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Occurrence of HAAs and THMs in Tap Water of The Bizerte City area (Tunisia): Portrait and Modeling

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Abstract

Haloacetic acids (HAA) and Trihalomethanes (THM) are found in large amount as disinfection by-products (DBPs) in finished drinking waters. Conventionally, THM have been used as surrogates for DBP. The aim of this present study is to consist a portrait and a model of spatial-temporal formation of HAA as a function of THM species combination in drinking water samples from Tunisia districts. The analysis of HAA and THM and other physico-chemical parameters were accomplished into a six-month sampling program. Also, The occurrence of these DBP depending on seasonal variation reflects very different DBP amounts and the concentrations of HAA are between 19 and 115 $\mu g.L^{-1}$ while these of THM are between 46 and 123 $\mu g.L^{-1}$. Statistical correlations between HAAs and THMs were developed and statistically significant correlation between total THM and HAA were found (Pearson's correlation coefficient, $0.955 < R^2 < 0.608$; $p < 0.0005$. Finally, multivariate linear regression analysis of the concentrations observed show that the levels in each HAA can be predicted from the THM combination.

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1. Introduction

Disinfection by-products (DBPs) are formed at the same time as the disinfectants are added at raw water [1,2]. Their training formation in the network continued when there was a presence of natural organic matter (NOM) in sufficient amount and residual disinfectant [3,4]. The infectious diseases of water origin in our society are eliminated mainly by the disinfection of drinking water. However, the process of disinfection has negative side effects [5]. In disinfected drinking water, more than 600 different DBPs have been identified [6]. Reproductive and developmental problems and birth defects have been linked to DBPs and especially cancer of the liver, reins, and large intestine [7]. Besides, Haloacetic acids represent the major fraction of non-volatile DBPs after the most common volatile fraction of DBPs, which are THM [8-10]. Therefore, the US Environmental Protection Agency (US EPA) have set a maximum contamination level (MCL) of 60 $\mu g.L^{-1}$ for HAA5

(MCAA, DCAA, TCAA, MBAA, and DBAA) [11], and maximum contaminant level 80 $\mu g.L^{-1}$ for total THM concentrations in drinking water [12]. Moreover, The European Union (EU) [13] has set MCL levels 100 $\mu g.L^{-1}$ for total THM concentrations. While the World Health Organization (WHO) has published guidelines for MCAA, DCAA and TCAA and guidelines for each of the four THM species [14]. The Tunisian drinking water guideline is the EU guidelines.

The formation of DBP has not yet been identified by an exact mechanism. In literature, some parameters have been identified, which have specific significance in the formation of HAAs and THMs in treated waters like the disinfection dose, the natural organic matter (NOM), the contact times with chlorine, the pH, and the temperature pretentious the quantity and the type of formed DBP. [15-17]. The concentrations of NOM are generally estimated as total organic carbon (TOC) and UV absorption at 254 nm (UV_{254} nm).

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Other studies demonstrate that the presence of bromide in disinfected water sources can lead to a change in the speciation of DBP toward brominated species [18,19]. Further notes that, the pH, which expressively pretentious THMs, has a lower impact related to the HAAs. The temperature had a reliable impact with a reducing DBP formation at lower value. Increasing the contact time with the disinfectant cause an increasing in the formation of the HAAs and THMs. Finally, the precursors involved in the formation of DBPs were found to be specific to water sources [20].

Traditionally, trihalomethanes have been the most studied DBPs and mostly used as surrogates of DBPs. In order to better understand and predict the presence of HAA in drinking water, several studies have attempted to model their training, either using information generated from distribution networks [21-23], or using information generated in the laboratories based on simulations of chlorination of some water. Several empirical models on the formation of THMs have been developed. On the other hand, few models on the formation of HAA are currently available. Furthermore, no information has been published on HAA in Tunisia.

