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Models for predicting HAA$_5$ formation as a function of pH, chlorine dose and UV$_{254}$ in a drinking water system

Bechir Hammami

Department of Chemistry, College of Science, Qassim University, Buraidah 51452, Saudi Arabia

Faculty of Sciences of Bizerte FSB, University of Carthage, 7021 Jarzouna, Tunisia

Abstract

In water disinfection, the predominantly disinfectant used for drinking water is chlorine. The generation via reactions with natural organic matter (NOM) in chlorine disinfection of drinking water consequently results the formation of disinfection by-products (DBP). The paramount of these DBPs, are haloacetic acids (HAA) that have different factors touching their concentrations, which are, bromide concentration, pH, temperature, free chlorine dose, contact time and NOM. However, their formation mechanisms are still being searched. In this research, we developed a multivariate linear regression model of analysis based on the use of water quality parameter in order to predict the concentrations of different compounds of HAA$_5$ and total HAA$_5$. The effects of pH, free-Cl$_2$ and NOM level on yields as well as the speciation of HAA in chlorinated water are studied. The results of this investigation showed that the obtained experimental water quality parameter data presented average value that are; pH= 7.25, free-Cl$_2$= 2.84, UV$_{254}$=0.16. A strong relationship between HAA formation and the studied water quality parameter was revealed to be R^2>0.885. The regression coefficient R^2 values of the established models varied between 0.70 and 0.97, indicated an excellent predictive aptitude for water quality parameters and HAA$_5$ in drinking water. The obtained statistical evaluation indicates that under the measurements of pH, chlorine dose and UV$_{254}$ values, the formation of HAA$_5$ in water can be described by the multiple linear regression technique. Moreover, these Contaminants Modeling are relevant for the study of human health effects through the exposure to DBPs and taking in consideration that the consumed water was collected from different resources with different properties.

Keywords: Chlorination. Disinfection by-products. Drinking water. Haloacetic acids. Speciation

1. Introduction

Disinfection by-products found in tap water were formed when a disinfectant reacts with natural organic matter (NOM) and/or bromide/iodide presented in a raw water source [1,2,3]. The most common disinfection by-products after trihalomethane (THMs) found in drinking water are the haloacetic acids (HAAs) and there are nine chloro- and bromo-HAAs in total [4,5,6,7]. The haloacetic acids are classified as mono halogenated acetic acid (MXAA) (monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA)), dihalogenated acetic acid (DXAA) (dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA)) and trihalogenated acetic acid (TXAA) (trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA),

dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA)). These components are classified as possible human carcinogens by the United States Environment Protection Agency (EPA) [8]. The presence of these compounds in drinking water causes a serious health concern [9,10]. In the US EPA guidelines, the maximum contaminant levels (MCL) specified in the DBP Stage I Rule are 60 µg.L^{-1} for the sum of five HAAs (HAA5: MCAA, DCAA, TCAA, MBAA, DBAA)[11] and the World Health Organization (WHO) have established guideline values for MCAA, DCAA and TCAA at 20, 50, and 200 µg.L^{-1}, respectively, in finished drinking water, though as provisional [12].

DBPs are formed when NOM, that remains after the treatment procedures, reacts with the used disinfectants. Therefore, to gain a better

understanding of the origins and occurrence of the creation of DBP, very extensive research has been carried out to detect the levels of DBP and their precursors [13,14,15], the reaction pathways and the physical parameters that lead to DBP's formation [16]. Besides, DBP precursors can be organic matter [17,18,19] or inorganic matter, such as bromide and/or iodide present in the natural water source [20,21,22]. Physical parameters, such as the pH, the type of disinfectants, the contact time, the temperature and the disinfectant dose have also been extensively studied and they are well known by their ability to alter the formation of HAAs [23,24,25].

