

Trihalomethanes formation in Iranian water supply systems: predicting and modeling

Ali Akbar Babaei, Leila Atari, Mehdi Ahmadi, Kambiz Ahmadiangali, Mirzaman Zamanzadeh and Nadali Alavi

ABSTRACT

Trihalomethanes (THMs) were the first disinfection by-products discovered in drinking water and are classified as probable carcinogens. This study measures and models THMs formation at two drinking water distribution systems (WDS1 and WDS2) in Ahvaz City, Iran. The investigation was based on field-scale investigations and an intensive 36-week sampling program, from January to September 2011. The results showed total THM concentrations in the range 17.4–174.8 µg/L and 18.9–99.5 µg/L in WDS1 and WDS2, respectively. Except in a few cases, the THM concentrations in WDS1 and WDS2 were lower than the maximum contaminant level values. Using two-tailed Pearson correlation test, the water temperature, dissolved organic carbon, UV₂₅₄, bromide ion (Br⁻), free residual chlorine, and chlorine dose were identified as the significant parameters for THMs formation in WDS2. Water temperature was the only significant parameter for THMs formation in WDS1. Based on the correlation results, a predictive model for THMs formation was developed using a multiple regression approach. A multiple linear regression model showed the best fit according to the coefficients of determination (R^2) obtained for WDS1 ($R^2 = 0.47$) and WDS2 ($R^2 = 0.54$). Further correlation studies and analysis focusing on THMs formation are necessary to assess THMs concentration using the predictive models.

Key words | modeling, prediction, trihalomethanes, water distribution system

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ABBREVIATIONS

BDCM bromodichloromethane
BFM bromoform
CFM chloroform
DBCM dibromochloromethane
DBPs disinfection by-products
DOC dissolved organic carbon
MCL maximum contaminant level
MDLs method detection limits
NOM natural organic matter
SUVA specific ultraviolet absorbance
THMs trihalomethanes
TOC total organic carbon
TTHM total trihalomethane
UVA ultraviolet absorbance

WDS water distribution system
WTP water treatment plant

INTRODUCTION

Chlorine is a widely used disinfectant because of its efficiency, cost-effectiveness, and prevention of water-borne disease transmission (Sadiq & Rodriguez 2004; Pavon *et al.* 2008; Siddique *et al.* 2014). Most surface waters contain natural and anthropogenic organic matters that are trihalomethanes (THMs) precursors (Panyapinyopol *et al.* 2005). Chloroform (CHCl₃), bromodichloromethane

(CHCl₂Br), dibromochloromethane (CHClBr₂), and bromoform (CHBr₃) are the main THM species.

Recently, reproductive consequences of THMs in drinking waters such as spontaneous abortion, stillbirth, and intra-uterine growth reduction, and harmful effects on the liver, kidneys, bladder, and central nervous system have been reported (Legay *et al.* 2010; Richardson & Postigo 2012). Numerous studies have described the formation and relevant health risks of THM compounds (Sohn *et al.* 2004; Kumar *et al.* 2014). Toxicological information and guidelines related to THMs (mg/L) are shown in Table 1.

The formation of THMs during chlorination of drinking water needs to be monitored to ensure compliance with guidelines. A mathematical model that can simulate disinfection by-products (DBPs) is very useful in predicting THMs formation. Such models have been developed for various purposes, such as identification of the significant operational and water quality parameters controlling the formation of THMs, investigation of the kinetics of their formation, and THMs prediction as an alternative to field measurements (Sadiq & Rodriguez 2004). Modeling THMs requires the extension of experimental and mathematical relationships between THM levels in treated water and water quality and operational parameters if it is to be effective in THMs formation (Di Cristo *et al.* 2013; Al-Omari *et al.* 2014). The presence of THMs in chlorinated waters depends on the pH, water temperature, contact time between water and chlorine, type and dose of disinfectant, bromide ion concentration, and nature and concentration of natural

organic matter (NOM) (Ristoiu *et al.* 2009; Fooladvand *et al.* 2011). Numerous models have been developed to predict THMs formation in drinking waters by recognizing the effective parameters (Chowdhury *et al.* 2009; Abdullah & Hussona 2013). These predictive models employ different water quality parameters, and individual models typically use three to eight parameters. However, the interaction parameters are typically not included in the modeling of THMs (Sohn *et al.* 2004).