In Tunisia which has a Mediterranean climate, chlorine is the most used disinfectant for different water sources that have different qualities as well. Thus, diverse water sources have been chosen to investigate the quantitative relationships between the studied compounds. This study provides a good case for assessment of HAA and THM levels in finished drinking waters from different sources. The outcomes are designed to model HAA levels on the derivation of THM levels.

The objective of this research is not only to highlight a picture of the special simultaneous evolution of HAA and THM in the distribution network of Bizerte but also to point to the modelization of this evolution in order to predict the HAA level with THM as surrogate. The followed methodology uses first the consistency of generating a database of HAA and THM, then it develops models that describe the evolution of the polar studied DBPs based on the other non-polar studied DBPs.

DBAA, TBAA, and BCAA) were purchased from Fluka (Buchs, Switzerland) with purity >98%. THM

2. Materials and methods
2.1. Standard solutions
Seven HAAs (MCAA, DCAA, TCAA, MBAA, mixture solution ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) were bought from Supelco. The solvent methanol of residue analysis grade and sulfuric acid was supplied by Fisher Scientific (Loughborough, UK), whereas anhydrous sodium sulphate and methyl tert-butyl ether of residue analysis grade were obtained from Fluka. Laboratory grade water was from Milli-Q water purification system (Millipore, Bedford, MA). A manual solid phase microextraction holder fitted with 100mm polydimethylsiloxane fiber is supplied by Supelco. The HAAs individual aqueous standard solutions of 1000 $mg.L^{-1}$ were prepared by weight in Milli-Q water. The mixtures aqueous standards solutions were prepared weekly or daily, depending on their concentrations. Before analysing and using for calibration and quantification studies. All solutions were stored in the dark at 4°C and warmed to ambient temperature before use.

2.2. Areas of study
Drinking water supply systems in Bizerte is based on surface water. Given that, it was not possible to make a hydraulic swing of the studied network to get the information on the time and kinetic of disinfection reaction, we have chosen the sampling points depending on the geographic distance from the water treatment plant (WTP) to the end of the network. As a matter of fact, to verify that the sampling points represent variable contact time, an intensive campaign of measurement of free residual chlorine have been performed in the distribution system. A sampling program was carried out starting from 2010 to 2014 with the aim of covering the hot season (August): Campaign 1 and the cold season (January): Campaign 2. During each campaign, there were three samples taken per monitoring point. Bizerte's WTP supplies are carried through an exclusive distribution pipe network and further details of about this process and the sampling points are given in Table 1. Raw and finished water quality parameters of Bizerte's WTP are reported in Table 1. The pH, water temperature (T), and UV_{254} were measured on site. In this study the samples Were collected from the storage tanks whose distances are known precisely.

Table 1

Description of water treatment plant of Bizerte and sampling points and operational parameters with %RSD in parenthesis

Source	WTP	Sampling locations		Operational parameters		
surface water (raw water)	Coagulation					
	Flocculation	Raw water				
	Filtration	Sand filtration	Su	Pre-chlorine dose ($mg.L^{-1}$)		Post-chlorine dose ($mg.L^{-1}$)
	Chlorination	Treated water		3		2.5

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			Raw water			Finished water		
		Zone 1 (7 km)	pH	TOC (mg.L^{-1})	UV$_{254}$ (Cm^{-1})	pH	TOC (mg.L^{-1})	UV$_{254}$ (Cm^{-1})
		Zone 2 (20 km)	7.68 (11.8)	6.5 (3.2)	0.179 (2.6)	7.20 (7.5)	3.83 (4.6)	0.086 (2.6)
		Zone 3 (43 km)						
Distribution (Storages tanks)	Flow capacity 113 (ML/d)	Zone 4 (45 km)	Pre-chlorine dose (mg.L^{-1})			Post-chlorine dose (mg.L^{-1})		
		Zone 5 (48 km)	1.5			2.2		
		Zone 6 (58 km)	Raw water			Finished water		
		Zone 7 (59 km)						
		Zone 8 (62 km)	pH	TOC (mg.L^{-1})	UV$_{254}$ (Cm^{-1})	pH	TOC (mg.L^{-1})	UV$_{254}$ (Cm^{-1})
		Zone 9 (66 km)	7.51 (9.5)	4.86 (7.6)	0.154 (3.1)	7.31 (5.9)	3.11 (5.1)	0.075 (3.3)

(Winter label appears rotated alongside the second Raw water/Finished water block.)

