Experimental Investigation of Trihalomethane Formation and Its Modeling in Drinking Waters

K. Özdemir[1,*], Y. Yildirim[1], I. Toröz[2] and V. Uyak[3]

[1]Department of Environmental Engineering Bülent Ecevit University, Zonguldak, Turkey
[2]Department of Environmental Engineering Istanbul Technical University, Istanbul, Turkey
[3]Department of Environmental Engineering, College of Engineering, Pamukkale University, Denizli, Turkey

*Corresponding author: Fax: +90 372 2574023; Tel: +90 372 2574010/1135; E-mail: kadirozdemir73@yahoo.com

This research developed models using multiple linear regression analysis for the prediction of trihalomethane formation in coagulated Istanbul drinking water sources. The power-law model (model 1), using only ΔUV_{272} as the designed parameter, proved the best model to describe the formation of trihalomethane. The other model (model 2), included pH, total organic carbon, chlorine dosages, ultraviolet absorbance at 254 nm (UV_{254}), specific ultraviolet absorbance (SUVA) and differential absorbance at 272 nm (ΔUV_{272}). The root-mean-square error (RMSE), normalization mean square error (NMSE), regression coefficient (R^2) and index of agreement (IA) were used as statistical variables to evaluate the model performance. The better prediction results were obtained by model 1 for root-mean-square error, normalization mean square error, R^2 and index of agreement as 9.14, 0.015, 0.95 and 0.99, respectively.

Keywords: Drinking water, Trihalomethane, Differential absorbance at 272 nm (ΔUV_{272}), Modeling.

INTRODUCTION

Chlorine is commonly used as a disinfectant to eradicate pathogenic organisms in drinking waters[1,2]. However, when water containing the organic precursor compounds is chlorinated, disinfection by-products such as trihalomethanes and halo acetic acids may be generated[3-9]. Due to the adverse health effects of disinfection by-products on human being, many industrialized countries have developed stringent regulations for the control of disinfection by-products[10,11]. Meanwhile, some international regulatory agencies worldwide have set maximum contaminant levels for disinfection by-products like trihalomethanes. The United States environmental protection agency (USEPA) and European Union (EC) have set to the maximum contaminant levels of four trihalomethane species (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) of 80 µg/L[12-14]. The limit for trihalomethanes is 100 µg/L in Turkey. The formation of disinfection by-products depends on many factors such as solution pH, temperature, the concentration and content of natural organic matter, disinfectant dose, bromide concentration and reaction time[15-18]. For instance the yield of trihalomethanes has been observed to increase with increasing pH[19,20]. Furthermore, several surrogate parameters (total organic carbon, UV_{254} and specific ultraviolet absorbance) have been used to represent the reactivity of natural organic matter (NOM) and disinfection

by-products formation. Among these parameters, specific ultraviolet absorbance is most widely used as a predictive parameter for natural organic matter reactivity[21-23]. However, the differential absorbance at 272 nm (ΔUV_{272}) has been practically used as a spectrophotometric indicator to monitor the formation of disinfection by-products as a result of the chlorination of water reservoirs including natural organic matter [24-26]. Many investigators have suggested several empirical models for understanding the complex nature of disinfection by-products precursors and their reactions with chlorine[27-29]. An extensive form of the different models available to estimate the formation of trihalomethanes.was presented by Lyn and Taylor[30]. In other words, empirical and kinetic trihalomethane formation models were quantified as a power function of various quality parameters and generally obtained by linear and non-linear multi regression analysis[31,32]. Moreover, some researches extended the number of fitting parameters to include total organic carbon, specific ultraviolet absorbance, chlorine dosage, contact time, pH and bromide concentration for modeling the formation of trihalomethanes[33-36].

Developed[14] the model for trihalomethane formation in the chlorination of enhanced coagulated and finished water in Istanbul. They used the chlorine dose, coagulant dose, reaction time and dissolved organic carbon (DOC) values as model variables. Also established[35] the model prediction of trihalomethane and halo acetic acid formation based on pH, contact

time, chlorine dosage and specific ultraviolet absorbance by using multiple linear regression analysis (R^2 = 0.96). In this model, the model regression coefficients of trihalomethane and halo acetic acid were found as 0.88 and 0.61, respectively.

The objective of this study is to develop a statistical model for the prediction of trihalomethanes formation in coagulated water samples that are chlorinated. Within this scope, three Istanbul reservoirs known as Terkos lake water, Büyükçekmece lake water and Ömerli lake water were studied in jar test experiments. In this study, we attempted to develop a fitting model representing the formation of trihalomethanes during chlorination of coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples under the different chlorination conditions with respect to multiple linear regression analysis. The model variables used were ΔUV_{272}, chlorine dosage, total organic carbon, specific ultraviolet absorbance, chlorination pH and alum dose.

EXPERIMENTAL

Sample collection: Raw water samples were taken from three lakes of Terkos, Ömerli and Büyükçekmece in Istanbul. Approximately 2 million m^3 of per day of drinking water is provided from these reservoirs. Raw water samples were collected as a grab sample by treatment plant personnel and shipped to the water quality laboratory of the Istanbul Water Utilities Administration (ISKI) on a same day. When water samples were received at the laboratory, they were kept in the dark in a refrigerator at +4 °C to prevent biological activity prior to use.

