Journal of ENVIRONMENTAL Treatment Techniques

*J. Environ. Treat. Tech.*
*ISSN: 2309-1185*
Journal weblink: http://www.jett.dormaj.com

# Trihalomethane Formation Potential in Rural Drinking Water: A Case Study Project of Seven Villages - Marvdasht Fars

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Received: 28/07/2019 Accepted: 08/09/2019 Published: 30/02/2020

## Abstract

Trihalomethanes have been known as carcinogen material for human by IARC. Considering the Project of seven villages drinking water is supplied from the Droodzen dam and Groundwater and water disinfection with chlorine is performed, this study was carried out to determine THM concentrations in drinking water of Project of seven villages. In this descriptive-cross-sectional research, 32 samples were taken from different points of drinking water distribution system after the villages map meshing so that covers all parts of the system in Spring and Summer seasons in 2017. The reason for these two seasons been variations in the concentration of organic substances in water resources and consequently the concentration of THMs precursors produced and the effect of temperature on the formation of THMs. Gas chromatography technic was used in with electron capture detector for analyzing samples of THM for each of four components including Chloroform, Bromodichloromethane,Dibromocholoromethane and Bromoform. The average concentration of THMs in Spring for Chloroform, Bromoform Bromodichloromethane ,Dibromocholoromethane and THMs were 22.25±7.98,11.42±3.90, 7.43±2.72 , 5.95±2.51 and 47.06±15.70 µg/Lit and in summer were 14.69±4.11,7.55±1.99, 4.93±1.51 ,3.95±1.49 and 31.13±7.97 µg/Lit, respectively. Concentration of trihalomethanes and total trihalomethanes in Project of seven villages drinking water distribution system is lower than the national and international standards and the drinking water consumers arenot at risk of exposure to trihalomethanes.

**Keywords:** Trihalomethanes, Village, Distribution network, Drinking water

## 1 Introduction

Disinfection is considered as the most important and conventional water treatment process, which aims to remove bacterias, viruses and parasites [1, 3]. The various physical and chemical factors having their own advantages and disadvantages are used to disinfect drinking water. The criteria of selecting an appropriate disinfectant involve disinfecting power, producing facility, accessing, applying and un-disturbing water quality [4].

Trihalomethane (THM) is regarded as one of water disinfection by-products since it is produced in chlorinated water by reacting natural organic materials such as humic and fulvic compounds and chlorine injected into water. A daily increase in applying chlorine in water treatment and abundance of natural organic material or those derived from discharging human and underground wastewater into water produce about 780 by-products in water, of which halogen compounds are a main part. THMs are considered as one of the most important disinfection by-products [5], which are devoid of specific odor in water although they associate with physiological hazards [6].

A group of researchers in United States environmental protection agency (US EPA), Switzerland and Netherlands found new compounds in chlorinated water, which had not been observed in drinking water earlier (1974). These compounds belonging to the family of chlorinated organic material were named trihalomethane (THMs) [5]. Chloroform, bromoform, dibromochloromethane and dichlorobromomethane are regarded as the most famous THMs, among which chloroform is absorbed through mouth, breathing and cutaneous contact, while three other compounds are absorbed by digestive system [4]. Recent epidemiological studies have represented the abundant negative impacts of THMs including sudden abortion, birth defects, stillbirth, some effects in reproduction such as congenital abnormalities and damage to specific organs such as liver, kidney and nervous system and adverse impact on circulatory system [4]. Considering the health hazards of THMs, US EPA published rules for controlling TMHs in drinking waters (1979). Based on this rule, the maximum allowed value of total THMs in drinking water entitled mean annual value was 100 (µgr/L) which decreased to 80 (µgr/L) from 1998 to now [7]. Further, the institute of standards and industrial research of Iran, drinking water-physical and chemical specifications announced that the maximum of THMs concentration in 1997 is equal to 200 (µgr/L) chloroform [8]. THMs concentration in drinking water is affected by some factors such as temperature, concentration and nature of natural organic material, consumed chlorine concentration, pH, bromide ion concentration and chlorine contact time with water [9, 12]. An addition of temperature results in increasing reaction rate and consequently chlorine consumption which leads to the enhancement of producing disinfection by-products [2, 13, 15].