2.3. Sampling and analytical strategies

The water quality parameter analyzed in this study included pH, TOC, Free-Cl2 and UV254. The analysis of pH used pH meter, TOC were directed with a Shimadzu TOC-5000 equipped with a Pt catalyst (American Public Health Association 1998) [24], the residual free chlorine (Free-Cl2) was measured by iodometric method [25] and UV254 were measured on site.

The concentrations of bromide were measured using ion chromatography (Metrohm 792 Basic IC) fitted with an (Metrohm 6.2828.100, 150 mm) column and an eluent composition of (1.28 mM NaHCO$_3$ / 0.48mM Na$_2$CO$_3$) [26].

The studied HAA (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, dibromoacetic, tribromoacetic and bromochloroacetic) were analyzed following a previously optimized procedure [27,28]. While, the THM (chloroform, dichlorobromomethane, chlorodibromomethane and bromoform) were determined by the formerly optimized method developed by [29]. For the extraction of HAA and THM a head space solid phase microextraction (HS-SPME) were used [26,29].

2.4. Determination of HAAs

HAAs Concentrations were determined by an Agilent 6890 gas chromatograph system equipped with a [63]Ni electron capture detector (GC-ECD) operated by HP Chemstation software. The analytical column purchased from Supelco (Bellefonte, PA, USA) was SPB-1701, coated with 14% cyanopropyl-phenyl, 86% dimethylpolysiloxane (30m x 0.32mm id, 0.25mm film thickness). The temperature of the injector and the detector were respectively 250 and 300°C, while the oven's temperature was programmed as 40°C for 2min, then increased to 120 °C at 5 °C.min^{-1} and then to 250 °C at 25 °C.min-1 for 10min. Helium was used as carrier gas with a flow rate 1.5 mL/min. The derivatization of HAAs into their methyl esters was carried out with acidic methanol esterification [27]. The injector was operated in the splitless mode. Nitrogen was utilized as a make-up gas at 60 mL/min [26].

2.5. Determination of THMs

The determination of THM and the optimization of HS-SPME conditions were performed by a Hewlett-Packard 6890 gas chromatograph equipped with a split/splitless injection port, an [63]Ni electron capture detector (GC-ECD) and worked by HP Chemstation software was used for the experiments. The injector was used in splitless mode (4 min) and held isothermally at 250 °C. The column used for analysis was VOCOL (60 m×0.32 mm ID, 1.8 μm film thickness, Supelco). The initial oven temperature was set at 60 °C for 4 min, ramped at 15 °C/min to 210°C and held for 15 min. The ECD system was maintained at 300 °C. The Carrier gas was helium at a flow rate of 1.5 ml/min and the flow rate of the make-up gas was 60 ml/min with nitrogen. [29].

2.6. Statistical analysis

Correlation between total THM and HAA was examined through simple linear regression analysis using an SPSS 9.0 package, introducing individually THMs level as the independent variable, and each studied HAA level as the dependent variable. Multivariate linear regression analysis was used to elucidate THM combination as predictors for the HAA compounds with statistical significance $p < 0.005$.

3. Results and discussion
3.1. Occurrence of HAAs

The outcomes of this evaluation showed that the studied HAAs were detected in all the water samples retained of the distribution network. All of the experiments were conducted in triplicate, and the average concentration of HAA in the distribution system were between 19.34 μg.L^{-1} and 115.48 μg.L^{-1} (Table 2). The concentration levels of HAA exceeded the MCL (60 μg.L^{-1}) recommended by the EPA at the storage tank at the end of the network (Zone 7) because HAA formation continues as long as the water passes through the distribution network. The major species of HAA found in the water under study are MCAA, TCAA and DBAA.