Coagulation procedure: Coagulation of Terkos lake water, Büyükçekmece lake water and Ömerli lake water was carried out using alum ($Al_2SO_4 \cdot 18H_2O$) doses ranging from 20 to 120 mg/L using a jar-test. Jar tests were prepared by using a Phips and Bird six paddle jar-test apparatus. The Jars were round beakers with 1 L capacity. Rapid mixing was at 150 rpm for 2 min; flocculation was carried out at 40 rpm for 30 min. After coagulation, coagulated samples were stood for 60 min for settling and then they were filtrated through a 0.45 µm membrane filter.

Chlorination procedure: Chlorination of the raw water samples was conducted in accordance[37] with Standard Methods 5710 B. Before chlorination. the pH of the samples were buffered to pH 7 by using a phosphate buffer (adjusted with HCl and NaOH solution if necessary). Chlorine stock solution was prepared from 5 % sodium hypochlorite and the concentration (5 mg/mL) was obtained calorimetrically by the DPD method. The chlorinated samples were placed in to 125 mL amber glass bottles with polypropylene screw caps and TFE-faced septa. These were then incubated in a dark room for 24 h. Sodium sulfite solution was used as a quenching agent for all the chlorinated samples prior to performing UV spectro-photometric and trihalomethane analysis.

Analytical procedure: Trihalomethane measurements were performed by liquid-liquid extraction (LLE) with *n*-pentane. For trihalomethanes, a total of six trihalomethane calibration standards were prepared using certificated commercial mix solutions (Accu Standard, Inc., purity > 99 %). Samples were analyzed by gas chromatography (GC) equipped with a micro electron capture detector (µECD) for trihalomethane analyses. A capillary column of 30 m × 0.32 mm ID × 1 µm film thickness was used (DB-1 J&W Science). The sample was injected in split/splitless mode with helium as the carrier gas and nitrogen gas as a make-up gas. The minimum quantification limits for trihalomethane species ranged between 0.5 and 1µg/L. Dissolved organic carbon concentrations were measured on a Schimadzu 5000 total carbon analyzer equipped with AS auto sampler according to method 5310 B in standard methods[37]. The instrument provided reliable, accurate and reproducible data with a minimum detection limit of 2 µg/L C. The readings of UV absorbance at 254 nm and the differential UV absorbance at 272 nm were determined with a Shimadzu 1608 UV/VIS spectrophotometer.

Methodology and performance of the model: The model development was carried out using the total trihalomethane (TTHM) concentrations from experimental chlorinated raw water samples. The general relationship between concentration and explanatory variables is given as follows:

$$C = F(x_o, \ldots, x_k) \qquad (1)$$

where X_i (i = 2,.....k) are explanatory variables

In many studies, investigators used a power-law model for the function F. So, the concentration can be expressed as follows:

$$C = F(x_o, \ldots, x_k) = 10^{B1} X_2^{B2} \ldots X_k^{Bk} \qquad (2)$$

where k is the number of explanatory variables. Taking logarithms of both sides, thus;

$$\log C = B_1 + B_2 \log(X_2) + \ldots + B_k \log(X_k) \qquad (3)$$

where B_1 is the intercept, B_2-B_k is the partial slope coefficients. In this respect, two different multiple regression models can be proposed.

Model-1: In this model the relationship between the concentration and explanatory variables is linear and a power-law is used. The model equation may be explained as follows:

$$\log C = \log[B_o] + B_1[\log(X_1)] + B_2[\log(X_2)] + \ldots + B_k[\log(X_k)]$$

Model-2: In this model the relationship between concentration and explanatory variables is linear and a power-law is not used. The model equation may be explained as follows:

$$C = B_o + B_1 X_1 + B_2 X_2 + \ldots + B_k X_k$$

In order to quantify the model performance, predicted values and observed data have been evaluated with the following statistical measures (RMSE, index of agreement, R^2, normalization mean square error, FB and PE) as employed by many researchers[38-40]. The root-mean-square error (RMSE) is:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (O_i - P_i)^2} \qquad (4)$$

The normalization mean square error (NMSE):

$$NMSE = \frac{\sum_{i=1}^{N} (O_i - P_i)^2}{\sum_{i=1}^{N} (P_i)^2} \qquad (5)$$

Square of correlation coefficient (R^2):

$$R^2 = \frac{\left(\sum_{i=1}^{N} (O_i - O_m)(P_i - P_m) \right)^2}{\sum_{i=1}^{N} (O_i - O_m)^2 (P_i - P_m)^2} \qquad (6)$$

Index of agreement (IA);

$$IA = 1 - \frac{\sum_{i=1}^{N}(O_i - P_i)^2}{\sum_{i=1}^{N}\left[|O_i - O_m| + |P_i - P_m|\right]^2} \qquad (7)$$

where O_i and P_i are the observed and predicted total trihalomethane concentration values on day i, N is the number of days in the test set. O_m and P_m represent the means of the observed and predicted total trihalomethane concentration.

These indices make assessments of the global performance of the model. Root-mean-square error represents differences observed and predicted data. index of agreement varies between 0 and 1, the latter representing perfect agreement between observed and predicted values. R^2 represents the square of the correlation coefficient, achieving perfect agreement when R^2 is equal to 1. The perfect agreement between observed and predicted values are indicated when NMSE = 0.

Scatter diagram and factor of exceedance: A scatter diagram represents agreement between predicted and observed data sets. A value above the y = x line indicates a situation of over-prediction and the reverse is true for a situation of under-prediction.