Some previous researches suggested several empirical models related to the mechanisms of DBP formation [26]. Several models were expressed as multiparameter function and they resulted from linear and nonlinear multi-regression analysis [27]. The different parameters of raw water and treatment plants which are used for building these empirical models are; the amount of total organic carbon (TOC) or dissolved (DOC), the ultraviolet light absorbance at 254nm (UV254), the chlorine dose, the bromide quantity, pH, temperature and reaction time [28,29,30,31,32]. Most of these models are considered as specific water sources, and they are unsuitable in other aquatic places that have different conditions [33]. A study showed that a water treatment plant distributing water at pH 5.5 produced as much THM as HAA, while factories that have a pH above seven produced more THM than HAA [34]. In addition to the effects of pH on the formation of THMs and HAAs, many DBPs tend to be hydrolyzed under alkaline pH conditions (pH> 8.0) [35].

The improvement of an efficient and accurate model concerning the quality of water parameters is essential to get a prediction methodology for the formation of DBPs [36,37]. Between these parameters UV254 is perhaps the most widely used for describing NOM [38]. However, aromatic and humic substances present the essential form of NOM, which have the higher absorption at 254nm [39]. The aromatic compounds were generally considered to be the primary precursors for HAAs and many DBPs because they contain significant amounts of aromatic fractions that are extremely reactive with chlorine and other oxidants.

The objective of this study is to develop statistical models for the prediction of HAA5 formation and the elimination of NOM. This study is the first investigation in Tunisia related to modeling of HAA5

formation in tap water of Bizerte. Besides, there are no other studies that has been done for the prediction of HAA5 formation in Tunisian water so far. Therefore, in this research we try to apply multi linear regression analysis to predict the formation of HAA5 during chlorination of Bizerte reservoir water with water quality parameters specifically organic matter content (expressed as UV254). However, this is the first investigation to determine the relationships between quality water parameter and different compounds of HAA5 formed from NOM fractions derived from different sources. The contamination level of HAA5 was used to predict HAA5 formation. In addition, the correlations between UV254, pH, chlorine dose and formation of HAA5 were determined for the studied water sources. The efficiency of the contaminant model was evaluated through the examination of various statistical parameters, including regression coefficient (R2), the F statistic, and the α value for linear regression. These statistical evaluations are intended to provide contaminant modeling of HAA5. In addition, these models were developed to provide a better understanding on the formation of HAA in water treatment plant and the chlorine demand of treated water.

2. Experimental:

2.1. Study area and water sampling

Drinking water supplied in Bizerte comes from surface **sources**. Eighty-six drinking water samples were taken for the analysis of HAA, 6 samples of raw water, 6 samples after sand filtration, 6 samples from finished water reservoir at Bizerte's WTP and 68 samples from different seven representative points of the distribution system during eight-month sample program.

Water samples were collected using a 200-mL amber glass bottles with PTFE-faced septa and propylene screw caps. Ammonium chloride (NH_4Cl) as dechlorinating agent were added to the sample in order to produce a concentration of $100mg.L^{-1}$, headed to stop further disinfection by-products formation. All samples were transported to the laboratory, transferred to a refrigerator at 4°C away from light and analyzed within two days from being collected [40].

2.2. Experimental analysis

The water quality parameter analyzed in this study included pH, TOC, Free-Cl_2 and UV_{254}. The analysis of pH used pH meter, TOC were directed with a Shimadzu TOC-5000 equipped with a Pt catalyst [41], the residual free chlorine (Free-Cl_2) was

measured by iodometric method [42] whereas UV_{254} were measured on site.

HAA5 (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, dibromoacetic, tribromoacetic and bromochloroacetic) were analyzed following a previously optimized procedure [43]. Briefly, 40 mL Tap water samples were treated with sulfuric acid, anhydrous sodium sulfate and methyl tert-butyl ether (MtBE). Then, 2mL of the MtBE extract were evaporated to dryness and the following reagents; 0.1 g of anhydrous sodium sulfate, 30 µL of concentrated sulfuric acid and 50 µL of methanol were added. The HAAs were derivatized at 55°C for 10 min and the Headspace-solid-phase microextraction (HS-SPME) is applied during 10 min at 25°C with 100-mmpolydimethylsiloxane fiber to extract the formed haloacetates. Finally, the corresponding haloacetates were desorbed for 2 min in the injector port of the gas chromatograph at 250°C equipped with electron capture detection (GC-ECD).