The present study is the first attempt to evaluate THMs formation and to develop a predictive model based on multiple regression analysis using raw and treated water characteristics, operational conditions, and the properties of drinking water in two water distribution systems (WDS1 and WDS2) in Ahvaz, Iran. Ahvaz has a population of 1.2 million, and its drinking water is supplied by two water treatment plants (WTP1 and WTP2). The Karun River is the major source of raw water for WTP1 and WTP2. The deterioration of the quality of this river's water is a serious public concern; it receives tonnes of untreated municipal, industrial, and agricultural wastewaters annually. Recently, due to reduced precipitation in the region, the river's pollution has been concentrated, especially in terms of organic matter. Furthermore, the conventional treatment process used in local WTPs cannot guarantee organic matter removal. Consequently, the risk of THMs formation in the finished water is increasing.

In this research, we presented the profile of THMs and factors leading to their formation in WDS1 and WDS2. In

Table 1 | Toxicological information and standards/guideline related to THMs (mg/L) (Sadiq & Rodriguez 2004; USEPA 2006; WHO 2008; ISIRI 2009)

Compounds	Toxicological information		Regulatory					
	Animal	Human	WHO (2008)	USEPA (2006)	Health Canada (2007)	AUS–NZ (2004)	UK (2000)	IR–IRAN (2009)
CHCl ₃	Liver tumor	B2	0.300	–	–	–	–	0.300
CHCl ₂ Br	Kidney tumor	B2	0.060	–	0.016	–	–	0.060
CHClBr ₂	Colon tumor	C	0.100	–	–	–	–	0.100
CHBr ₃	Liver tumor	B2	0.100	–	–	–	–	0.100
TTHM	–	**	**	0.080*	0.100	0.250	0.100	**

UK: United Kingdom.

Aus–NZ: Australia–New Zealand.

B2: Probable human carcinogen (sufficient laboratory evidence).

C: Possible human carcinogen.

* MCL.

** The sum of the ratios of the THMs level to the WHO guideline values should not exceed 1.

addition, based on these results, we developed a predictive multiple regression model and conducted a sensitivity analysis on the model.

MATERIALS AND METHODS

Description of WTPs

WTP1 and WTP2, which supply the water requirements of about 1 million inhabitants of Ahvaz, were monitored and the formation of THMs was modeled. Both plants use conventional treatment process trains and are mainly fed with the Karun River. These plants supply about 500,000 m³ of treated water to the city daily. The treatment trains consist of prechlorination, coagulation by the addition of poly aluminum chloride, flocculation, sedimentation, rapid sand filtration with a backwashing period of 8–12 hours, and final chlorination (typically up to 2.5 mg/L).

Sampling procedure

We designed the sampling period to cover both cold and warm seasons and so consider the impact of seasonal changes on the water quality. A 36-week sampling period

was carried out from January to September 2011. Samples were taken from various locations to provide a comprehensive evaluation of the water quality in WDS1 and WDS2 (Table 2). Ninety water samples were collected to determine THM species. Thirty-six samples were taken from WDS1 and 54 from WDS2. Sampling in the distribution networks was performed biweekly at 10–12 a.m. Before collecting each sample, the faucet was opened for about 5 minutes to collect a representative sample and to ensure that each water sample came from the distribution network (Rodriguez et al. 2007).

For measurement of THMs, tap water was collected in 125-mL amber glass bottles with polypropylene screw caps and TFE-faced septa. Before sampling, we added a sodium thiosulfate solution (10%) to the bottles to eliminate residual chlorine and to prevent further formation of THMs until analysis. Special care was exercised during sampling to avoid any air bubbles in the sample. The samples for analyzes of dissolved organic carbon (DOC), UV absorbance at 254 nm (UV₂₅₄), bromide ion, and ammonia were collected in 1 L amber glass bottles. Before sampling, the bottles were washed with detergent, rinsed with deionized ultra-pure water, and placed in an oven at 400 °C for 1 hour. Once collected, the samples were stored in the dark at 4 °C and analyzed within 24 hours. The temperature,

Table 2 | Sampling points and the physico-chemical parameters studied in WDS1 and WDS2

Sampling points	Parameters									
	Temperature (°C)	pH	DOC (mg/L)	UV ₂₅₄ (1/cm)	SUVA (L/mg m)	Ammonia (mg/L)	Br ⁻ (µg/L)	Chlorine dose (mg/L)	Free residual chlorine (mg/L)	THMs (µg/L)
WDS1										
Filtered water	–	–	36	36	36	36	36	–	–	–
Sp1-1	18	18	–	–	–	–	–	36	18	18
Sp1-2	18	18	–	–	–	–	–	–	18	18
WDS2										
Filtered water	–	–	54	54	54	54	54	–	–	–
Sp2-1	18	18	–	–	–	–	–	54	18	18
Sp2-2	18	18	–	–	–	–	–	–	18	18
Sp2-3	18	18	–	–	–	–	–	–	18	18

Sp1-1 and Sp2-1: At the outlet of the storage tank before leaving the plant.