The factor of exceedance (FOEX) is a useful measure of the extent of over- or under-prediction. If N pairs of observed (O_i) and predicted (P_i) values are plotted in a scatter diagram and if $N_{(O_i > P_i)}$ is the number of over-predictions, for example the number of pairs where $O_i > P_i$, then factor of exceedance can be defined as[39]:

$$FOEX = \left[\frac{N_{O_i > P_i}}{N} - 0.5\right]100 \qquad (8)$$

If factor of exceedance is equal to -50 %, then all points lie below the y = x line, indicating all the modeled results are under-predicted. If factor of exceedance equals +50 % then all the modeled results are over-predicted. If factor of exceedance equals 0 % then one observes optimum distribution of data where there are half-under- and half-over-predictions.

RESULTS AND DISCUSSION

Effects of coagulation process on trihalomethane precursors: A substantial amount of trihalomethane precursors leading to the formation of trihalomethanes during the chlorination of waters has been removed by the coagulation process. Within this goal, Terkos lake water, Büyükçekmece lake water and Ömerli lake water were coagulated using an alum dosage range of 20-120 mg/L. Fig. 1 shows the change of DOC and UV_{254} values in Terkos lake water, Büyükçekmece lake water and Ömerli lake water by alum coagulation. The percentage reductions in DOC values were 20, 10 and 8 % with the alum dose of 20 mg/L at Terkos lake water, Büyükçekmece lake water and Ömerli lake water, respectively. These removal ratios were increased to 65, 47 and 41 % with the highest alum dose of 120 mg/L. Likewise, the highest UV_{254} removal was observed the alum dose of 120 mg/L for all coagulated raw waters. For instance; as the UV_{254} values decreased from 0.16 to 0.118 cm^{-1} with the alum dose of 20 mg/L in Terkos lake water, this value decreased significantly to 0.035 cm^{-1} with an alum dose of 120 mg/L. In other words, the ratio of UV_{254} removal for Terkos lake water increased from the percentage of 26 to 78 % with the alum dosage range of 20-120 mg/L. Similar trends were observed for the other coagulated raw water samples with regard to UV_{254} removals (Fig. 1). Comparing the percentage reduction in DOC and UV_{254} values for the three coagulated water samples, DOC was removed by coagulation to a lesser extent than the change in UV_{254}. This result suggests that coagulation preferentially removed UV-absorbing chromospheres. This observation is in accordance with the results of prior studies[14,41].
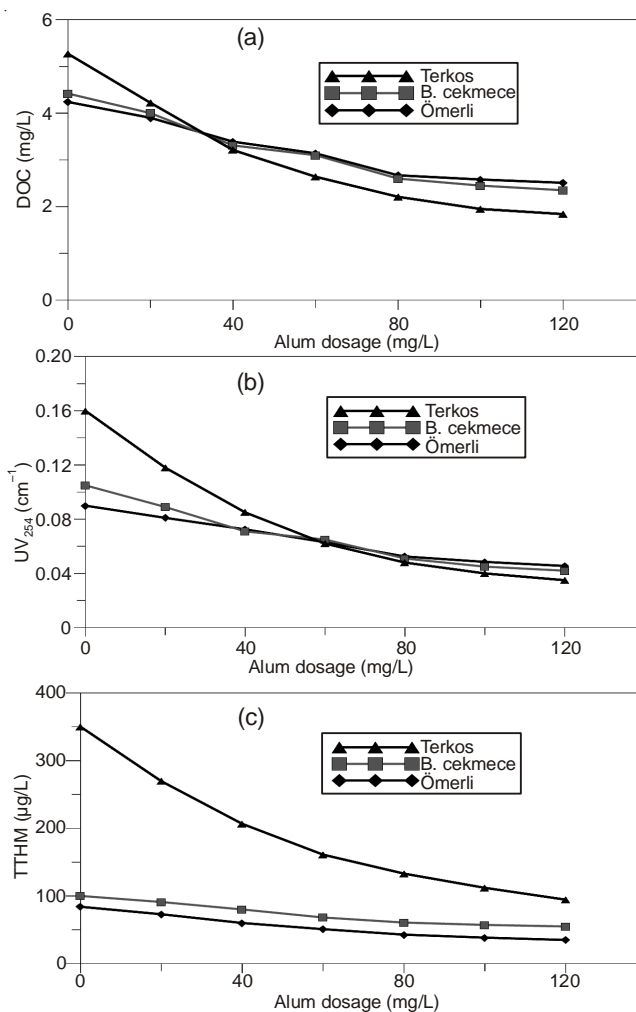

Fig. 1. Coagulation of Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples with the alum dosage range of 20-120 mg/L; (a) DOC removal (b) UV_{254} removal (c) TTHM removal

The variation of the amount of total trihalomethane formation during the chlorination process (chlorine doses ranged from 2 to 10 mg/L) of coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water with the alum dose ranging from 20 to 120 mg/L in reaction time of 24 h is also shown in Fig. 1. Among the chlorinated water samples, the highest total trihalomethane removal of 73 % was accounted for by the highest alum dose of 120 mg/L in chlorinated Terkos lake water samples (Fig. 1). Furthermore, since the hydrophobic content of the natural organic matter contained more activated aromatic carbon structures than that of the hydrophilic content, the

highest total trihalomethane formed in the 24 h reaction time was determined in Terkos lake water samples with the specific ultraviolet absorbance level of 3.04 L/mg.m. This finding suggests that the hydrophobic structures into the natural organic matter played a greater role in trihalomethane formation and also were more susceptible to coagulation than the hydrophilic portion of natural organic matter with low SUVA values (< 3 L/mg m) such as the Büyükçekmece lake water (SUVA = 2.38 L/mg m) and Ömerli lake water (SUVA = 2.12 L/mg m). These experimental results are also consistent with previous studies[18,35].

