

**Presence and seasonal variation of trihalomethanes (THMs) levels in drinking tap water in Mostaganem Province in northwest Algeria**Benhamimed El-Attafia<sup>1</sup>, Moulessehou Soraya<sup>2</sup><sup>1</sup> Department of Biology, University of Mostaganem, Algeria<sup>2</sup> Department of Biology, University of Djilali Liabes, Sidi Bel Abbes, Algeria**Type of article:** Original**Abstract**

**Background:** The use of chlorine to disinfect water, produces various disinfection byproducts such as trihalomethanes (THMs). These compounds are formed when free available chlorine reacts with natural organic matter in raw water during water disinfection. Epidemiologic studies have shown an association between long-term exposure to THMs and an increased risk of cancer, all of them are suspected of having carcinogenic effects.

**Aim:** The aim of this study was to determine the presence of THMs in the drinking tap water of Mostaganem Province (Algeria) in order to assess the seasonal variation in trihalomethane levels in tap water and to identify the season of high risk to the consumer.

**Methods:** This analytical study was conducted in Mostaganem Province, Algeria in March, July, September and December 2015. Primarily, we proceeded to collect 30 samples from different areas of Mostaganem Province which were marked with a higher level of residual chlorine for the year 2015; secondly, we utilised the HS-SPME method for determination of trihalomethanes in drinking tap water over a period of four months. For comparison of trihalomethanes values, we used ANOVA.

**Results:** The results obtained show variability in total THM concentrations from one district to another, with a maximum of 198 µg/l recorded in the Achaacha district during July, but the lowest value 07.84 µ g/l is noted at Salamandre city during the same period, noting that these values decrease progressively during the winter period.

**Conclusion:** Our drinking tap water samples include a large quantity of THMs with different concentrations, where the dibromochloromethane and the bromoform constitute the major portion of THMs.

**Keywords:** Analyse, Drinking water, Trihalomethanes, Seasonal variation

**1. Introduction**

Chlorine is applied to drinking water in order to deactivate microorganisms and/or to ensure the residual concentrations in drinking water distribution systems, thus protecting water from microorganisms' regrowth (1). As a result of disinfection of natural water, trihalomethanes (THMs) are a commonly monitored class of drinking water disinfection by-products (DBPs). Trihalomethanes are formed when free available chlorine reacts with natural organic matter in raw water when the water is being treated with disinfection (2, 3). They are all considered to be possible carcinogens (4). Due to concerns regarding their possible health effects, the maximum contaminant levels (MCL) for total THMs in drinking water has been set by the United States Environmental Protection Agency (USEPA) at 100µg/L (1). Several standard methods that can be used to measure THM concentrations in drinking water have been provided by USEPA. Numerous methods can be found in the literature for measuring THMs concentrations in drinking water. Solid-phase microextraction (SPME) which was invented by Pawliszyn and co-workers (5) is a recent and very successful new approach to sample preparation. This technique has been successfully applied to the analysis of THMs (6, 7) and volatile organic compounds in water samples (8).

**Corresponding author:**

Benhamimed El-Attafia, Department of Biology, University of Mostaganem, Algeria.

Tel.: +2130665678223, E-mail: [a.benhamimed@yahoo.com](mailto:a.benhamimed@yahoo.com)

Received: September 10, 2016, Accepted: February 18, 2017, Published: May 2017

iThenticate screening: February 28, 2017, English editing: May, 01, 2017, Quality control: May 12, 2017