Sp1-2 and Sp2-3: At the end of the distribution system.

Sp2-2: At the midpoint of the distribution system.

pH, and free residual chlorine of the water samples were measured *in situ*. The pH and free residual chlorine were determined by a digital Multi 1000 Cl/pH meter (Palintest Company) and the water temperature was measured with a digital thermometer.

Analytical procedures

Ammonia was analyzed according to the method suggested by the HACH Company, using a DR5000 spectrophotometer (HACH, Germany). Bromide concentration was measured using an ion chromatograph (2695 Alliance model, Waters) equipped with an electrochemical detector (2465 model, Waters) in the calibration range of 6–200 µg/L.

The water samples were filtered with pre-washed glass-fiber filters (GFC-0.45 µm, 47 mm diameter) prior to analyzing DOC and UV₂₅₄. DOC was analyzed using a TOC-VCSH analyzer (Shimadzu, Japan), and UV₂₅₄ was determined using a DR5000 spectrophotometer (HACH, Germany) following American Public Health Association (1998). The specific UV absorbance (SUVA) values were calculated with Equation (1).

$$\text{SUVA (L/mg C.m)} = 100 [\text{UV}_{254}/\text{DOC}] \quad (1)$$

where 100 is a conversion factor (cm/m).

THM species analysis was carried out with the head space technique using a gas chromatograph (6890 model, Agilent) equipped with a µECD detector. A capillary fused silica DB-1701 column 30 m × 0.32 mm × 1.0 µm film thickness was used. Injections were made in splitless mode, with helium as carrier gas and nitrogen as makeup gas. Sample volumes of 10 mL were filled in 20 mL glass vials and spiked with 50 µL of the internal standard (10 mg/L p-bromofluorobenzene). The vials were immediately sealed with Teflon coated septa and aluminum crimp caps. After equilibration (10 minutes at 70 °C) a volume of 100 µL of the head space was injected splitless into a gas chromatograph. The temperature program was: initial 40 °C for 1 minute, 5 °C/min to 100 °C for 0 minute, 100 °C/min to 200 °C for 3 minutes. A linearity regression function was set up based on calibration measurement. There was good linearity in the detected range, and correlation coefficients (R^2) were 0.9989, 0.9999, 0.9996, and 0.9992 for CHCl₃,

CHCl₂Br, CHClBr₂, and CHBr₃, respectively. Water samples were spiked with a specific amount (1, 10, and 20 µg/L) of four THMs to determine the recovery. The average recoveries of the four THMs were in the range of 84–92% ($n = 7$) and relative standard deviations were 4.5–9.1% indicating acceptable precision and accuracy of the analytical procedure. The method detection limits (MDLs) were determined from the standard deviation of 1 µg/L spiked samples. The corresponding MDLs for CHCl₃, CHCl₂Br, CHClBr₂, and CHBr₃ were 0.15 µg/L, 0.11 µg/L, 0.12 µg/L, and 0.15 µg/L, respectively.

Modeling procedure

A multiple regression model was developed for analysis of THMs formation within these two distribution systems, using the forward selection procedure of SPSS 17. The dependent variable was THMs concentration in the distribution systems, and the filtered (i.e. after sand filters) and treated water (i.e. in the distribution systems) qualities and operational parameters from WTP1 and WTP2 were considered as the independent variables. The variables were tested for normality using the Kolmogorov–Smirnov test. We implemented several regression techniques, including linear, logarithmic, exponential, and quadratic in an attempt to formulate and adopt the equations exhibiting the highest coefficient of determination.

RESULTS AND DISCUSSION

Average seasonal values of the filtered (i.e. after sand filters) and distributed water quality parameters and operational parameters of WTP1 and WTP2 are shown in Table 3. These parameters were analyzed as they are important in THMs formation. Apart from the ammonia concentration and Cl₂ dose, whose values were almost two times greater in WDS1 than in WDS2, the values of the remaining parameters were comparable in the two distribution systems. Importantly, it was observed that the values of some of the parameters measured in WDS1 and WDS2 increased as the water temperature increased due to seasonal change from about 17 °C in winter to 30 °C in summer. According to Table 3, the humic nature of NOM (as indicated by

Table 3 | Average values of filtered and finished water quality parameters and operational parameters in WDS1 and WDS2