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Based on the study of Fazli in Zanjan (2013), the mean concentration of total THMs were quantified in the winter and summer of 2013. Further, the mean concentration of chloroform, bromoform, dibromochloromethane and dichlorobromomethane and total THMs in water distribution network during winter were determined as 4.7 ± 1.44, 4.72 ± 1.25, 3.08 ± 0.43, 1.98 ± 0.14 and 14.19 ± 3.09 (µgr/L) , respectively, while their concentrations in summer were obtained as 4.21 ± 1.83, 4.71 ± 1.8, 3.65 ± 0.81, 2.22 ± 0.14 and 14.81 ± 4.4 (µgr/L) , respectively, which were within the range suggested by the guideline of national and international standard [16]. According to Babaei (2011), total THMs concentration in Ahwaz during winter, spring and summer varied between 20.5-86 (µgr/L), 18.92-66.06 (µgr/L) and 17.35-174.7 (µgr/L), respectively. Further, total THMs concentration was higher than the value allowed by EPA 80 (µgr/L) in six cases and that allowed by the institute of standards and industrial research of Iran and guideline of world health organization (WHO) in three cases [17]. Regarding the assessment of THMs concentration in the drinking water of Tehran city, Mazlomi et al. (2010) reported that despite pre-chlorination in input tank and mean residual chlorine in output tank, chloroform concentration in both tanks was equal to 0.94 , which was very less than the THMs concentration allowed in drinking water in Iran and WHO 2002 (µgr/L). Further, the maximum concentration of THM was determined in May [18]. The present study was conducted during the spring and summer of 2017. To this end, three villages of Abbas Abad, Majd Abad and Kamar Zard with the total of nine stations were selected among the seven-village project of Marvdasht County in Fars province. Sampling was repeated three times on each village position and data were selected as maximum concentration. Drinking water tank involved a combination of Doroodzan dam and underground wells waters.

## 2 Materials and Methods

Regarding sample collection, 40ml glass Bottle having teflon doors were used. Before sampling, the dishes were completely washed, placed for 3hr at 300 $^0$C to evaporate their organic and volatile materials perfectly and they reached room temperature in desiccator. Further, 20ml normal sodium thiosulfate (4 drops of 10% solution) was added into sampling dish to remove residual chlorine in water and prevent from forming THMs in sampling dish after sampling based on US EPA standard [19]. Due to the volatility of THMs, no bubble or air should be in sample dish and its door should close completely during sampling [20]. Furthermore, the water tap of sampling area was left open for at least 5min in order to exit the stagnant waters existing within pipe and enter the water flowing within main pipes into sampling tap [20]. Sampling was iterated three times on each position having sampling tap. Thus, the sample-containing dishes were stored at 4$^o$C and transferred to laboratory for analyzing in order to determine sampling measurement. EPA method 7030 was used to prepare and extract volatile organic compounds from drinking water and EPA method 3260 was utilized for their recognition and measurement in order to measure THMs concentration. Regarding EPA method 3260, gas chromatography with mass spectrometric detection (CG-MS) was used [20].

Some methods such as modified trapping [25, 26], direct liquid injection [27], dynamic headspace sampling [28], solid phase micro-extraction [29] and liquid phase micro-extraction [30, 32] were reported along with the conventional method of liquid-liquid extraction technique [21, 24]. Three villages of Abbas Abad, Majd Abad and Kamar Zard located in Marvdasht County of Fars province with the total of nine stations were selected for sampling. Further, sampling was repeated three times on each position. The water existing in tank was provided from Doroodzan dam and underground (well) waters, which were combined in the main tank. The parameters of temperature, pH, free residual chlorine and TOC were measured. Three positions were considered for sampling in order to study the change and value of THMs compounds in the steps of transfer and distribution network. First position was located in Kamar Zard village after the main tank. Regarding second position, it was placed within 15km distance from chlorination site and the main tank in Abbas Abad village, in which THMs concentration were measured to assess the role of water pipeline in THMs concentration. Finally, third position was located at the farthest point and within 25km distance in Majd Abad village.