Table 2

HAA concentrations ($\mu g.L^{-1}$) in Bizerte drinking water (n=3).

	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BCAA
Average	18.26	5.63	9.67	4.64	11.96	7.38	6.83
(SD)	10.09	2.36	6.19	2.49	6.54	4.38	2.67
Min	6.65	2.36	2.56	1.65	3.02	1.36	1.74
Max	32.39	8.96	18.97	8.70	21.74	13.81	10.91
Median	16.56	5.347	7.857	3.93	10.84	6.90	7.44

3.2. Occurrence of THMs

The levels of THMs formed following the chlorination addition point in WTP showed that the studied THM ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) were detected in all water samples. The concentration of TTHMs was ranged from 46.55 to 123.24 $\mu g.L^{-1}$. Minimum, average, and maximum values are summarized in Table 3. The THM concentration in water treated samples were almost below the MCL of the USEPA. The detected THM in all analyzed water samples did not exceed the drinking water standards of the EU and the USEPA. Brominated THMs were the main and most ample species. They are fonds with an average concentration about 90%.

Table 3
THM concentrations ($\mu g.L^{-1}$) in Bizerte drinking water (n=3).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
Average	9.92	17.52	29.17	30.67
(SD)	4.44	3.69	4.25	13.12
Min	3.63	12.81	21.03	9.11
Max	15.6	22.25	35.46	48.93
Median	10.59	17.89	29.13	33.04

3.3. Seasonal variations of HAAs and THMs

The seasonal variation and spatial providence of DBPs in a drinking surface water distribution system located in a Bizerte region reflected the occurrence of a sensible significant seasonal variation in water quality occur (Fig. 1). Moreover, the investigation of a great number of collected samples presented that the seasonal and geographical variations of both groups HAA and THM were mainly important in this region [4,30]. A significant change in temperature influences directly the reaction kinetics, and the characteristics of the NOM and its reactivity vary during the season. The bromide concentration range was between 18 and 49 $\mu g.L^{-1}$, these values (<50 $\mu g.L^{-1}$) are considered relatively low, and it may be explained by the fact that the water source was distant from the coastline where there was no salt intrusion. These results are similar to those reported previously by Alomirah et al. and Cowman and Singer [31,32].

It is important to note that The HAA levels in summer, on average, were about two times higher than in winter, whereas average THM in spring were about three times higher than in winter (Fig. 1). The proportions of the different THM and HAA found during this work were similar to the results found by other authors [33,34]. Both the studied HAAs and THMs reflected an increase of the detected concentration at the start of the distribution system and stabilized by the end. This increase could be explained by the fact that the assimilation of NOM by biofilm microorganisms results in on another NOM more hydrophobic and the reaction of oxidation of organic matter by chlorine continues [35]. As a result of their high intra-seasonal changes, the control of the annual average levels of both groups of DBPs can differ extensively because of their spatio-temporal portrait.
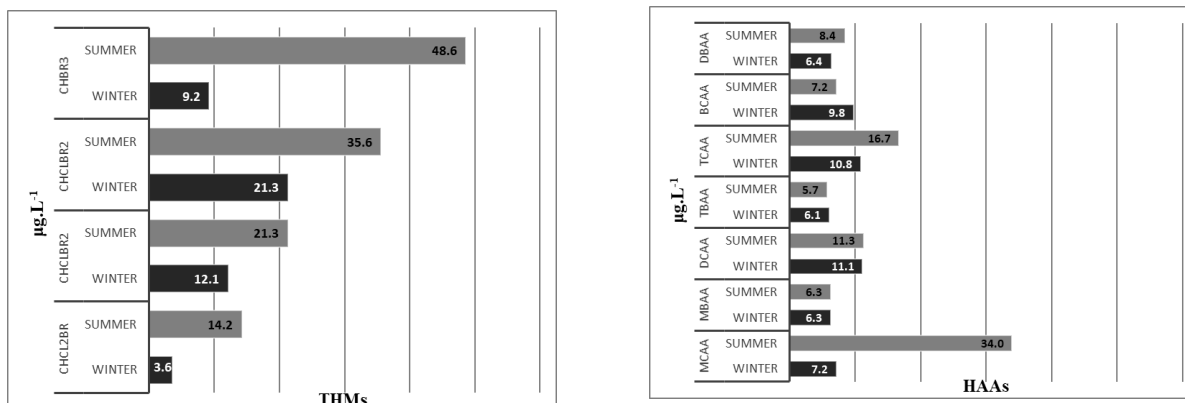