Season	Filtered water quality parameters					Operational parameter					Distributed water quality parameters				
	DOC (mg/L)	UV ₂₅₄ (1/cm)	SUVA (L/mg m)	Br (µg/L)	Ammonia (mg/L)	Cl ₂ dose (mg/L)	Temperature (°C)	pH	Residual Cl (mg/L)						
WDS1															
Winter N = 12	1 (0.09)	0.016 (0.004)	1.6 (0.44)	140 (2.23)	0.077 (0.046)	2.35 (0.05)	17.19 (2.19)	7.86 (0.07)	0.89 (0.42)						
Spring N = 12	0.82 (0.09)	0.018 (0.003)	2.2 (0.56)	160 (6)	0.048 (0.022)	2.24 (0.03)	26.3 (2.7)	7.9 (0.07)	0.87 (0.3)						
Summer N = 12	0.72 (0.07)	0.015 (0.005)	2.07 (0.72)	170 (6.3)	0.031 (0.011)	2.26 (0.1)	30 (2)	7.9 (0.05)	0.75 (0.33)						
Total N = 36	0.86 (0.15)	0.016 (0.004)	1.98 (0.63)	157 (13.7)	0.052 (0.035)	2.28 (0.08)	24.76 (5.6)	7.9 (0.06)	0.84 (0.35)						
WDS2															
Winter N = 18	0.9 (0.14)	0.015 (0.005)	1.6 (0.35)	141 (6)	0.028 (0.013)	1.14 (0.04)	17.42 (1.98)	7.87 (0.11)	0.88 (0.14)						
Spring N = 18	0.68 (0.09)	0.011 (0.003)	1.74 (0.68)	162.6 (4.4)	0.011 (0.003)	1.07 (0.01)	26 (2.86)	7.87 (0.06)	0.92 (0.15)						
Summer N = 18	0.79 (0.18)	0.016 (0.007)	2 (0.67)	171.6 (9.4)	0.011 (0.003)	1.16 (0.09)	30.67 (2.5)	7.89 (0.08)	0.57 (0.36)						
Total N = 54	0.79 (0.16)	0.014 (0.006)	1.8 (0.6)	158.5 (14.6)	0.017 (0.011)	1.12 (0.07)	24.7 (6)	7.87 (0.08)	0.79 (0.28)						

Note: Standard deviations are shown in parentheses.

SUVA) in the distribution systems increased linearly as the water temperature increased. Bromide also showed a similar trend, and its concentration increased in both distribution systems from about 140 to 171 µg/L. Overall, the elevated concentrations of these parameters in summer resulted in the increased concentrations of THMs in the WDS1 and WDS2 distribution systems.

As shown in Table 4, we observed seasonal and spatial variations in the THMs concentrations. The total concentrations of THMs of Ahvaz's drinking water in winter, spring and summer were 20.5–86 µg/L, 18.92–66.06 µg/L, and 17.35–174.75 µg/L, respectively. In addition, the total THMs concentrations in WDS1 and WDS2 were 17.35–174.75 µg/L and 18.92–99.5 µg/L, respectively. As shown in Figure 1, the maximum seasonal average of the THMs in both distribution systems was related to summer temperature. For WDS1, the maximum value was 70.47 ± 22.3 µg/L and occurred at the end of the distribution system (i.e. Sp1-2), whereas the value for WDS2 was 89.22 ± 60.8 µg/L, measured at the midpoint of the distribution system (i.e. Sp2-2). The minimum average concentration was related to the finished water of the treatment plants, where the THMs concentrations were 25.97 ± 5.17 µg/L and 31.54 ± 8.63 µg/L in Sp1-1 and Sp2-1, respectively. The one-way ANOVA-Tukey test was used to compare the average concentrations of THMs between seasons as well as at the sampling points. Comparison of the average concentration of THMs between sampling points (Table 5) showed a significant difference between the primary point and endpoint of both WDS1 and WDS2 ($p_{\text{value}} < 0.05$). Thus, we observed an increase in the THMs levels as the distance from treatment plants increased. This spatial variation is related to the long residence time of water within the distribution systems (Rodriguez *et al.* 2007).

As shown in Figure 1 and Table 4, the brominated THM species were the predominant THM compounds in all of the sampling points of WDS1 and WDS2, accounting for about 80% of the total THMs concentration, whereas, chlorinated THM species accounted for only 20%. Prior studies also reported brominated compounds as the major THM species (Kampioti & Stephanou 2002; Duong *et al.* 2003).