© 2017 The Authors. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

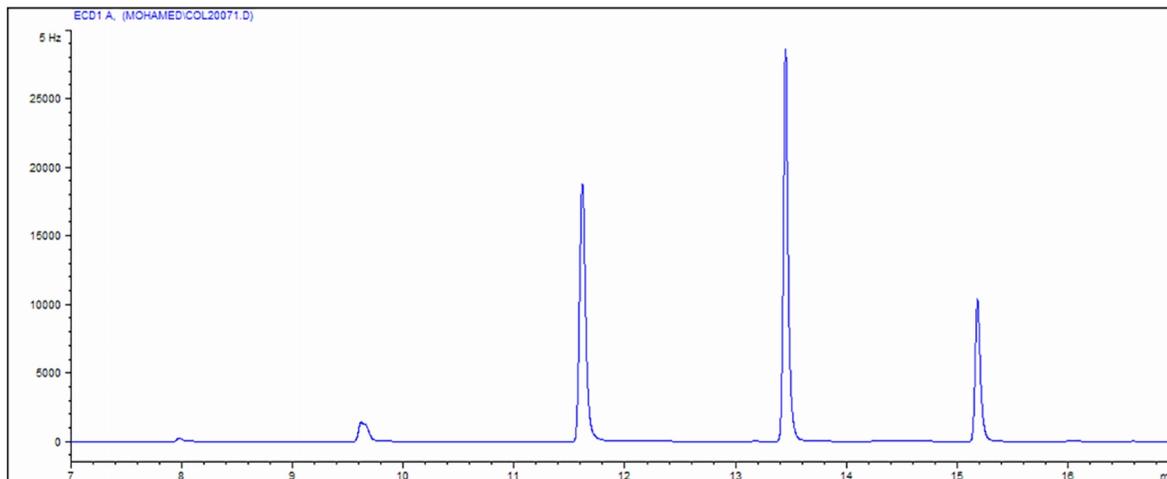
## 2. Material and Methods

Three company samples were taken at different areas of Mostaganem Province which had high concentration markings of residual chlorine during the year 2015, sampling was done over several months, the first sampling was in March, the second was in July, the third levy was in September and the last one was in December. All the samples were collected in 22-ml amber glass vials and were capped with PTFE-faced silica septa. Before sampling, a sodium sulphite (50  $\mu$ l of a 1.5 g/l Na<sub>2</sub>SO<sub>3</sub> solution) was added to bottles to eliminate any remaining residual chlorine and to stop further chlorination by-products (CBP) formation. The vials were completely filled to avoid evaporation of volatile compounds. The samples were transported to the laboratory, transferred to a refrigerator (set at 4 °C) and analysed within 2 days of collection (9-11). The samples were collected in 22-ml amber glass vials which were capped with PTFE-faced silica septa. To eliminate any remaining residual chlorine and to stop further chlorination by-products (CBP) formation, sodium sulphite (50  $\mu$ l of a 1.5 g/l Na<sub>2</sub>SO<sub>3</sub> solution) was added to bottles before sampling. In order to avoid evaporation of volatile compounds, the vials were completely filled. The samples were then transported to the laboratory and placed into a refrigerator (set at 4 °C), and were analysed within 2 days of collection (9-11). In this research, we have used a rapid and sensitive method for extraction and determination of trihalomethanes in drinking water by headspace solid-phase microextraction (HS-SPME) combined with a capillary gas chromatography-electron capture. Headspace solid-phase microextraction (HS-SPME) was performed using a Supelco No. 5-7300 manual solid-phase microextraction fiber assembly fitted with a 100  $\mu$ m poly (dimethylsiloxane) fiber. The fiber was conditioned at 250 °C for 1 hour prior to use, and blank desorption were performed. For SPME analysis, an aliquot of 2 ml of contaminated water was added in a 4-ml vial (Supelco). After placing a 0.8-cm long stir bar in each vial and 25 w/v% sodium chloride salt, it was sealed with a headspace cap with a PTFE-faced. The sampling times from 5 to 50 minutes were selected with constant stirring (750 rpm) to speed up phase equilibrium. Once sampling was complete, the fiber was immediately retracted back into the needle and transferred without delay to the injection port of the gas chromatograph injector for desorption. A desorption time of 4 min at 250 °C was enough for a quantitative desorption of all the analytes studied (9-11).