2.3. Statistical analysis

The correlation between HAA5 and studied parameters (pH, UV_{254}, Free-Cl_2) was examined through the multiple linear regression analysis. The specific variables of pH, UV_{254} and Free-Cl_2 were used to predict the significance correlation of HAA5 levels. On the one hand, the HAA5 levels were used as the independent variable and pH, UV_{254}, Free-Cl_2 levels were used as the dependent variable at the 0.05 level of significance. On the other hand, Multi-Linear regression analysis was performed using Excel 2010 software to determine the Pearson's correlations between pH, UV_{254}, Free-Cl_2 and the HAA5 compound. The linear regression coefficient (R^2), P-value, and equation were obtained for HAA5.

3. Results and Discussion
3.1. Evolution of water quality parameters

Many factors involved in the formation of DBPs, their combined effects on DBP levels is difficult to predict. The levels of DBP present in water networks depend on the respective characteristics of the raw water, the treatment strategies, and the distribution network. One of the most important water quality parameters is the NOM in terms of concentration and type and propensity to originate from HAA, frequently measured using surrogate parameters. Total organic carbon (TOC), dissolved organic carbon (DOC) and UV254 are the most commonly used surrogate parameters. Furthermore, UV absorbance at 254nm reflects the concentrations of main DBPs precursors in water, that can be used to specify the nature and reactivity of the precursor. Although, other work proposes granular activated carbon (GAC) adsorption as one of the best available technologies for removing NOM in drinking water treatment [44]. They propose a GAC adsorption of intermediate aromatic halogenated DBPs during chlorination, rather than a GAC adsorption of NOM prior to chlorination.

The results of the measurements of these parameters are recorded in Table 1. For pH, a relatively small decrease (3 to 6%) during treatment is observed. In addition, the variations in TOC and UV254 during treatment are significant (Fig. 1). These two parameters undergo a reduction of 50% for the TOC and 25% for the UV254 in the station. This result shows that the effectiveness of the water treatment can be considered as adequate.

The evolution in TOC in the WTP and along the distribution network is shown in Fig.1. We note that this parameter decreases as the water moves away from the treatment plant and the distance increases. The lowest TOC contents are observed at the end of the network. Thus, the reduction in TOC exceeds 50% between the start of the network to the end. Moreover, this decrease is due to the fact that the residence time of the water increases and this is what makes the reaction of organic matter by chlorine continues throughout the distribution network. The evolution of UV absorbance at 254 nm is different from that of TOC (Fig. 1). While TOC tended to decrease with residence time, the UV254 appeared to increase.

Table 1: water characteristics in the areas of study

Raw water			WTP effluents			
Water after sand filtration			Different points of the distribution system.			
pH	TOC (mg.L^{-1})	UV_{254} (Cm^{-1})	pH	TOC (mg.L^{-1})	UV_{254} (Cm^{-1})	Cl_2 (mg.L^{-1})
7.4 (10.3)	5.43 (**5.1**)	0.182 (**12.6**)	7.3 (**13.5**)	3.83 (**9.2**)	0.141 (**7.6**)	3.51 (**10.2**)
7.5 (**6.2**)	5.31 (**4.2**)	0.184 (**8.9**)	7.2 (**2.5**)	2.74 (**7.5**)	0.171(**6.8**)	2,62 (**8.4**)

(**RSD**): Relative standard deviations.