We compared the THMs concentration in the various seasons to determine whether seasonal values differed significantly, and indeed statistical analysis (ANOVA) did

Table 4 | Seasonal average of THMs ($\mu\text{g/L}$) values in Ahvaz drinking water

Season	WDS1					WDS2				
	CFM	BDCM	DBCm	BFM	TTHM	CFM	BDCM	DBCm	BFM	TTHM
Winter N = 12	2.7 (0.79)	5.73 (2.46)	14.4 (6.8)	18.76 (10.12)	41.6 (19)	2.44 (0.39)	5.3 (0.9)	13.8 (2.48)	19.21 (5.48)	40.75 (7.13)
Spring N = 12	1.83 (0.83)	4.6 (1.44)	12.17 (5.73)	15.21 (8.87)	33.8 (13.7)	1.2 (1.02)	4.09 (1.6)	14.6 (5.73)	20.05 (4.95)	39.94 (11.9)
Summer N = 12	3.52 (4)	8.96 (7.22)	20.78 (10.64)	21.17 (7.91)	54.45 (24.3)	4.1 (4)	10.5 (7.68)	24.9 (19.05)	22.48 (15.13)	61.98 (42.6)
Total N = 36	2.69 (2.4)	6.43 (4.73)	15.79 (8.6)	18.38 (9)	43.3 (20.8)	2.58 (2.68)	6.62 (5.28)	17.77 (12.45)	20.58 (9.64)	47.56 (27.4)
										54

Note: Standard deviations are shown in parentheses.

reveal a difference ($p_{\text{value}} < 0.05$). However, this difference was only significant for the values measured in summer and spring ($p_{\text{value}} < 0.05$). The seasonal variations in THMs concentration are likely due to the seasonal difference of the water temperatures and bromide concentrations. As shown in Table 3, the maximum level of the water temperature and bromide concentrations in WDS1 and WDS2 were in summer. The seasonal differences in the water temperature can affect reaction rates between chlorine and precursors. Thus, high levels of reaction rates result in the formation of higher levels of THMs (Sohn *et al.* 2001). The experimental results from batch studies indicated that increased water temperatures in summer yielded a greater THM formation potential for the Karun River water. The summer values were 1.2–1.6 times higher than those of the spring and fall seasons (Fooladvand *et al.* 2011).

Unlike in colder seasons, summer's higher bromide concentration can be due to the elevated water temperature and higher evaporation rate in the water source (Toroz & Uyak 2005). We observed higher concentration of the bromide in the Karun River during summer than in spring and winter.

We compared the THMs concentrations obtained in this study with the standard values set by the regulatory agencies (i.e. USEPA and WHO). Overall, we observed that the THMs concentrations in WDS1 and WDS2 were less than the maximum contaminant level (MCL) values set by these agencies. However, the concentration of the THMs exceeded the MCL value at a number of sampling times (Figure 2(a) and 2(b)). As can be seen from Figure 2, almost all of the days when the THMs concentrations exceeded the MCL set values were in summer. This observation is consistent with studies reporting the higher likelihood of THMs formation in warmer seasons (Whitaker *et al.* 2003; Hassani *et al.* 2010).

Correlation results for THMs with independent variables

A two-tailed Pearson test was employed to determine the correlation matrix for the THMs with regard to the water quality and operational parameters in WDS1 and WDS2 (Table 6). As shown in Table 6, we observed a positive and significant correlation ($r = 0.413$, $p_{\text{value}} = 0.012$)