Effect on coagulant dose on pH values: As shown in Table-1, prior to coagulation, pH values measured for each raw water sample and these varied from 8.3 to 7.65. After coagulation, pH values started to decrease with respect to alum dosage. For instance the pH values of coagulated Terkos lake water with an alum dose of 20 mg/L fell from 8.1 to 7.7. Similar findings were observed for Büyükçekmece lake water and Ömerli lake water samples at an alum dosage of 20 mg/L. The highest pH decrement was measured for the highest alum dosage as 120 mg/L at all water sources. Moreover, as compared to the ratio of DOC removal for coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples at an alum dose of 120 mg/L, the highest DOC reductions determined as 2.51, 2.33 and 2.05 mg/L were observed for the lowest pH values which ranged from 6.49 to 6.31 (Table-1). This also showed that pH values decreased with increasing alum doses.

Effect of chlorine dosage on trihalomethane formation: As the chlorine dosage was increased from 2 to 10 mg/L, the amount of trihalomethane that was formed within 24 h reaction time increased significantly (Table-1).

Further, in this study, kinetic experiments were carried out for raw and coagulated water samples to provide data on trihalomethane formation in 24 h reaction time with an applied chlorine dose range of 2 to 10 mg/L and for incremental additions of coagulated waters (20 to 120 mg/L). According to Table-1, the highest trihalomethane formation within 24 h was found at the highest chlorine dosage of 10 mg/L for each raw water sample before coagulation. The total trihalomethane values of Terkos lake water, Büyükçekmece lake water and Ömerli lake water were 236.7, 100.1 and 84.12 µg/L, respectively, at the chlorine dose of 10 mg/L and the reaction time of 24 h. The highest ratios of trihalomethane removal for coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples were determined as 73, 46 and 62 %, respectively, also at the highest chlorine dosage (10 mg/L). Greater trihalomethane formation and removal ratios were also observed for the Terkos lake water at the chlorine dose of 10 mg/L. These results suggested that as the hydrophobic fraction of natural organic matter like Terkos lake water samples was mostly composed of activated aromatic structures including one-two ring aromatic carboxylic acids, one and two ring phenols and tannin, it produced more trihalomethanes than the hydrophilic fraction of natural organic matter.

Since the hydrophobic portion of natural organic matter was preferably removed compared to that of the hydrophilic portion during the coagulation process, Terkos lake water had the highest ratio of trihalomethane removal. This result is also confirmed by other published findings[7,42].

Effects of trihalomethane precursors on trihalomethane formation: Dissolved organic carbon, SUVA and UVA_{254} are the main organic parameters used for understanding of natural organic matter reactivity in water sources. Among these parameters, SUVA is an effective surrogate parameter, used for predicting of natural organic matter precursor, leading to trihalomethane formation. For the three water samples studied, SUVA values decreased commonly with respect to applied alum dosages (Table-1). As shown Fig. 2, the highest trihalomethane formation as 388 µg/L was determined in Terkos lake

TABLE-1
CHARACTERISTICS OF ORGANIC PARAMETERS IN TERKOS LAKE WATER, BÜYÜKÇEKMECE LAKE
WATER AND ÖMERLI LAKE WATER SAMPLES DURING THE COAGULATION AND CHLORINATION PROCESSES

Water resources	Alum (mg/L)	DOC (mg/L)	UV_{254} (cm⁻¹)	$SUVA_{254}$ (L/mg-m)	$TTHM_{24hr}$ (µg/L)	ΔUV_{272} (cm⁻¹)	DOC (%)	UV_{254} (%)	$TTHM_{24hr}$ (%)
Ömerli lake water	0	4.24	0.0900	2.12	84.12	0.047	0	0	0
	20	3.90	0.0810	2.08	73.02	0.0465	8	10	9
	40	3.39	0.0725	2.14	60.11	0.041	20	19	20
	60	3.14	0.0630	2.01	50.98	0.0395	26	30	32
	80	2.67	0.0525	1.97	42.87	0.0405	37	42	39
	100	2.58	0.0485	1.88	38.44	0.038	39	46	43
	120	2.51	0.0455	1.81	34.97	0.0355	41	49	45
Büyükçekmece lake water	0	4.42	0.1050	2.38	100.12	0.046	0	0	0
	20	4.00	0.0890	2.23	91.12	0.0345	10	15	13
	40	3.31	0.0710	2.15	80.12	0.0285	25	32	29
	60	3.10	0.0650	2.11	68.25	0.027	30	38	39
	80	2.60	0.0510	1.96	60.75	0.0265	41	51	49
	100	2.45	0.0450	1.84	57.26	0.0245	45	57	54
	120	2.35	0.0420	1.79	55.02	0.024	47	60	58
Terkos lake water	0	5.27	0.1600	3.04	350.23	0.06	0	0	0
	20	4.22	0.1180	2.80	269.67	0.056	20	26	23
	40	3.21	0.0850	2.65	206.64	0.053	39	47	41
	60	2.64	0.0620	2.34	161.11	0.049	50	61	54
	80	2.21	0.0480	2.17	133.09	0.043	58	70	62
	100	1.95	0.0400	2.05	112.07	0.037	63	75	68
	120	1.84	0.0350	1.90	94.56	0.034	65	78	73