Therefore, this could be explained by the fact that the assimilation of NOM by biofilm microorganisms' results in a NOM even more hydrophobic than the original NOM. Consequently, the free residual chlorine in the distribution network contributes directly to the formation of disinfection by-products. It appears that the concentration of DPB increases when the free residual chlorine decreases in the network. As it is shown in fig. 1, a much faster decrease in the concentration of free chlorine was found from R5 to R7. This decrease in the concentration of free chlorine is due because the reaction of NOM by chlorine continues as the residence time of water increases at the end of WTP. The formation of HAA will be more favored when the contact time of chlorine with the NOM present in the water is longer.

3.2. Evaluation of the method

The methods that were used to estimate the limit of detection (LOD), accuracy and precision evaluations were supposed to be on a linear model and provided acceptable results for HAA5 (Table 2). A calibration study was performed by spiking Milli-Q water with studied analytes in tested concentration ranges from 0.1 to 200 µg.L^{-1} designed for the estimation of the linearity of the used method. In addition, the correlation coefficients (R2) in linear range of each analyte are presented in Table 2. The LOD 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 0.07 and 0.82 µg.L^{-1}. Besides, the R2 coefficients can be considered good (R2>0.9928). 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 10 to 50 µg.L^{-1}. 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 the described conditions using external calibration on 1 and 3 days, respectively. Relative standard deviations for Run-to-run precision ranged between 6 and 17% and for Day-to-day precision between 9 and 18% with a standard deviation (SD) of no more than 2 (Table 2).
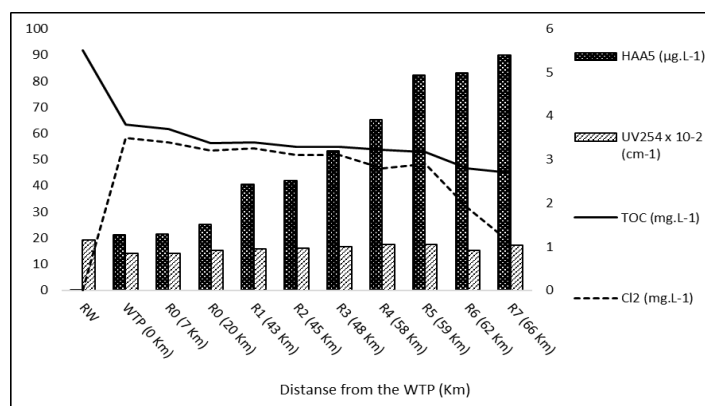

Fig 1. The evolution of HAA5 against studied water quality parameters (UV254, TOC and free-Cl2) in the areas of study

Table 2: Linearity, LOD, accuracy and precision studies for the used method for HAA5 species

| Compound | Linear range (µg L^{-1}) | Instrument precision (RSD%) | | LOD (µg L^{-1}) | R^2 |
		Concentration (µg L^{-1})	Repeatability[a] (mean $\pm$ SD) (µg L^{-1})	Reproducibility[b] (mean $\pm$ SD) (µg L^{-1})		
MCAA	5-200	50	50.2$\pm$1.5 (8)	48.5$\pm$0.2 (17)	0.82	0.9928
DCAA	0.1-200	20	21.9$\pm$1.9 (10)	20.1$\pm$0.8 (18)	0.07	0.9972
TCAA	0.1-100	10	6.2$\pm$1.4 (17)	5.9$\pm$0.9 (12)	0.08	0.9961
MBAA	1-200	10	11.8$\pm$0.3 (6)	10.8$\pm$2.2 (14)	0.32	0.9947
DBAA	0.1-100	10	6.5$\pm$0.6 (11)	5.8$\pm$2.1(9)	0.09	0.9959

