

Trihalomethanes Formation Potential in Water Supply System of Bandar Abbas (Southern Iran): from Source to Distribution Network

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Abstract

Background: Pre-chlorination of raw water containing natural organic matters may lead to forming harmful disinfection by-products such as trihalomethanes (THMs), the measurement of which needs expensive advanced analytical instruments. This study was conducted to anticipate THMs formation potential in Bandar Abbas drinking water system using cheap and simple experiments and a mathematical model.

Methods: In a 24 week sampling program, 96 samples were collected weekly from raw water (RW), clarification (CE), filtration (FE), and disinfection effluent (DE). After measuring the Dissolved Organic Carbon (DOC), residual chlorine, contact time, temperature and pH of water, THMs concentration was calculated using a mathematical model.

Results: The means of DOC concentration in RW, CE, FE and DE were 5.56, 4.21, 3.50, and 3.01 (mg/l), respectively. The mean of temperature values varied from 22.28 in RW to 21.25 in DE and the mean of pH variations was measured from 6.75 in DE to 8.37 in CE. Also, the mean of residual chlorine concentration was 0.0 to 1.72 in RW and DE, respectively.

Conclusion: The means of calculated THMs were $37.92 \pm 4.82 \mu\text{g/l}$, $51.15 \pm 9.44 \mu\text{g/l}$, and $52.71 \pm 8.37 \mu\text{g/l}$ for CE, FE, and DE respectively; this did not meet the related EPA standard (30-40 $\mu\text{g/l}$); therefore, further detailed studies should be conducted to resolve the consumers' concerns in this regard.

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Keywords: Organic Matters; Disinfection by-Products; Trihalomethanes; Prediction model

Introduction

Organic matters in water consist of a range of natural and synthetic compounds, having a wide variety of chemical compositions and molecular sizes. The amount of natural organic matters (NOMs) in water differs with climate and the hydrological regime as well as a number of other environmental factors. So, the character of NOM can vary with source and season.¹⁻³ Chlorine has been used for water disinfection in many water treatment plants.⁴ During the chlorination, chlorine may react with NOM in the raw water and lead to production

of many disinfection by-products (DBPs), such as trihalomethanes (THMs).⁵⁻⁸ DBPs have the potential to create unpleasant taste and odor in drinking water that cannot be removed completely by conventional treatment processes.⁹⁻¹¹ Many of the DBPs have been classified as probable or possible carcinogens; thus, the presence of DBPs in drinking water is considered as a human health risk factor; therefore, occurrence of DBPs in drinking water has been regulated in most countries.¹²⁻¹⁴

Measurement and detection of THMs and other disinfection-by-products requires advanced analytical

instruments while purchase and preparation of the instruments is not possible for many water supply systems, so models for THMs formation potential (THMFP) prediction have been developed. In recent years, mathematical models for DBPs prediction have been used in water distribution and network systems.^{15,16} Among them, linear, non-linear and multiple regressions have been the mostly used models in water treatment facilities.¹⁷ Based on reported developed models for prediction of THMs in drinking waters, THMs formation is related to many factors such as pH, contact time with the chlorine concentration and properties of chlorine, chlorine residual, temperature, and concentration of bromine.¹⁸⁻²⁷

Bandar Abbas (BA) city, center of Hormozgan province, with about 700,000 population is located in warm and humid climate in the south of Iran. Drinking water resource of BA is surface water, Esteqlal Minab Dam (EMD), which is located 90 km far from BA. Water treatment plant of BA is structured in two distinct parts. The first section, which is adjacent to the EMD, includes pre-chlorination unit, mixing, coagulation and flocculation and sedimentation tank (Pulsator system). To control the nuisance factors such as algae, chlorine is added to raw water at the first section of the water treatment plant. The second part, including filtration and final chlorination, is located in Bandar Abbas city, 90 kilometers away from the first part of water treatment plant. After final disinfection, water is transported to BA drinking water reservoirs.

Objectives: Due to the high health risks related to THMs and lack of access to advanced and expensive instruments for detecting THMs in all parts of the country, this study was conducted to anticipate the capacity and possibility of the THMs formation in Bandar Abbas drinking water system, using cheap and simple experiments and a mathematical model.