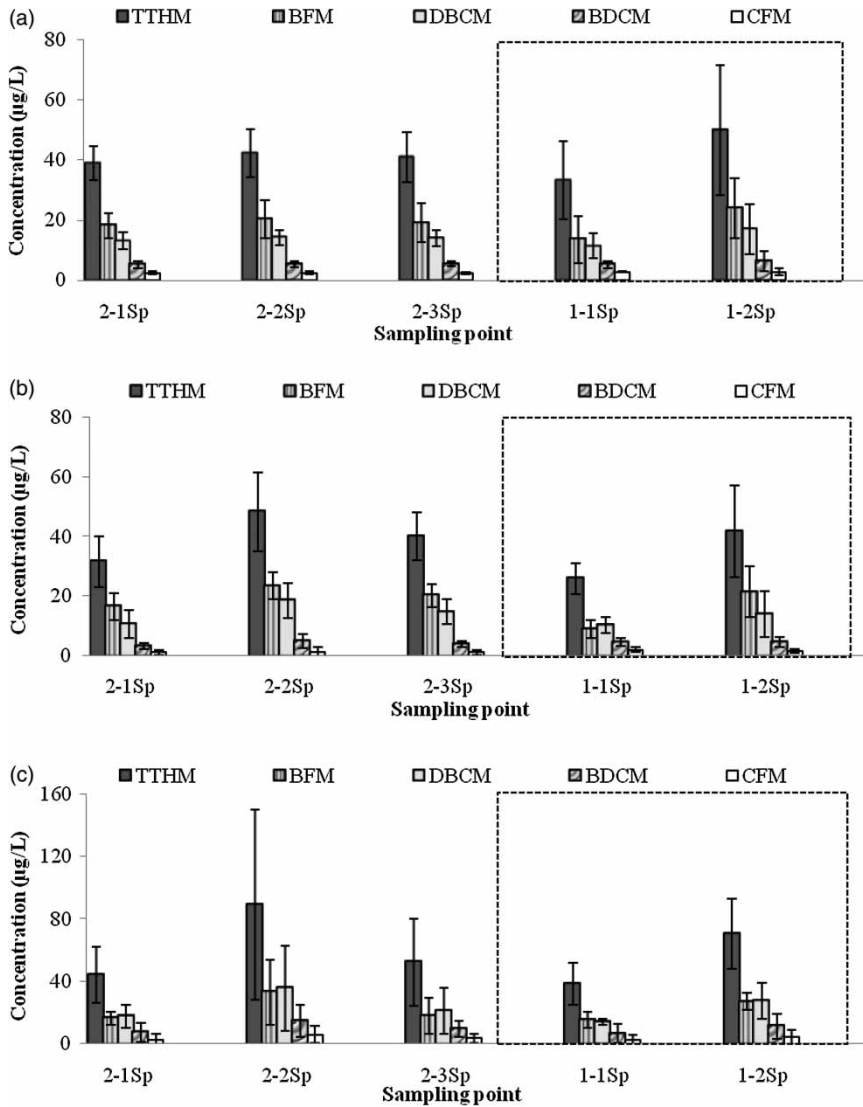


Figure 1 | Spatial variation of THMs at sampling points of WDS2 (unselected parts) and WDS1 (selected parts): (a) winter; (b) spring; and (c) summer.

Table 5 | Comparison of the probability values of THMs concentration between seasons, sampling points and distribution systems

Season		<i>P</i> value	Location		<i>P</i> value	DS	<i>P</i> value	
WDS1	Winter	Spring	0.59					
	Winter	Summer	0.25	Sp1-1	Sp1-2	0.001*		
	Summer	Spring	0.03*					
	Between seasons						WDS1	WDS2
WDS2	Winter	Spring	0.9	Sp2-1	Sp2-2	0.04*		
	Winter	Summer	0.04*	Sp2-1	Sp2-3	0.7		
	Summer	Spring	0.036*	Sp2-2	Sp2-3	0.19		
	Between seasons			Between points		0.04*		

*THMs average difference is significant at the 95% confidence interval.

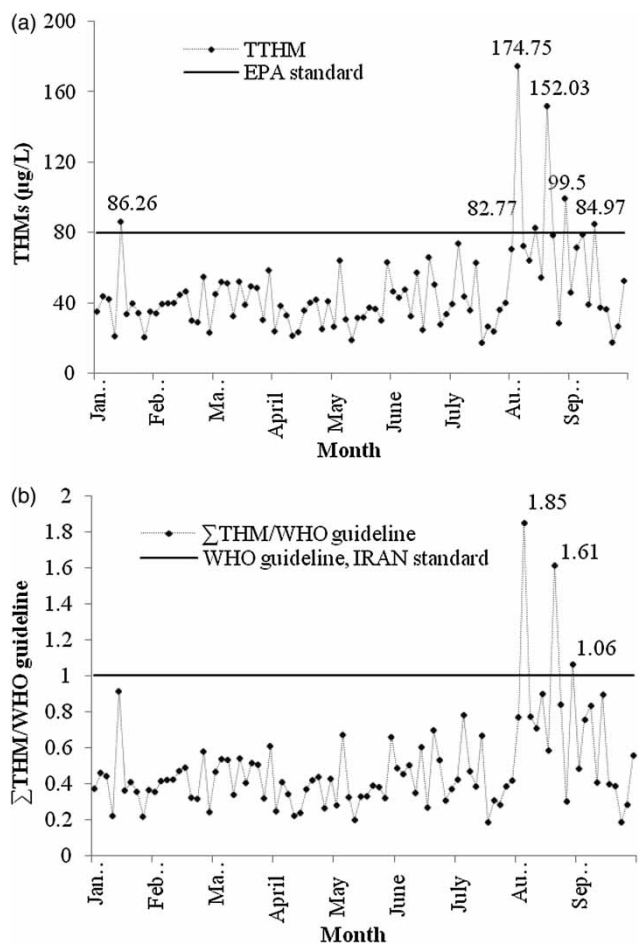


Figure 2 | Comparison between THMs concentration and (a) EPA standard and (b) WHO guideline and Iran standard.