[a] n=5, [b] n=5 replicate x 3 days

3.3.HAA levels in tap water

The concentrations of HAA5 in Bizerte's water distribution network are presented in Table 2. The results of this evaluation showed that the HAAs studied were detected in all the water samples taken after the pre-chlorination point. While, the DPBs were not detected in the samples of non-chlorinated water. The average concentration of HAA5 in the distribution system are between 21.30 $\mu g.L^{-1}$ and 89.82 $\mu g.L^{-1}$ (Table 3). As a result, we notice slightly higher levels during the second year of evaluation. In addition, the Concentration levels of HAA5 exceeded the MCL (60 µg.L-1) recommended by the EPA at the storage tank, which is 58 km away from the WTP and reaches their maximum level at the end of the network because HAA formation continues as long as the water passes through the distribution network. This can also be explained by the fact that, the formation of HAA will be more favored, when the contact time of chlorine with the assimilate NOM by biofilm microorganisms present in the water is longer. Also, the free-Cl2 decreases in the network, so the concentration of HAA increases.

A number of studies on the occurrence of HAA in drinking water in different countries have been carried out. Levels of reported HAA have exceeded 100 µg.L-1 in some studies, while the median values range between 15 $\mu g.L^{-1}$ and 40 $\mu g.L^{-1}$ [5,25,45,46]. Because, the sources of water, the method of treatment and the disinfection practices are not the same, it is difficult to compare them, but they often give an idea of general trends. Thus, the concentrations of HAA measured in this work have levels similar to those reported by some authors

3.4. HAA5 correlations

The study of a set of possible relationships for the occurrence of HAAs was possible with the determination of the relative importance of the water quality parameters. Therefore, this would assist in determining whether the levels of water quality parameters can be used as a surrogate for HAA levels or not. This would be essential for quality control and routine monitoring in water services. As observed in fig.3, there are moderate correlations between HAA5 and pH, Dose Cl2 and UV254 for the sites under study.

The representativeness of this sample for the whole dataset was checked by the average HAA5 amounts at the 0.05 level of significance. Moreover, Standardized beta coefficient is used to study which of the independent variables have a greater effect on the dependent variable in a multiple regression analysis. Also, the regression analysis that have been standardized so that the variances of dependent and independent variables are one. Fig. 3 illustrates actual and predicted values of HAA5 as well as standardized beta coefficient. The water quality parameters considered as variables were compared to each other. Furthermore, the strength of the effect of each individual independent variable to the dependent variable was accomplished by a standardized beta coefficient comparison. The higher the absolute value of the beta coefficient highlighted the stronger effect for the HAA5 formation is found with the variable UV254 (0.620) with standard deviations (0.404) fig.3 (a). The range of predicted HAA5 values is 13 to 90 µg/L and validation values were predicted within 5 µg/L, while 95% of all values were predicted within 8 µg/L fig.3 (b).

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Table 3: Concentrations of HAA5 (µg.L-1) in the areas of study

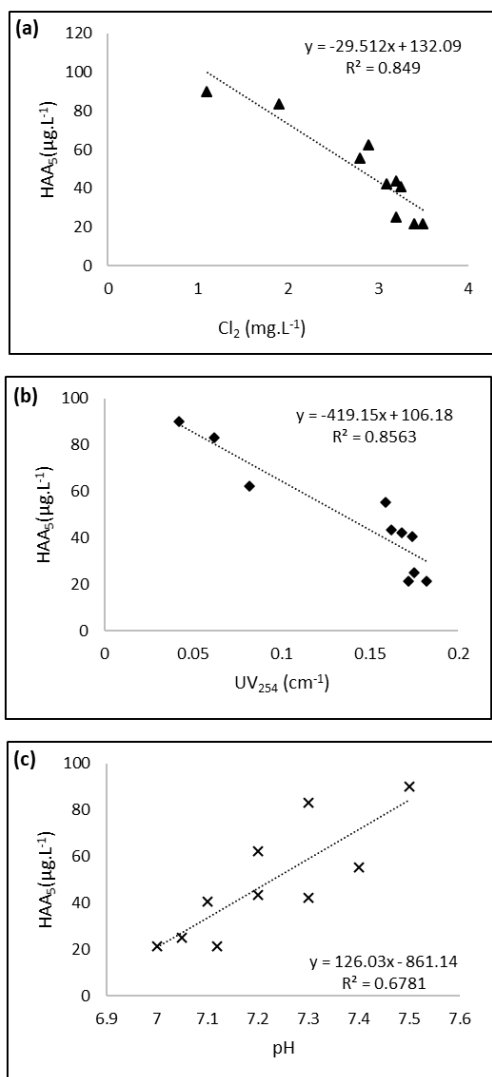|	MCAA	MBAA	DCAA	TCAA	DBAA	HAA5
Average (SD)	18.42 (5.44)	5.94 (10.04)	10.54 (0.94)	12.87 (1.57)	7.63 (7.07)	55.40 (14.21)
Min	5.42	3.71	2.59	2.42	2.89	21.30
Max	32.39	8.96	18.97	21.74	10.91	89.82
Median	16.56	5.61	7.85	10.84	7.30	47.74
% dominance	27.69	8.936	15.85	19.35	11.46	