Dissolved organic carbon (DOC); Specific ultraviolet absorbance (SUVA); Total trihalomethane (TTHM)

water samples with SUVA value of 3.04 L/mg m. On the contrary, the lowest trihalomethane formation of 187 µg/L was observed in Ömerli lake water samples with SUVA value of 2.54 L/mg m. In other words, greater trihalomethane yields were generated from waters with higher SUVA values, such as Terkos lake water.
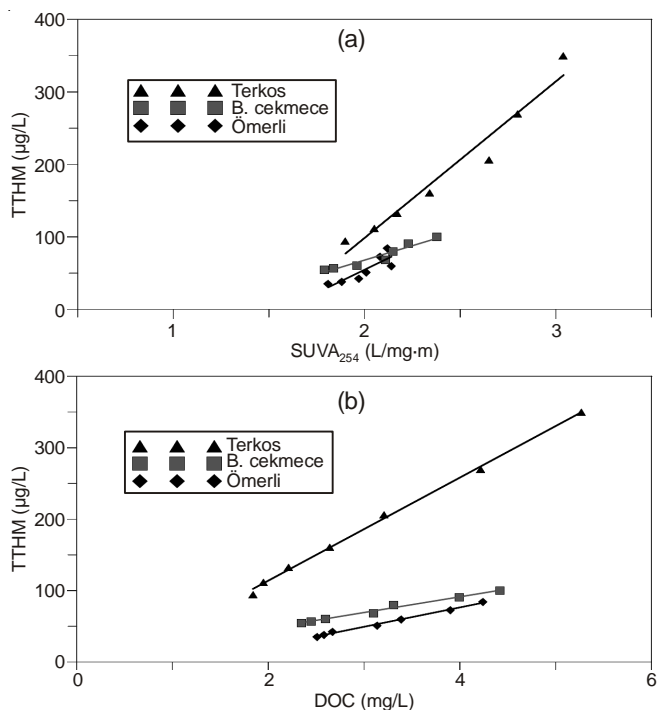

Fig. 2.   (a) Relationship between total trihalomethane concentrations and SUVA$_{254}$ at different Cl$_2$ to DOC ratios in Istanbul reservoirs (b) Relationship between total trihalomethane concentrations and DOC at different Cl$_2$ to DOC ratios in Istanbul reservoirs

In this study it was determined that while strong correlations were established between SUVA and total trihalomethane formation for Terkos lake water and Büyükçekmece lake water samples for the various alum dosages and chlorination conditions, it was not so strong for the Ömerli lake water samples. The corresponding linear regression coefficients (R^2) for Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples were quantified as 0.96, 0.92 and 0.73, respectively. Dissolved organic carbon and UV$_{254}$ have also been widely used as surrogate parameters for monitoring trihalomethane formation. As shown in Fig. 2, good correlations were achieved between DOC, UV$_{254}$ and trihalomethane concentrations for three coagulated water samples with R^2 = 0.99. The UV$_{254}$ and DOC values decreased with increasing alum doses. However the trihalomethanes yields increased during chlorination as the UV$_{254}$ and DOC values increased. The higher trihalomethane values were presented in Terkos lake water samples that had more activated functional groups leading to more trihalomethanes production at various chlorine dosages ranged from 2 to 10 mg/L.

Relations between ∆UV$_{272}$ and trihalomethane formation: Previous studies have demonstrated that the correlations between the differential absorbance at 272 nm (∆UV$_{272}$) and trihalomethanes formation were very strong and linear[6,24,25] with R^2 > 0.95. In this part of the work, a series of experiment

was conducted for coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples to provide of trihalomethane formation in 24 h reaction time *versus* three Cl$_2$/DOC (0.8, 1.6 and 3.2) and different alum doses (20-120 mg/L) (Fig. 3).
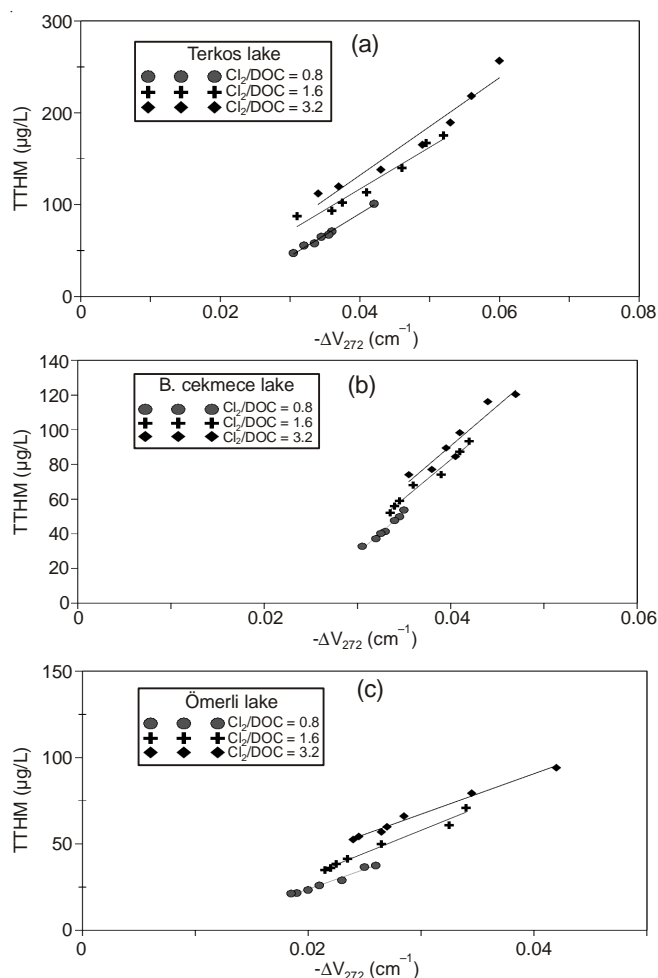