Recovery percentage (%R) and relative standard deviation (RSD) were used to validate the method of THMs measurement. Table 1 represents the values of %R and %RSD related to the method of THMs measurement which was used in the present study. Recovery percentage between 80-120% is considered as acceptable based on recommended standard method [33]. As shown in Table 1, the obtained recovery percentages were in the above-mentioned range. Thus, THMs measurement was regarded appropriate with respect to validation. Further, THMs measurement was proper with respect to accuracy since RSD less than 20% is considered as acceptable [33]. The data were analyzed by using the statistical tests of Kolmogorov-Smirnov test, PP plots and paired and one-sample t-tests. Figures 1 and 2 demonstrate the mean concentration of each THM and total THMs in the spring and summer of 2017 based on EPA standard.

## 3 Results

The comparison of mean, standard deviation, range, minimum and maximum of 95% of changes in THMs concentration in the area under study is summarized in Tables 2 and 3. Based on the results, the mean concentrations of chloroform, bromoform, dibromochloromethane and dichlorobromomethane in all samples during spring were obtained 22.25, 11.42, 5.95 and 7.43µgr/L, respectively, while their values in summer were 14.69, 7.55, 3.95 and 3.93µgr/L, respectively. Further, the mean concentration of total THMs was determined 47.06 and 31.13µgr/L in spring and summer, respectively. The THM concentrations related to two seasons of spring and summer were compared by using paired and one-sample t-tests (Tables 4 and 5), indicating that no significant difference was observed between total THMs concentration in spring and summer. As shown, the mean concentration of chloroform, bromoform, dibromochloromethane and dichlorobromomethane and total THMs in all samples were less than the allowed value suggested by EPA.

## 4 Discussion

Considering the results in Table 2, the minimum and maximum concentration of total THMs in the samples related to spring were determined 30 and 73 µgr/L, respectively, while these values in the samples of summer were 25 and 48 µgr/L, respectively. The maximum concentration of chloroform, bromoform, dibromochloromethane and dichlorobromomethanene among all samples related to the spring and summer of 2017 were obtained as 36.87, 17.89, 11.03 and 12.29 µgr/L and 24.24, 11.87, 7.88 and 8.78 µgr/L, respectively. THMs concentration in two seasons of spring and summer was compared by using paired-sample t-test (Table 4), which represents an insignificant difference between total THMs concentration in spring and summer. Thus, no seasonal change was observed in the present study.

Based on one-sample t-test (Table 5) and comparison with total THMs concentration in two mentioned seasons, the mean concentration of total THMs in spring was different from EPA standard significantly ($p<0.000$). Further, the result was confirmed in summer. Fazli (2013) measured the mean concentration of total THMs in Zanjan during the winter and summer of 2013. Additionally, the mean concentration of chloroform, bromoform, dibromochloromethane and dichlorobromomethane and total THMs existing in water network during winter and summer were reported as $4.7 \pm 1.44$, $4.72 \pm 1.25$, $3.08 \pm 0.43$, $1.98 \pm 0.14$ and $14.19 \pm 3.09$ µgr/L and $4.21 \pm 1.83$, $4.71 \pm 1.8$, $3.65 \pm 0.81$, $2.22 \pm 0.14$ and $14.81 \pm 4.4$ µgr/L, respectively, which were within the range suggested by the guideline of national and international standard [16]. Mazlomi et al. (2010) assessed THMs concentration in the drinking water of Tehran city and found that despite pre-chlorination in input tank and mean residual chlorine in output tank, chloroform concentration in both tanks was equal to 0.94, which was very less compared to the THMs concentration allowed in drinking water in Iran and WHO 2002 (µgr/L). Further, the maximum concentration of THM was obtained in May [18].

Table 1: Values related to THMs measurement

| Std. Deviation | Recovery percentages | Parameters | Std. Deviation | Recovery percentages | Parameters |
|---|---|---|---|---|---|
| 3/55 | 80/82 | Bromodichloromethane, $CHCl_2Br$ | 1/13 | 81/05 | Chloroform, $CHCl_3$ |
| 2/23 | 83/35 | Bromoform, $CHBr_3$ | 4/67 | 87/73 | Dibromochloromethane, $CHBr_2Cl$ |