between THMs and water temperature in WDS1, while the Pearson correlation test for WDS2 indicated that the THMs concentration has a positive and significant correlation with several parameters, including temperature ($r=0.472$, $p_{\text{value}} < 0.01$), DOC ($r=0.352$, $p_{\text{value}} < 0.01$), UV_{254} ($r=0.311$, $p_{\text{value}} = 0.022$), Br^- ($r=0.485$, $p_{\text{value}} < 0.01$), and chlorine dose ($r=0.48$, $p_{\text{value}} < 0.01$). In addition, this test showed a negative correlation between the THMs and free residual chlorine ($r=-0.521$, $p_{\text{value}} < 0.01$) in WDS2. The remaining parameters (i.e. pH and ammonia) did not show a correlation with the formation of THMs due to slight variations.

The positive correlations of the THMs with temperature and with soluble organic matter (DOC, UV_{254}) indicate that the THMs formation increased as the water temperature and soluble organic matter in surface water increased. This observation agrees with the results reported by several

researchers (Toroz & Uyak 2005; Ye et al. 2009). In addition, a negative and significant correlation observed in this study between the free residual chlorine and THMs concentration shows that the seasonal variations in water temperature influenced the reaction rates between chlorine and THMs precursors. This influence led to the decay of more chlorine and reduction of the free residual chlorine, and therefore a higher demand for chlorine dose (Toroz & Uyak 2005).

A positive and significant correlation was seen between the THMs and the Br^- concentration, indicating the elevated THMs concentration with increase of the Br^- concentration (Zha et al. 2014). In addition, the low UV_{254} and SUVA values in the drinking water demonstrated that the hydrophilic fraction of NOM was greater than the hydrophobic fraction. Therefore, formation of the brominated THMs was expected due to the higher reaction tendency of NOM with Br^- than with chlorine (Liang & Singer 2003). In addition, in the presence of chlorine and bromine ions in water containing NOM, the haloform substitution efficiency (i.e. CHX_3 produced per mole X_2 consumed) for bromine is greater than that for chlorine because the bromine has higher electron density and lower bond strength than chlorine atoms (Westerhoff et al. 2004).

Modeling THMs formation within distribution systems

Various regression models were exercised to develop a structured model for THMs prediction in the distribution systems. The sample size (n), significance (P_{value}), and coefficient of correlation (R^2) for each model are presented in Table 7. Based on the coefficients of determination, the best fit was obtained from the linear regression model for both WDS1 ($R^2 = 0.47$, $P_{\text{value}} < 0.05$) and WDS2 ($R^2 = 0.54$, $P_{\text{value}} < 0.05$). However, the coefficient of determination value of the THMs linear predictive model for WDS2 was greater than that for the WDS1 (Table 7). This observation holds true for overall comparison of the various regression models applied for WDS1 and WDS2, probably because the number of samples was greater for WDS2 than that for WDS1. Furthermore, the greater coefficient of determination for WDS2 can be attributed to more significant correlation values between THMs and independent variables in WDS2 than in WDS1. The coefficient of determination obtained in this study was comparable to those

Table 6 | Pearson correlation matrix for water quality and operational parameters of WDS1 and WDS2

	Temperature	pH	DOC	UV ₂₅₄	SUVA	Ammonia	Br ⁻	Free residual chlorine	Cl ₂ dose	THM
WDS1										
Temperature	1									
pH	0.253	1								
DOC	-0.663*	-0.405*	1							
UV ₂₅₄	-0.141	-0.058	0.174	1						
SUVA	0.229	0.158	-0.393*	0.828*	1					
Ammonia	-0.590*	-0.107	0.332*	0.221	0.006	1				
Br ⁻	0.930*	0.321	-0.676*	-0.070	0.294	-0.469*	1			
Free residual Cl	-0.243	-0.151	0.139	-0.091	-0.168	-0.226	-0.243	1		
Cl dose	-0.452*	-0.354*	0.527*	0.523*	0.189	0.477*	-0.366*	-0.095	1	
THM	0.413*	0.015	-0.004	-0.132	-0.122	-0.210	0.323	-0.324	0.168	1
WDS2										
Temperature	1									
pH	0.011	1								
DOC	-0.213	-0.232	1							
UV ₂₅₄	0.079	-0.058	0.632*	1						
SUVA	0.211	0.139	0.078	0.810*	1					
Ammonia	-0.599*	-0.020	0.421*	0.099	-0.160	1				
Br ⁻	0.901*	-0.083	-0.184	0.077	0.175	-0.601*	1			
Free residual Cl	-0.483*	-0.097	-0.303*	-0.556*	-0.473*	0.032	-0.399*	1		
Cl dose	0.119	-0.292*	0.550*	0.497*	0.173	0.098	0.148	-0.187	1	
THM	0.472*	-0.198	0.352*	0.311*	0.084	-0.052	0.485*	-0.521*	0.48*	1