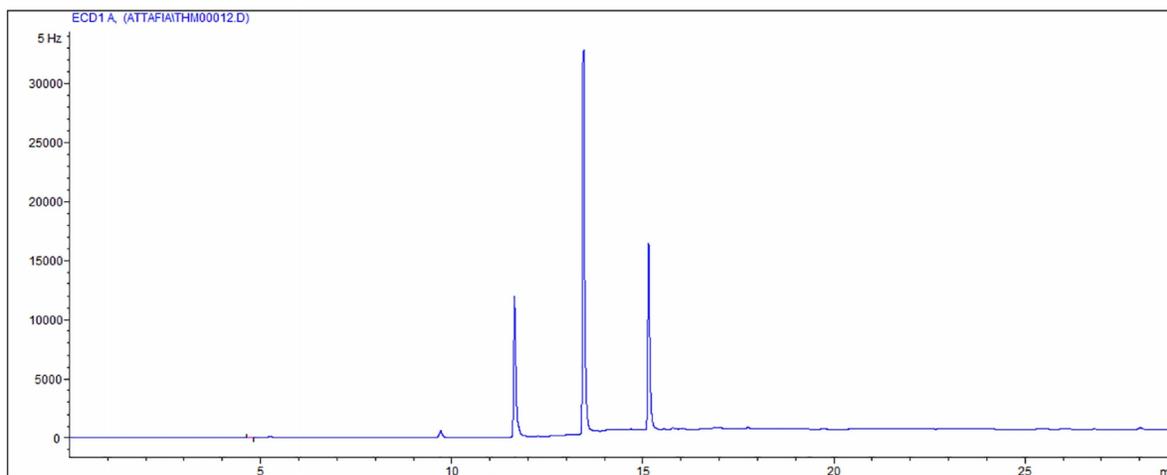
## 3. Results and Discussion

The identification of the four analytes was deduced from their retention times and quantification was performed using the peak area measurement as well comparison with responses of a mixed trihalomethanes standard based on multi-level calibration from 5 to 100  $\mu$ g/L; a typical chromatogram of the four standard THMs (50 ppm) is displayed in Figure 1. Figure 2 shows the chromatogram obtained by solid phase micro extraction (SPME) for the analysis of one sample water named (plateau area) at Mostaganem Province. This chromatogram, indicate clearly peak saturation for the dibromochloromethane and bromoform, this phenomenon confirmed the richness of our drinking water samples by bromide ions in the source. All samples analysed contained considerable and variable amounts of trihalomethanes during the four months (March, July, September and December). The maximum value was registered in July at 198  $\mu$ g/l at Achaacha district, located at 10.000 meters, this value exceeds the norm which is limited at (100  $\mu$ g/l) (12-14). However, the lowest value was marked in December with only 6.94  $\mu$ g/l in the region of Salamandre, situated at 10 meters at the coastal location. This variability is due to several factors involved in the formation of THMs such as water temperature, pH, organic matter rate, residual chlorine, turbidity, contact time and other parameters of the quality of the drinking water; which have an essential role in the formation of these compounds (15-18). The results of analyses of total trihalomethanes in drinking tap water at Mostaganem Province are shown in Figure 3. According to the experimental results which have been presented in Table 1, the concentration of THMs on the sample points vary from one month to another. In all samples and during the four months of analysis of trihalomethanes in drinking water, Achaacha district had the greatest value respectively (198  $\mu$ g/L, 179.56  $\mu$ g/L, 134.4  $\mu$ g/L and 126.65  $\mu$ g/L), as a consequence of higher values of water temperature and residual chlorine. Also, this region is known for its high rate of waterborne diseases, which can lead municipal authorities to increase the chlorination rate above the permitted standard. This increase in the level of chlorine can lead to the formation of chlorinated by-products such as trihalomethanes in the presence of organic matter, these higher values on the mentioned sample points can also be the organic pollution which can penetrate into the drinking water as a result of the outdated water supply system in this region, however, the lowest values were respectively recorded in P epini ere city with 6.47  $\mu$ g/L in December and Salamandre city with 6.94  $\mu$ g/L in March. Depending on trihalomethanes concentration evolution during all months for the year 2015, primarily, July shows the highest concentration of total THMs in all sample points except in Beymouth city which scored a rate of 21.95  $\mu$ g/L and remains lower compared to other sampling sites; and secondly, the month of September which marked interesting rates for all sample points; On the other hand, it was observed that in the month of March, the rate of total trihalomethane is slightly higher than in December, with 134.4  $\mu$ g/L and 126.65  $\mu$ g/L respectively. Our results are in accordance with those found in the United States, Europe and Egypt (17-20) indicating that the water temperature