Fig. 1. Seasonal variations of DBPs for water distribution system of Bizerte

3.4. Evaluation of the method

The methods that were used to estimate the LOD, accuracy and precision evaluations were supposed on a linear model and provided acceptable results for each species HAA and THM (Table 4). A calibration study was performed by spiking Milli-Q water with HAA analytes in tested concentration ranges from 0.1 to 200 μg.L^{-1} and from 1 to 50 ng.L^{-1} for THM designed for the estimation of the linearity of the used method. The correlation coefficients (R^2) in linear range of each analyte are presented in Tab. 4. To sum up, the R2 coefficients can be considered good ($R^2 > 0.9935$). The limit of detection for each compound was calculated by comparing the signal-to-noise ratio (S/N) of the

lowest detectable concentrations to S/N=3. The limits of detection for HAA were between 0.05 and 0.90 μg.L^{-1} and between 2.1 and 7.5 ng.L^{-1} for THM. The precision of the method was estimated by carrying out five independent extractions of the studied compounds from Milli-Q water at various spiked levels ranging from 5 to 50 μg.L^{-1} for HAA and 50 ng.L^{-1} for THM. The repeatability (Run-to-run) and the reproducibility (Day-to-day) of the proposed methods were determined by the measurements of five replicates of spiked Milli-Q water under described conditions using external calibration on 1 and 3 days, respectively (Tab. 4).

Table 4
LOD, accuracy and precision data for the used method for HAA species with %RSD in parenthesis.

Analyte species	Linear range (μg.L^{-1})	R^2	LOD HAA (μg.L^{-1}) THM (ng.L^{-1})	Instrument precision (RSD%)		
				Target value (μg.L^{-1})	Repeatability[a] (mean $\pm$ SD) (μg.L^{-1})	Reproducibility[b] (mean $\pm$ SD) (μg.L^{-1})
MCAA	5-200	0.9959	0.90	50	13.13$\pm$ 0.4 (6)	18.28$\pm$0.5 (9)
DCAA	0.1-200	0.9965	0.12	20	19.23$\pm$0.3 (5)	21.05$\pm$0.8(14)
TCAA	0.1-100	0.9976	0.05	5	5.18$\pm$2.1 (14)	5.76$\pm$0.9 (14)
MBAA	1-200	0.9935	0.15	10	11.52$\pm$1.9(18)	9.55$\pm$0.5 (11)
DBAA	0.1-100	0.9966	0.07	5	6.31$\pm$1.1 (10)	4.76$\pm$0.2(8)
CHCl$_3$	0.001-0.05	0.9968	2.1	0.005	0.054$\pm$1.0(11)	0.061$\pm$0.3(7)
CHCl$_2$Br	0.001-0.05	0.9952	7.5	0.010	0.058$\pm$2.2(8)	0.041$\pm$1.5(15)
CHClBr$_2$	0.001-0.05	0.9947	2.8	0.005	0.063$\pm$1.6(8)	0.043$\pm$1.4(9)
CHBr$_3$	0.001-0.05	0.9979	3.2	0.005	0.046$\pm$0.5(7)	0.057$\pm$0.9(12)