Fig. 3.   Correlations between ∆UV$_{272}$ values and total trihalomethane concentrations at different Cl$_2$ to DOC ratios at pH 7 and in a reaction time of 24 h for; (a) Terkos lake water, (b) Büyükçekmece lake water, (c) Ömerli lake water

The correlations between ∆UV$_{272}$ values and total trihalomethane 24 h for each coagulated water sample were presented in straight lines with R^2 ≤ 0.98. Among the water samples, Terkos lake water had a higher ∆UV$_{272}$ and total trihalomethane values than the other water sources. Its trihalomethane yield and ∆UV$_{272}$ values were 236.36 µg/L and 0.07 cm^{-1}. Likewise, the highest trihalomethane and ∆UV$_{272}$ values monitored were the Terkos lake water samples which had the highest SUVA level of 3.04 L/mg m because its hydrophobic organic carbon content included more activated aromatic compounds. The ∆UV$_{272}$ parameter is a very useful indicator for monitoring trihalomethane formation from the chlorination of water samples. Therefore, in this research, we tried to apply multiple linear regression analysis to model only between ∆UV$_{272}$ and trihalomethane formation during the chlorination of coagulated Istanbul water sources.

Modeling of the trihalomethane formation: In this study, two different multiple regression models were developed for

predicting the concentrations of TTHM based on the use of alum dose, chlorine dose, total organic carbon, SUVA, UV_{254} ΔUV_{272} and pH for coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water samples. The multiple regression models obtained for this study is as follows:

$$TTHM = 15.559 + 1003114^* \, (\Delta UV_{272})^3 \quad \text{Model (1)}$$
$$TTHM = 620.492 - 0671^* \, \text{Alum dose} - 0.569^*$$
$$HOCl - 57.289^* \, TOC + 5035.846^* \, \Delta UV_{272} - 155.658^*$$
$$SUVA^* \, pH + 373.733 \, UV_{254} \quad \text{Model (2)}$$

As seen from Table-2, model-1 gives better prediction performances compared to model-2. Model-2 performance shows that factor of exceedance equals to 0.00 %, meaning optimum distribution of data where there are half-under- and half-over-predictions. However, model-1 performance of factor of exceedance equals to -11.11 %, indicating some of the modeled results are under-predicted. If other statistical measures are evaluated, the better results are obtained by model-1 for root-mean-square error, normalization mean square error, R^2 and index of agreement as 9.14, 0.015, 0.95 and 0.99, respectively. The performance results of the models are presented at Table-2. Fig. 4 presents the comparisons between measured and predictive values for two total trihalo-methane model. As seen in Fig. 4, both models give acceptable total trihalomethane prediction values. At most points in Fig. 4, model-1 gives better prediction values than does model-2.

TABLE-2
MODEL PERFORMANCE RESULTS

	RMSE	NMSE	R^2	IA	FOEX
Model-1	9.14	0.015	0.95	0.99	-11.11 %
Model-2	12.50	0.028	0.90	0.97	0.00 %

Root-mean-square error (RMSE); Normalization mean square error (NMSE); Regression coefficient (R^2); Index of agreement (IA); Factor of exceedance (FOEX)
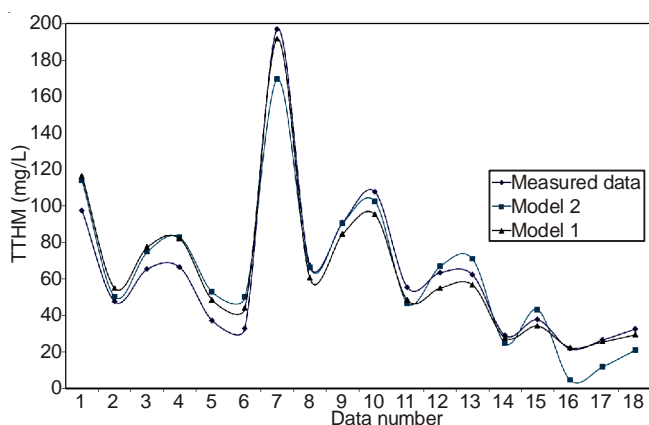

Fig. 4.　Time series plot of observed and predicted total trihalomethane concentrations for two different models

For instance; the value of measured total trihalomethane in Fig. 4 at point 16 is 21.16 µg/L, while it is calculated as 22.44 and 4.53 µg/L using model-1 and model-2, respectively. In the mean time, although the intermediate total trihalome-thane values obtained with using model-1 and model-2 are very closely to measured total trihalomethane data, model-2 gives better prediction values in respect to model-1 at these

total trihalomethane values. Fig. 5 presents the results of vali-dation analysis for two models. To evaluate the model results more accurately, Figs. 5 and 6 show the results of observed and predicted total trihalomethane values for model-1 and model-2, respectively.
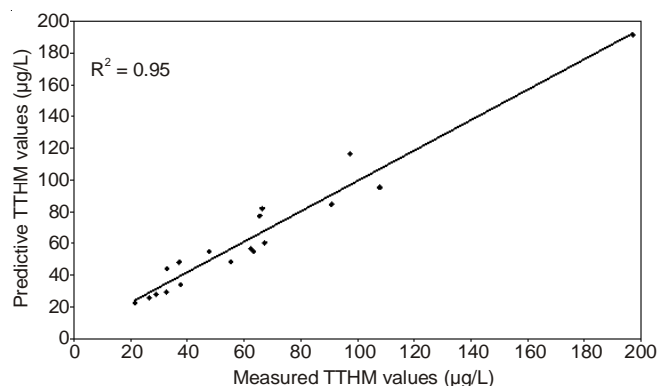