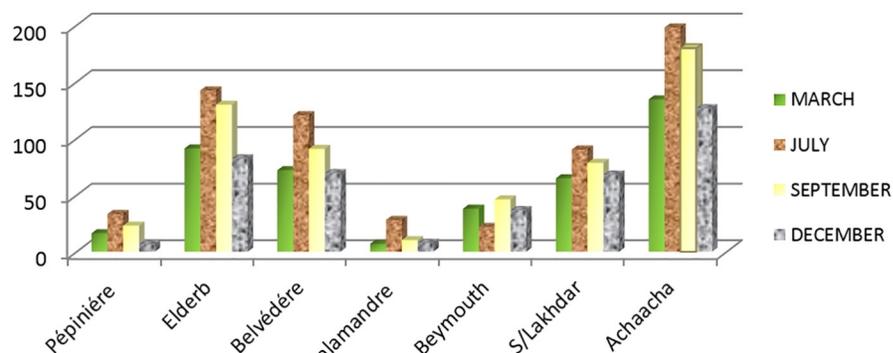
decreases in winter, which is a disadvantage in the production of the disinfection by-products while the concentration of THMs increases in summer and autumn sees the temperature rise depending on the season and the emissive use of chlorination to ensure safe water (21, 22). These results have proved the dominance of brominated species in all the samples analyzed, whereas chlorinated species like chloroform ( $\text{CHCl}_3$ ) and bromodichloromethane ( $\text{CHBrCl}_2$ ) were not detected on some of the sample points ( $0.00 \mu\text{g/L}$ ) or have marked low levels in others, which is illustrated in Table 1, for example the Achaacha sample had the highest total trihalomethanes ( $198 \mu\text{g/l}$ ) in July. The concentration of bromoform ( $\text{CHBr}_3$ ) was  $98.69 \mu\text{g/l}$ , followed by chlorodibromomethane ( $\text{CHClBr}_2$ ) with  $62.34 \mu\text{g/l}$ ; when, bromodichloromethane ( $\text{CHBrCl}_2$ ) and chloroform ( $\text{CHCl}_3$ ) were  $31.31$  and  $5.76 \mu\text{g/l}$  respectively. The dominance of bromine species than chlorinated species can be explained by water vapors mixed with precipitation, as well as industrial and petroleum brine discharges which can contaminate water sources with bromides (22-24). Sketchel et al. showed the dominance of bromoform ( $\text{CHBr}_3$ ) and chlorodibromomethane ( $\text{CHClBr}_2$ ) in the Mediterranean regions (22, 25-27). Similar results are also observed in the region of Bizerte (Tunisia) (10), in addition, the presence of bromide ions further favors the formation of bromine THM products (24, 26). The presence of bromide causes the formation of THMs brominated (28); while the concentrations of chloroform decrease proportionally (27, 28). Given the coastal location of our study site, this translates into the dominance of bromides, which are mostly found in salt water. Sea water vapours and saltwater mixed precipitation may increase the concentration of bromides in the soil, surface water and groundwater in coastal areas (29). So, our samples of tap water ions are rich in bromides, the presence of brominated by-products depends on the presence of bromides in the source (24, 26).



**Figure 1.** Chromatogram obtained for a 50 ppb THM standard. GC±MS was performed following headspace sampling by SPME. Analytes in order of elution were: 1)  $\text{ChCl}_3$ , 2)  $\text{ChCl}_2\text{Br}$ , 3)  $\text{ChClBr}_2$ , 4)  $\text{ChBr}_3$ .



**Figure 2.** Chromatogram of Plateau area tap water sample by (HS-SPME)-CG-ECD; Peaks: 1)  $\text{ChCl}_3$ , 2)  $\text{ChCl}_2\text{Br}$ , 3)  $\text{ChClBr}_2$ , 4)  $\text{ChBr}_3$ .



**Figure 3.** Concentration of total trihalomethanes in the tap water at Mostaganem Province during four months of analysis.

**Table 1.** The variation in trihalomethane levels in tap water at Mostaganem Province during four months (March, July, September and December) for the year 2015.

Sampling points (location)	Trihalomethanes rate in µg/l															
	March				July				September				December			
Pépinière	00	1.01	2.01	13.23	1.79	3.02	5.32	23.15	0.75	1.01	3.48	17.75	00	1	2.03	3.44
Eldb	7.5	14.25	17.13	52.23	16.69	17.52	30.33	77.82	14.09	15.52	29.3	70.76	9.08	10.06	17.3	46.04
Belvédère	0.32	4.88	18.02	48.66	3.65	8.56	20.2	88.14	0.32	5.23	17.2	84.19	1	2.4	11.02	55.01
Salamandre	0.2	0.44	1.1	5.2	3.12	6.22	7	11.67	0.24	0.62	1.1	8.3	00	00	0.75	7.09
Beymouth	00	1.7	3.24	33.04	0.48	2.38	7.82	11.27	2.5	5.75	8.05	30.04	00	2.02	3.25	31.4
S/Lakhdar	1	3.13	15.66	45	2.09	7.08	24.34	56.74	1.02	5.44	20.19	51.76	0.89	2.39	16.48	48.23
Achaacha	5.6	20.7	48	60.8	5.76	31.21	62.34	98.69	8.39	28.11	52.34	90.72	5.43	14.48	41.51	65.7