[a] n=5

[b] n=5 replicate x 3 days

3.5. Relationships between HAAs, THMs

The resolve of the relative importance of one DBPs on the other species is essential in order to find an assembly of probable relationships between the occurrence of HAAs and THMs. This associations can help if THM levels can be used as surrogate of HAA levels or not. A modest correlation between HAAs and THMs in studied water samples were observed (Fig. 2). The correlation between HAA and THM is based on the dataset collected in different geographic point of studied distribution system. The independent variables (CHCl$_3$, CHCl$_2$Br, CHClBr$_2$, CHBr$_3$) have a
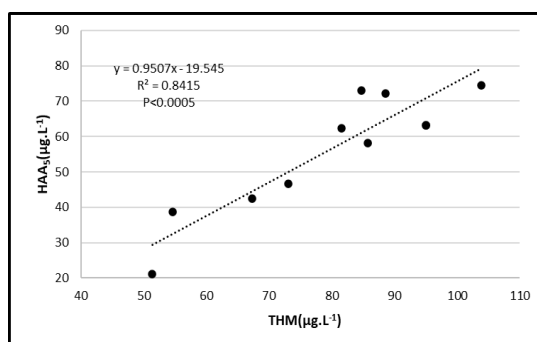
greater effect on the dependent variable (MCAA, DCAA, TCAA, MBAA, DBAA, BCAA, TBAA) in a multiple regression analysis represented by standardized coefficients, also called beta coefficients (Fig. 3). Also, the variances of dependent and independent variables present good correlation. The representativeness of HAA dataset was checked by comparing of the average of THM levels and no significant differences were discovered among them p<0.0005. Linear regression analysis exposes a high-level and statistically significant correlation between THM and HAA, Y=0.950X–19.545; Pearson's correlation coefficient R^2=0.845 (Fig. 2).

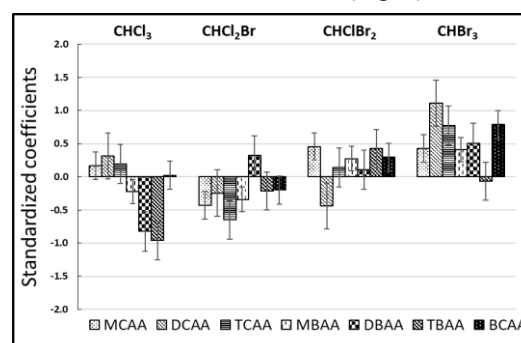Fig 2. The correlation between THM and HAA levels.

Fig 3. The strength of each considered THM on the

concentrations of studied HAA.

The range of predicted HAA$_5$ values is 16.42 to 108.12 µg.L^{-1} and validation values were predicted within 10 µg.L^{-1}, while 90% of all values were predicted within µg.L^{-1} (Fig. 4).

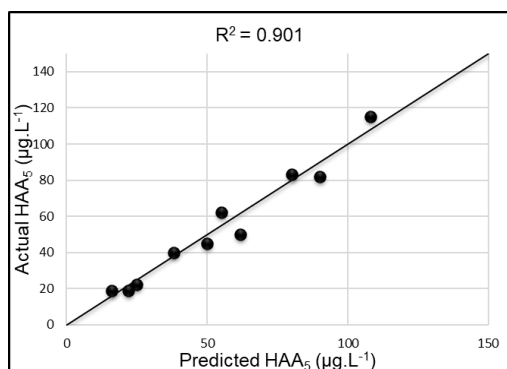
Fig. 4. Predicted and Actual amount of HAA5 (µg.L^{-1}).

3.6. HAA-THM Modeling

The moderate relationships found between HAAs and THMs, allows the development of an interesting multivariate linear regression models for DBPs. Multivariate regression-based modeling permits the simultaneous study of the significance of HAA individual determination on THM occurrence. After being established, these models can also be used as simulation method that has as objective which is the prediction of HAAs levels. In literature few authors have developed multivariate linear regression models for HAA formation but the most attention was given to modeling of THMs [36].

The coefficient of determination (R^2) determines the proportion of the variance in the dependent variable that is predicted from the independent variable. It indicates the level of variation in the given data set.