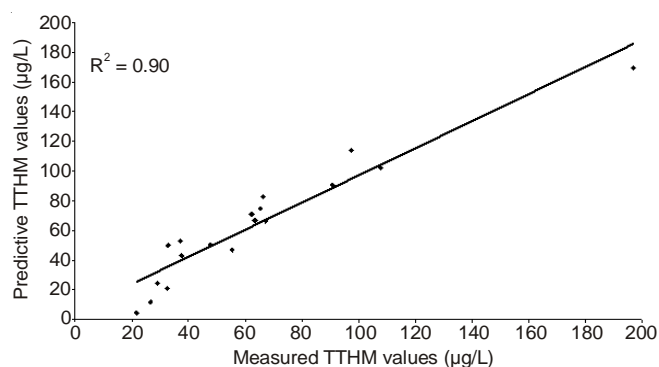Fig. 5.　The predicted and measured values of total trihalomethane for model-1

Fig. 6.　The predicted and measured values of total trihalomethane for model-2

The total trihalomethane model results show satisfactory prediction with R^2 values of 0.95 and 0.90 shown in Figs. 5 and 6. The modeling results are an appropriate level of expla-nation of the measured variables for Istanbul reservoirs. Further-more, the results demonstrate that under these experimental conditions which indicate the variations of pH, chlorine dosages, UV_{254}, SUVA, total organic carbon and ΔUV_{272} and the trihalomethane formation can be well described by the multiple linear regression technique.

In conclusion, the results of this study show that the trihalomethane formation in Istanbul drinking water sources can be predicted simply with model-1. In other words, the power-law model known as model-1 is the best model to describe the formation of trihalomethane for coagulated Istanbul reservoir waters under the given chlorination condi-tions. In the past, many studies have proposed several complex statistical equations for description of DBP formation[43-45]. In this study, the trihalomethane formation was firstly charac-terized by only one parameter with model-1. If model-2 is used to predict the TTHM concentrations, one has to know at least seven independent parameters. However, TTHM values can be predicted more accurately using only one independent parameter by model-1.

Discussion

In this paper, parameters affecting trihalomethane formation were investigated initially using surrogate organic parameters; DOC, SUVA and UV$_{254}$. The experimental results showed that the highest trihalomethane formation was observed at high concentrations of hydrophobic structures of natural organic matter for Istanbul drinking waters. Strong correlations were established between organic parameters and TTHM formation. These linear correlations were linear quantified with R^2 > 0.90 except for the Ömerli lake water samples which had high SUVA values. At the same time, two different models were developed for predicting of trihalomethane formation by using multiple linear regression analysis of data from coagulated Terkos lake water, Büyükçekmece lake water and Ömerli lake water sources under the given chlorination conditions. One of the models, known as model-2, was obtained as a linear equation including many variables such as pH, total organic carbon, chlorine dosages, UV$_{254}$, SUVA and ΔUV$_{272}$. The other model, known as model-1, is the best model to describe the formation of trihalomethane. By using either of the two models, it is possible to predict the trihalomethane formation in Istanbul drinking water resources. In order to quantify the model performance, root-mean-square error, index of agreement, R^2 and normalization mean square error were used as statically variables, respectively. According to these variables, the better results were obtained by model-1 for root-mean-square error, normalization mean square error, R^2 and index of agreement as 9.14, 0.015, 0.95 and 0.99, respectively. They are a satisfactory level of explanation of the observed variables. One of the most significant results of this research is that the trihalomethane formation can be practically predicted using model-1 with only one independent parameter, ΔUV$_{272}$. In other words, after the ΔUV$_{272}$ value is rapidly determined using a spectrophotometer, trihalomethane formation can be simply predicted by model-1 without using the other sophisticated models including several parameters.