Fig.2: Scatter plot showing the correlation between HAA5 and (a) free-Cl2 (b) UV254 (c) pH

Linear regression analysis reveals a high and statistically significant correlation between HAA5 and pH, UV254 and free-Cl2 severely; Pearson's correlation coefficient are correspondingly 0.678, 0.856 and 0.849; p<0.0005 fig.3 (a). Multivariate linear regression analysis shows that some HAA are

highly correlated to specific water quality parameters (Table 4). The concentrations of DCAA, TCAA and DBAA acids are highly correlated with the studied quality parameters r >0.9, p<0.0005 (Table 4). Thus, variation of specified quality parameters explains the variability of these HAA. MBAA that were also correlated with water quality parameters but have a lower correlation coefficient (r > 0.8, p<0.0005). MCAA was less correlated with specified quality parameters (r=0.6) (Table 4). The most chlorinated HAA (DCAA and TCAA) are those with the highest predictive capacity, and this explains the concentrations of five HAA examined. Surprisingly, the DBAA correlates significantly with studied variables.

Obviously, in the water disinfection process, the residence time is a significant physical parameter that represents the contact time of water with the chlorine dose. However, this parameter is a difficult variable to estimate in the absence of a hydraulic model (the variations in water main diameter, flow rates, and water demand). Since the contact time and distance vary proportionally, it was decided in this study to classify the sampling points by their distance from the water treatment plant. Therefore, samples were collected from the storage tanks which distances were known precisely [47,48].

For this reason, we have chosen to build our prediction model by performing simple and fast measurements of water physical-chemical parameters, which have a strong correlation. Therefore, for each tank in Bizerte's distribution network that represent the different sampling points for this study, we measure the pH, Cl2 and UV254 as they are the parameters with the greatest correlation. Besides, by applying the established prediction models we can estimate the concentrations of the different HAA species studied.
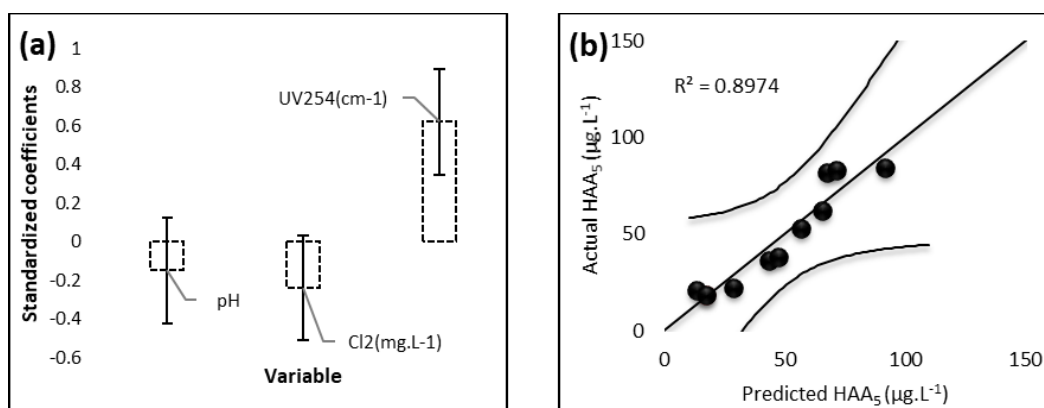

Fig. 3: (a) The strength of studied independent variable (b) Predicted and Actual amount of HAA5 (µg.L-1).