## 5. Conclusions

The presence of THMs in the drinking water has caused great concern since these components can cause cancer in humans. The monitoring of the THMs formation is crucial in order to make sure that the drinking water remains at the acceptable safety levels. The analysis of samples collected from various sources, shows a variability of our tap water by total THMs during four months (March, July, September and December). Despite the results it appears that the concentration of trihalomethanes decreases in winter, increasing in spring and fall season and usually reaching a maximum in summer. All the samples analyzed show clearly the dominance of brominated species (dibromochloromethane and bromoform) than chlorinated species in all seasons, this indicates the richness of our source in bromides. We recommend that the relevant authorities take appropriate actions to prevent and keep the THM concentrations within limits, especially in the hot months when their values are much higher, as long term consumption can cause health problems.

## Acknowledgments:

The authors would like to thank Mr. Rheda Driss, Professor in Charge of the Laboratory of Environmental Analytical Chemistry (LEAC), Faculty of Science, Bizerte (Zarzouna, Tunisia) and Mme. Moulessehou S. and the whole team of the laboratory of Biototoxicology (University Djilali Liabès, Sidi Bel-Abbes, Algeria).

## Conflict of Interest:

There is no conflict of interest to be declared.

## Authors' contributions:

Both authors contributed to this project and article equally. Both authors read and approved the final manuscript.

## References:

- 1) Rodriguez MJ, Serodes JB. Spatial and temporal evaluation of trihalomethanes in three water distribution systems. *Water Res.* 2001; 35(6): 1572–86. doi: 10.1016/S0043-1354(00)00403-6. PMID: 11317905.
- 2) Rook JJ. Formation of haloforms during chlorination of natural water. *Water Treat Exam.* 1974; 23(2): 234-43.