Models for HAAs levels were developed with good value of statistical coefficients of determination R^2 (between 0.60 and 0.95). Though, most of the variables are significant (p = 0.0005). The relatively values for formed HAAs in water were even much lower than THMs. Details for the HAAs Models predicting are offered in Table 5. Multivariate linear regression analysis shows that some HAA are highly correlated to specific THM. The concentrations of DCAA, BCAA, DBAA, and TBAA acids represented a strong correlation with THM (R^2 > 0.9) (Table 5). TCAA is also correlated with THM but with a lower correlation coefficient (R^2 > 0:8; p=0:0005). MCAA and MBAA are less correlated with THM (R^2 = 0.608 and 0.728 respectively).

The THM determination seems easier and faster than for HAA. Since these studied HAA are non-volatile compounds and they required as an essential step of derivatization, so that the corresponding haloacetates can be injected for detection by gas chromatography electron capture detection (GC-ECD). In general, this derivatization step is an esterification reaction and more precisely methylation reaction described in a previous work [27,28] which requires optimization control and monitoring of its yield. Using the strongest correlation obtained between HAA and THM (Fig. 2) and to avoid the laborious step of derivatization, THMs can be considered as an excellent surrogate for HAA. The calculated equations from these correlations may be beneficial for the approximation of HAA concentrations from THM.

Table 5

Predictive models for the determination of HAAs concentration from those of THMs

Haloacetic acids (Yi)	Model (Xi)[a] Regression coefficient Significance
DCAA	$Y_1 = 7.61 + 0.16 \times X_1 - 0.15 \times X_2 - 0.24 \times X_3 + 0.20 \times X_4$
	0.955
	$p < 0.0005$
BCAA	$Y_2 = -1.127 + 1.43 \times X_1 - 0.14 \times X_2 + 0.18 \times X_3 + 0.16 \times X_4$
	0.931
	$p < 0.0005$
DBAA	$Y_3 = 1.29 - 1.21 \times X_1 + 0.57 \times X_2 + 0.16 \times X_3 + 0.25 \times X_4$
	0.927
	$p < 0.0005$
TBAA	$Y_4 = -2.96 - 0.94 \times X_1 - 0.25 \times X_2 + 0.85 \times X_3 - 2.14 \times X_4$
	0.906
	$p < 0.0005$
TCAA	$Y_5 = 8.81 + 0.26 * X_1 - 1.09 * X_2 + 0.21 * X_3 + 0.36 * X_4$
	0.895
	$p = 0.0005$
MBAA	$Y_6 = 2.78 - 0.12 * X_1 - 0.23 * X_2 + 0.16 * X_3 + 0.81 * X_4$
	0.728
	$p = 0.0005$
MCAA	$Y_7 = 10.92 + 0.38 \times X_1 - 1.18 \times X_2 + 0.60 \times X_3 + 0.33 \times X_4$
	0.608
	$p = 0.0005$
[a]$X_1 = CHCl_3,\ X_2 = CHCl_2Br,\ X_3 = CHClBr_2,\ X_4 = CHBr_3$	

4. Conclusion

This study was designed to investigate the occurrence of HAAs and THMs in drinking water and to generate a reliable portrait of the evolution of these two DBP species in the drinking water of one region located in the north of Tunisia. The portrait shows that both two groups of DBPs not exceed the MCL preconized except for HAA at the end of the distribution system. The Seasonal variations analysis of DBPs showed that the highest concentrations of such substances were observed at the hot season. The range of HAA values in the distribution system is 19.34 µg.L-1 to 115.48 µg.L-1 and the range of predicted HAA5 values were 16.42 to 108.12 µg.L-1. The validation of these results showed that the error of prediction was low between the observed and the predicted data.

The resultant dataset displays a statistically significant correlation between total THM and HAA (Pearsons's correlation coefficient, $R2 = 0:8415$; $p < 0:0005$). Besides, studied HAA are highly correlated with studied THMs. Therefore, multivariate linear regression analysis of the concentrations observed show that the levels of studied HAA can be predicted from the THM amount. Finally, this allows to consider THM species as a surrogate of HAAs for the tap water of Bizerte. These outcomes were very imperative for epidemiological studies on health as well.

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