Table 2: Seasonal comparison of mean, standard deviation, minimum and maximum, and range of THMs concentration

| TTHM | CHCl3 | CHCl2Br | CHClBr2 | CHBr3 | Parameters | period |
|---|---|---|---|---|---|---|
| 30 | 12/15 | 4/9 | 3/13 | 6/75 | Minimum | Spring |
| 73 | 36/87 | 12/29 | 11/03 | 17/89 | Maximum | |
| 47/066 | 22/25 | 7/43 | 5/95 | 11/42 | mean | |
| 43 | 24/72 | 8/1 | 7/89 | 11/14 | Range | |
| 25 | 10/53 | 3/51 | 2/63 | 5/85 | Minimum | Summer |
| 48 | 24/24 | 8/78 | 7/88 | 11/87 | Maximum | |
| 31/133 | 14/69 | 4/93 | 3/95 | 7/55 | mean | |
| 23 | 13/71 | 5/27 | 5/25 | 6/02 | Range | |

Table 3: 95% Confidence Interval of the Difference THM concentration

| 95% Confidence Interval of the Difference | | Summer | 95% Confidence Interval of the Difference | | Spring |
|---|---|---|---|---|---|
| Lower limit | Upper limit | | Lower limit | Upper limit | |
| 26/71 | 35/54 | TTHM | 38/36 | 55/76 | TTHM |
| 6/45 | 8/65 | $CHBr_3$ | 9/26 | 13/59 | $CHBr_3$ |
| 3/12 | 4/78 | $CHClBr_2$ | 4/55 | 7/34 | $CHClBr_2$ |
| 4/08 | 5/77 | $CHCl_2Br$ | 5/92 | 8/94 | $CHCl_2Br$ |
| 12/41 | 16/96 | $CHCl_3$ | 17/83 | 26/67 | $CHCl_3$ |

Table 4: Comparison of THMs concentration by using paired-sample t-test

| TTHM | | Paired Differences | | | | | Sig. (2tailed) |
|---|---|---|---|---|---|---|---|
| | | Mean | Standard Deviation | Std. Error Mean | 95% Confidence Interval of the Difference | | |
| | | | | | Minimum | Maximum | |
| | $CHCl_3$ | 20/62 | 8/25 | 1/50 | 17/54 | 23/70 | 0/000 |
| | $CHCl_2Br$ | 32/91 | 12/48 | 2/28 | 28/25 | 37/58 | 0/000 |
| | $CHClBr_2$ | 34/14 | 12/96 | 2/36 | 29/30 | 38/98 | 0/000 |
| | $CHBr_3$ | 29/60 | 11/19 | 2/04 | 25/42 | 33/79 | 0/000 |

Table 5: Comparison of THMs concentration by using one-sample t-test

| TTHM | Test Value = 80 | | | |
|---|---|---|---|---|
| | Sig. (2tailed) | Std. Error Mean | 95% Confidence Interval of the Difference | |
| | | | Minimum | Maximum |
| $CHCl_3$ | 0/000 | -61/52 | -64/26 | -58/79 |
| $CHCl_2Br$ | 0/000 | -73/81 | -74/75 | -72/87 |
| $CHClBr_2$ | 0/000 | -75/04 | -75/89 | -74/19 |
| $CHBr_3$ | 0/000 | -70/50 | -71/86 | -69/15 |