REFERENCES

1. W.E. Elshorbagy, H. Abu-Qadais and M.K. Elsheamy, *Water Res.*, **34**, 3431 (2000).
2. M.W. LeChevallier, *J. Am. Water Works Assoc.*, **91**, 86 (1999).
3. H. Arora, M. LeChevallier and K.L. Dixon, *J. Am. Water Works Assoc.*, **89**, 60 (1997).
4. S.W. Krasner, M.J. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagan and E.M. Aieta, *J. Am. Water Works Assoc.*, **81**, 41 (1989).
5. S.D. Richardson, in ed.: R.A. Meyers, Drinking Water Disinfection by-Products, In: The Encyclopedia of Environmental Analysis and Remediation, Wiley, New York, vol. 3, pp. 1398-1421 (1998).
6. P. Roccaro and F.G.A. Vagliasindi, *Water Res.*, **43**, 744 (2009).
7. M.J. Rodriguez and J.B. Serodes, *Water Res.*, **35**, 1572 (2001).
8. J.J. Rook, *Water Treat. Exam.*, **23**, 234 (1974).
9. Y.F. Xie, Disinfection Byproducts in Drinking Water: Formation, Analysis and Control, CRC Press, Washington, DC, USA (2003).
10. S. Krasner, R.S. ChinnPastor, M. Sclimenti, H.Weinberg, G. Onstad and S. Richardson, *Epidemiology*, **13**, 108 (2002).
11. P.C. Singer, *J. Environ. Eng.*, **120**, 727 (1994).
12. F. Pontius, *J. Am. Water Works Assoc.*, **85**, 22 (1993).
13. US EPA National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts (D/DBP), *Final Rule*, **68**, 159 (2003).
14. V. Uyak and I. Toroz, *Environ. Monit. Assess.*, **121**, 503 (2006).
15. A. Adin, J. Katzhendler, D. Alkaslassy and C. Rav-Acha, *Water Res.*, **25**, 797 (1991).
16. B.D. Black, G.W. Harrington and P.C. Singer, *J. Am. Water Works Assoc.*, **88**, 40 (1996).
17. G.A. Cowman and P.C. Singer, *Environ. Sci. Technol.*, **30**, 16 (1996).
18. G.W. Harrington, Z.K. Chowdhury and D.M. Owen, *J. Am. Water Works Assoc.*, **84**, 78 (2000).
19. A.C. Diehl, G.E. Speitel, J.M. Symons Jr, S.W. Krasner, C.J. Hwang and S.E. Barrett, *J. Am. Water Works Assoc.*, **92**, 76 (2000).
20. P.C. Singer, A. Obolensky and A. Greiner, *J. Am. Water Works Assoc.*, **87**, 83 (1995).
21. J.P. Croue´, J.F. DeBroux, G.L. Amy, G. Aiken and J. Leenheer, in ed.: P.C. Singer, Natural Organic Matter: Structural Characteristics and Reactive Properties, In: Formation and Control of Disinfection By-Products in Drinking Water, American Water Works Association, Denver, USA (1999).
22. M. Kitis, T. Karanfil, J.E. Kilduff and A. Wigton, *Water Sci. Technol.*, **43**, 9 (2001).
23. M. Kitis, T. Karanfil, A. Wigton and J.E. Kilduff, *Water Res.*, **36**, 3834 (2002).
24. G.V. Korshin, W.W. Wu, M.M. Benjamin and O. Hemingway, *Water Res.* **36**, 3273 (2002).
25. G.V. Korshin, C.W. Li and M.M. Benjamin, *Water Res.*, **31**, 1787 (1997).
26. P. Roccaro, H.S. Chang, F.G.A. Vagliasindi and G.V. Korshin, *Water Res.*, **42**, 1879 (2008).
27. S. Platikanov, X. Puig, J. Martin and R. Tauler, *Water Res.*, **41**, 3394 (2007).
28. P.M.S.M. Rodrigues, J.C.G. Esteves da Silva and M.C.G. Antunes, *Anal. Chim. Acta*, **595**, 266 (2007).
29. J. Wang, H. Du, H. Liu, X. Yao, Z. Hu and B. Fan, *Talanta*, **73**, 147 (2007).
30. T.L. Lyn and J.S. Taylor, Modeling Compliance of Chlorine Residual and Disinfection by-Products, Proceeding of AWWA Water Quality Technology Conference, Miami, FL, USA (1993).
31. R. Sadiq and M.J. Rodriguez, *Sci. Total Environ.*, **321**, 21 (2004).
32. G. Solarik, R.S. Summers, J. Sohn, W.J. Swanson, Z.K. Chowdhury and G.L. Amy, Extensions and Verification of the Water Treatment Plant Model for Disinfection by-Product Formation. In: Natural Organic Matter and Disinfection By-Products, American Chemical Society, pp. 47-66 (2000).
33. G.L. Amy, R.A. Minear and W.J. Cooper, *Water Res.*, **21**, 649 (1987).
34. R.E. Rathbun, *Sci. Total Environ.*, **191**, 235 (1996).
35. V. Uyak, K. Ozdemir and I. Toroz, *Sci. Total Environ.*, **378**, 269 (2007).
36. P.D. WesterhoffReckhow, G. Amy, Z. Chowdhury, J. McClellan, J. Dundorf and Q. He, Role of Five Independent Treatment Processes on NOM Structure, DBP Precursor Removal and DBP Modeling Parameters, Proceeding of AWWA Annual Conference, June 11-15, Denver, USA (2000).
37. APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater, edn. 21, Washington, DC (2005).
38. M. Kolehmainen, H. Martikainen and J. Ruuskanen, *Atmos. Environ.*, **35**, 815 (2001).
39. R.S. Sokhi, R. San José, N. Kitwiroon, E. Fragkou, J.L. Pérez and D.R. Middleton, *Environ. Model. Softw.*, **21**, 566 (2006).
40. J.S. Willmott, *Bull. Am. Meteorol. Soc.*, **63**, 1309 (1982).
41. G. Crozes, P. White and M. Marshall, *J. Am. Water Works Assoc.*, **87**, 78 (1995).
42. V. Uyak and I. Toroz, *Environ. Technol.*, **26**, 261 (2005).
43. S.K. Golfinopoulos and G.B. Arhonditsis, *Chemosphere*, **47**, 1007 (2002).
44. A.D. Nikolaou and T.D. Lekkas, *Acta Hydrochim. Hydrobiol.*, **29**, 63 (2001).
45. H. Pourmoghaddas and A. Stevens, *Water Res.*, **29**, 2059 (1995).