*Correlation is significant at the 95% confidence interval (two-tailed).

Table 7 | THMs formation predictive models in WDS1 and WDS2

Distribution system	Formulated model	R ²	P _{value}	n
WDS1	Linear: $THM = -347.56 + 2.88(T) - 13.56(SUVA) + 151.46(D)$	0.47	<0.05	36
	Exponential: $THM = e^{-3.54+0.06(T)-0.32(SUVA)+2.79(D)}$	0.36	<0.05	36
	Quadratic: $THM^2 = -12,095.21 + 5.52(T)^2 + 2,039.95(D)^2$	0.32	<0.05	36
	Logarithmic: $THM = 0.1 \times 10^{-2}(T)^{1.17}(SUVA)^{-0.47}(D)^{3.87}$	0.34	<0.05	36
WDS2	Linear: $THM = -159.13 - 11.07(SUVA) + 0.54(Br) - 42.93(FCl) + 154.47(D)$	0.54	<0.05	54
	Exponential: $THM = e^{0.43-0.23(SUVA)+0.008(Br)-0.55(FCl)+2.53(D)}$	0.46	<0.05	54
	Quadratic: $THM^2 = -11,718.91 + 5.6(T)^2 - 3,184.63(FCl)^2 + 10,483.49(D)^2$	0.52	<0.05	54
	Logarithmic: $THM = 0.18 \times 10^{-2}(Br)^{1.24}(SUVA)^{-0.49}(FCl)^{0.27}(D)^{3.13}$	0.45	<0.05	54

Note: T: temperature (°C), D: chlorine dose (mg/L), SUVA: specific UV absorbance (L/mg m), Br: bromide ion (µg/L), FCl: free residual chlorine (mg/L).

presented in the literature (Golfopoulos & Arhonditsis 2002; Abdullah & Hussona 2013). Nikolaou *et al.* (2004) reported coefficients of determination ranging between 0.38 and 0.58, using field data for development of a predictive model for THMs formation. Although the model

developed in this research agreed with prior studies on THMs predictive models, it appears that the parameters affecting THMs formation in water treatment systems require further investigation to increase the precision of these predictive models (Nikolaou *et al.* 2004).

CONCLUSION

The highest concentration of THMs, which was observed in summer, was 174.75 µg/L. A comparison of seasonal THM values in the two distribution systems revealed, respectively, THM concentrations in summer 1.6 and 1.4 times higher than the average values obtained in the spring and winter seasons. The results of this study showed that the minimum and maximum concentrations of the THMs in WDS1 were related to the finished water samples and water samples taken from the furthest points of the distribution system, respectively; whereas, the values in WDS2 were related to the finished water samples and water samples taken from the midpoint of the distribution system, respectively. In general, except for a few cases, THM concentrations in the Ahvaz drinking water were lower than the MCL values. The brominated THM species were the predominant THM compound in the Ahvaz drinking water, accounting for 80% of the total THM concentration. The bromide ion level in water is the key factor in controlling THMs bromination. Significant correlations were observed between THMs and the individual variables including temperature, Br⁻, free residual chlorine, DOC, UV₂₅₄ and chlorine dose for WDS2. For WDS1, significant correlation was only observed with temperature. Among the THMs formation predictive models used, the highest coefficient of determination was obtained with the linear regression model for both WDS1 and WDS2. The development of a precise model for prediction of THM formation was a challenging task due to limited data, lack of proper knowledge of THM formation mechanisms, and continuous changes in parameters affecting THM formation. Based on the results of this study, it was concluded that further investigations are required to develop a more precise predictive model for THM formation in drinking WDSs based on laboratory-controlled experimentations as well as field-scale investigations. This research was the first field-scale study on modeling THMs formation in the Ahvaz drinking WDSs. The overall results may help to identify operational strategies for water utility operators to use in minimizing THMs formation and improving decision-making for management of public health risks associated with THMs.

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