- 3) Bellar TA, Lichtenberg JJ, Kroner RC. The occurrence of organohalides in chlorinated drinking waters. *J Am Water Works Assoc.* 1974; 66(12): 703–6.
- 4) Lekkas TD. *Halofoms and Related Compounds in Drinking Water.* Berlin: Springer; 2003: 193–214. doi: 10.1007/978-3-540-44997-3\_8.
- 5) Arthur CL, Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal Chem.* 1990; 62(19): 2145–8. doi: 10.1021/ac00218a019.
- 6) Stack MA, Fitzgerald G, O'Connell S, James KJ. Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry. *Chemosphere.* 2000; 41(11): 1821–6. doi: 10.1016/S0045-6535(00)00047-3. PMID: 11057623.
- 7) Cho DH, Kong SH, Oh SG. Analysis of trihalomethanes in drinking water using headspace-SPME technique with gas chromatography. *Water Res.* 2003; 37(2): 402-8. doi: 10.1016/S0043-1354(02)00285-3. PMID: 12502068.
- 8) Nakamura S, Daishima S. Simultaneous determination of 22 volatile organic compounds, methyl-tert-butyl ether, 1, 4-dioxane, 2-methylsoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography-mass spectrometry. *Analytica Chimica Acta.* 2005; 548(1-2): 79-85. doi: 10.1016/j.aca.2005.05.077.
- 9) Cancho B, Ventura F, Galceran MT. Solid-phase microextraction for the determination of iodinated trihalomethanes in drinking water. *J Chromatogr A.* 1999; 841(12): 197-206. PMID: 10371048.
- 10) Bahri M, Driss MR. Development of solid-phase microextraction for the determination of trihalomethanes in drinking water from Bizerte, Tunisia. *Desalination.* 2010; 250(1): 414-7. doi: 10.1016/j.desal.2009.09.067.
- 11) Serrano A, Gallego M. Rapid determination of total trihalomethanes index in drinking water. *J Chromatogr A.* 2007; (1-2): 26–33. doi: 10.1016/j.chroma.2007.03.101. PMID: 17420023.
- 12) *Guidelines for Drinking-Water Quality. 2nd Edition, Volume1, Recommendations.* World Health Organization. Geneva; 1993.
- 13) Health Canada. *Chlorinated disinfection by-products (SPCD).* 2000.
- 14) United States Environmental Protection Agency. National primary drinking water regulation: Disinfectants and disinfection by products, final rule, In federal Register Parts IV(40 CFR Part 9,141 and 142 December 1998: 69390-69476.
- 15) Nieminski EC, Chaudhuri S, Lamoreaux T. The occurrence of DBPs in Utah drinking waters. *J AWWA.* 1993; 85(9): 98–105.
- 16) Lee KJ, Kim BH, Hong JE, Pyo HS, Park SJ, Lee DW. A study on the distribution of chlorination by-products (CBPs) in treated water in Korea. *Water Res.* 2001; 35(12): 2861–72. doi: 10.1016/S0043-1354(00)00583-2. PMID: 11471686.
- 17) Ibarluzea JM, Goni F, Santamaria J. Trihalomethanes in water supplies in the San Sebastian area, Spain. *Bull Environ Contam Toxicol.* 1994; 52(3): 411-8. doi: 10.1007/BF00197830. PMID: 8142713.
- 18) Singer PC, Obolensky A, Greiner A. DBPs in chlorinated North Carolina Drinking Water. *J AWWA.* 1995; 87: 83–92.
- 19) Durmishi H, Bujar D, Vezi M, Ismaili A, Shabani Sh, Abdul. Seasonal Variation of Trihalomethanes Concentration in Tetova's Drinking Water (Part B). *World J Appl Enviro Chem.* 2012; 1(2): 42-52.
- 20) Souaya EMR, Abdullah AM, Mossad M. Seasonal Variation of Trihalomethanes Levels in Greater Cairo Drinking Water. *Mod Chem appl.* 2015; 3: 149. doi: 10.4172/2329-6798.1000149.
- 21) Toroz I, Uyak V. Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. *Desalination.* 2005; 176(1): 127-41. doi: 10.1016/j.desal.2004.11.008.
- 22) Baytak D, Sofuoglu A, Inal F, Sofuoglu SC. Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks. *Sci Total Environ.* 2008; 407(1): 286–96. doi: 10.1016/j.scitotenv.2008.08.019. PMID: 18805568.
- 23) Vinette Y. *Évolution spatio-temporelle et modélisation des trihalométhanes dans des réseaux de distribution d'eau potable de la région de Québec.* Mémoire du grade de maître ès sciences; Université Laval. Canada. 2001: 157.
- 24) Patelarou E, Kargaki S, Stephanou EG, Nieuwenhuijsen M, Sourtzi P, Gracia E, et al. Exposure to brominated trihalomethanes in drinking water and reproductive outcomes. *Occup Environ Med.* 2011; 68(6): 438-44. doi: 10.1136/oem.2010.056150. PMID: 20952554.
- 25) Sketchel J, Peterson HJ, Christofi N. Disinfection by product formation after biologically assisted GAZ treatment of water supplies with different bromide and DOC content. *Water Res.* 1995; 12(29): 2635-42. doi: 10.1016/0043-1354(95)00130-D.

- 26) Villanueva CM, Gagniere B, Monfort C, Nieuwenhuijsen MJ, Cordier S. Sources of variability in levels and exposure to trihalomethanes. *Environ Res.* 2007; 103(2): 211–20. doi: 10.1016/j.envres.2006.11.001. PMID: 17189628.
- 27) Aizawa T, Magara Y, Musashi M. Effect of bromide ions on trihalomethanes (THMs) formation in water. *Aqua.* 1998; 3: 41.
- 28) Bond T, Huang J, Graham NJ, Templeton MR. Examining the interrelation ship between DOC, bromide and chlorine dose on DBP formation in drinking water- a case study. *Sci Total Environ.* 2014; 470-471: 469-79. doi: 10.1016/j.scitotenv.2013.09.106. PMID: 24176694.
- 29) Uyak V, Toroz I. Investigation of bromide ion effects on disinfection by-products formation and speciation in an Istanbul water supply. *J Hazard Mater.* 2007; 149(2): 445–51. doi: 10.1016/j.jhazmat.2007.04.017. PMID: 17517472.