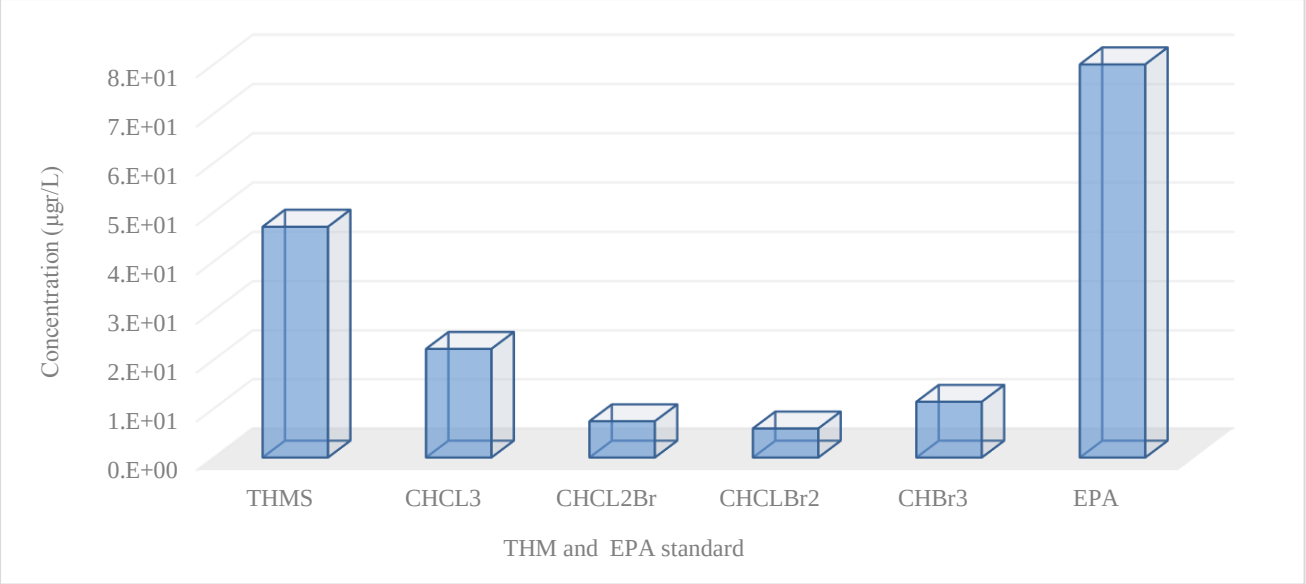


Figure 1: Mean concentration of THMs in spring based on EPA standard

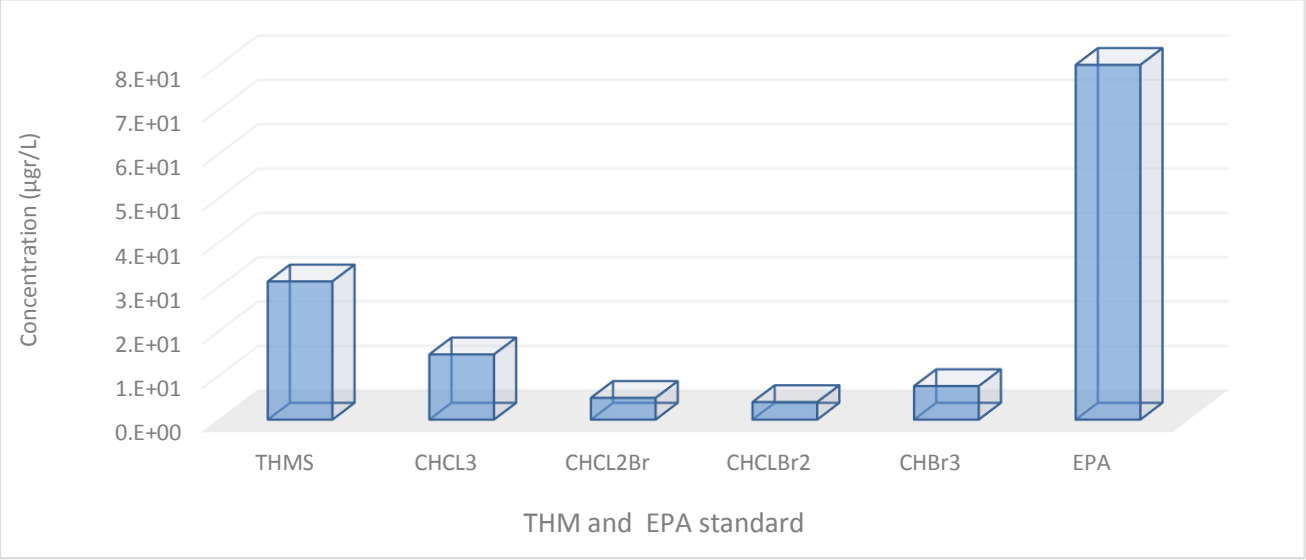


Figure 2: Mean concentration of THMs in summer based on EPA standard

## 5 Conclusion

Based on the results, the maximum concentration of chloroform, bromoform, dibromochloromethane and dichlorobromomethanene among all samples were measured as 36.87 ± 7.32, 12.29 ± 2.51, 11.03 ± 2.27, 17.89 ± 3.62 and 73 ± 14.67 µgr/L, respectively, which are less than the allowed value suggested by EPA. Thus, there is no problem about high THM concentration in the drinking water distribution network of seven-village project and consumers do not face with the risk of these disinfection by-products.

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