Table 4: Multiple linear regression equations of prediction.

Datasets		Model	R^2 Significance
1	MCAA	MCAA = -7.599-3.890*pH - 3.214*Cl_2+397.074*UV_{254}	0.609 / 0.012
2	DCAA	DCAA = -38.488+1.361*pH+0.173*Cl_2+204.218*UV_{254}	0.928 / 0.0005
3	TCAA	TCAA = 10.405-2.804*pH-3.174*Cl_2+182.168*UV_{254}	0.952 / 0.0005
4	MBAA	MBAA = 12.104-2.619*pH+0.506*Cl_2+68.040*UV_{254}	0.809 / 0.0005
5	DBAA	DBAA = -35.726+0.197*pH-2.698*Cl_2+330.640*UV_{254}	0.971 / 0.0005
6	HAA_5	HAA_5 = -59.304-7.7548*pH-8.407*Cl_2+1182.143*UV_{254}	0.897 / 0.0005

This simple and rapid technique was validated and tested by comparing the quantities estimated by the models with the quantities measured in this eight-month program of this study and a strong correlation was found between them. Therefore, these reliable prediction models may eventually be used to predict HAA quantities. Obviously, the quality of the water is site-specific can vary enormously from one region to another [49,50] but the simplicity of the measurements of these parameters can be promising for the application of this model in other water sources collected from different environments that have varying conditions and after doing a necessary study of correlation. The comparison between predicted and actual values for HAA model indicates that the model seems to be very satisfactory ($R2=0.8974$) and confirming datasets HAA amount in water samples taken during another period (June 2009) [40] from the same reservoir waters and chlorinated under identical conditions of present study. So that the multiple linear regressions are useful for modeling HAA levels in chlorinated water supplies through simple measures of correlated water quality parameters.

4. Conclusions

This study was conducted to evaluate the relationships between the raw water quality and the HAA formation consequential from chlorination at a water treatment plant. Empirical models of water quality parameters, and HAA5 formation were developed using real samples, which were collected through an eight-month program within 154 samples in seasonal variable conditions. Due to the fact that very little data about DBP are poorly presented now a days in the distribution system in Bizerte and in other regions of Tunisia, the generation of information using a modelling approach is very useful. The statistical regression analysis was used to develop the empirical models and only the variables that were statistically significant were considered in the models which are pH, free-Cl2 and UV254. Therefore, relationships of pH, free-Cl2, UV254 were confirmed and quantified. In this study, UV254 is a significant predictor of HAA5 but is also known to be a non-specified NOM. A Further study is needed for a better characterization of NOM (identification of hydrophobic fraction, as an example) and it would give better information about its effects on DBP

occurrence in water. The correlation and regression analysis for examining the relationship between independent variables and the dependent variables models showed promise and the relation appeared to be good. Besides, to test the validity of these models of contamination, data was analyzed and compared to predictive values. The validation results showed that there were no significant differences and the errors of prediction were low between the observed and the predicted data. Finally, the Contamination modeling results highlighted that, with the use of these models, it is possible to estimate HAA5 levels in chlorinated surface water supplies of Bizerte. This reliable model could be recognized as an essential methodological basis for predicting HAA formation in Tunisian regions taking in consideration the drinking water quality parameters.

5. Conflicts of interest

"There are no conflicts to declare".

6. References

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