Methods

In this study, the sampling period was 24 weeks during early March through the end of August 2012. Samples were collected from weekly raw water (RW), from Minab dam and treated water samples from a water treatment plant in Minab that uses a conventional treatment process (pre-chlorination, coagulation, flocculation, sedimentation), specially from clarifier effluent (CE). The other sampling locations were filtration effluent (FE) and disinfection effluent (DE) in water treatment plant in Bandar Abbas which uses filtration and final chlorination. One sample per week was taken from each defined location; thus, 96 samples were taken in total. Sampling containers were dark glass sterile bottles washed using detergent followed by diluted HCl and deionized water washing. Then, the bottles have been placed in 400°C oven to release of volatile organic matter for 60 minutes. In water sampling location,

temperature and pH of the samples were determined immediately. The samples were kept in dark and cool place (4°C) and sent to health school laboratory of BA in less than 4 hours after sampling. In the laboratory, DOC and residual chlorine were measured by TOC analyzer model DR B200 made in Germany and HACH digital chlorine-meter, respectively. After TOC measuring, Dissolved Organic carbon (DOC) was determined by acidifying the samples, in which Inorganic Carbon (IC) converted into Carbonic acid (H₂CO₃), also known as dissolved inorganic carbon (DIC). Measurement of pH using pH meter Elmetron Model CP-501 was conducted using the catalog. Mathematical THMs prediction model used in the present study was developed by Rodriguez et al. The parameters affecting the formation of THMs in this model include the amount of NOMs as DOC, chlorine contact time, chlorine residual, temperature, and pH of water (equation. 1).²²

$$\text{Equation 1: } TTHM = 0.044(\text{DOC})^{1.030} \times (t)^{0.262} \times (\text{pH})^{1.149} \times (D)^{0.277} \times (T)^{0.968}$$

In eq.1, DOC represents the NOMs as DOC concentration, t is chlorine contact time, pH is pH of water, T for water temperature, and D is residual chlorine dose. Statistical Package for the Social Sciences (SPSS) 19.0 for Windows was used to determine the relationship between THM potential and affecting parameters. Contact time for Pre-chlorinated water in clarification effluent was 45-minutes. In two other locations, the linear velocity equation was used to calculate the time. Based on the discharge rate and diameter of the transmission lines, linear velocity of water was calculated as 1 m/s. This velocity rate and the distance of pre-chlorination site to each location was used to determine the contact time. As Rodriguez model is a nonlinear regression, to transform it into the linear modes, the values were converted to logarithmic scale and then the multiple regression was fitted to the data so the dependent variables was considered as ln (TTHM) and the independent variables were ln (DOC), ln (pH), ln (temperature) and ln (residual chlorine). Then through determining the amount of (Beta), the effect of each parameter in THMs formation was estimated.

Results

Table 1 shows the results of DOC, pH, residual chlorine and water temperature in the tested samples for the four sampling locations. The statistical values for parameters affecting THMs formation in each sampling location are displayed in Table 2.

The calculated contact times for clarifier, filtration and disinfection effluents were 45 min, 11.5 hr and 12.1 hr, respectively. Because of lack of chlorination in raw water, no value for THMs was calculated. The averages of calculated THMs concentration in

Table 1: Results of DOC, pH, residual chlorine, water temperature measurements in the tested samples

Sample no	DOC (mg/l)				Temp (°C)				pH				Residual chlorine (mg/l)			
	RW	CE	EF	DE	RW	CE	EF	DE	RW	CE	EF	DE	RW	CE	EF	DE
1	6.37	4.58	3.87	3.44	23.54	22.51	21.49	21.50	7.78	8.27	8.21	6.81	0.00	0.70	0.52	1.59
2	6.11	3.78	3.20	2.84	25.07	22.51	22.00	22.00	7.99	7.98	7.45	6.60	0.00	0.84	0.57	1.89
3	5.94	4.29	3.63	3.24	24.05	23.03	22.51	23.03	7.78	8.50	8.31	7.01	0.00	1.30	0.66	1.57
4	5.42	3.80	3.32	2.93	22.51	22.00	22.51	22.00	7.56	8.50	7.77	6.60	0.00	0.93	0.61	1.71
5	6.05	3.92	3.32	2.54	22.00	21.49	21.49	20.98	8.21	8.62	8.07	6.70	0.00	0.57	0.22	1.29
6	4.94	4.17	3.83	3.00	23.54	22.51	21.49	21.49	7.99	8.30	7.30	6.81	0.00	1.15	0.85	1.42
7	5.69	4.45	3.76	3.46	25.07	22.51	22.51	21.49	8.10	8.35	8.21	6.91	0.00	0.93	0.60	1.81
8	5.86	4.29	3.63	3.46	24.56	21.49	20.98	20.47	8.21	8.33	7.40	6.91	0.00	0.88	0.66	1.99
9	4.55	4.34	3.12	2.74	24.05	21.49	22.51	20.98	7.61	8.50	8.04	6.60	0.00	1.09	0.81	1.95
10	5.91	4.10	3.95	3.24	24.56	22.51	23.54	22.51	7.67	8.67	7.36	6.26	0.00	1.02	0.52	2.28
11	4.91	4.29	3.25	2.88	23.54	22.00	22.51	21.49	7.99	8.33	8.00	6.82	0.00	0.79	0.45	1.78
12	5.74	4.19	3.56	3.13	23.03	22.51	22.51	22.51	8.21	8.15	7.98	6.70	0.00	0.97	0.75	2.19
13	5.93	4.56	3.87	3.00	22.51	20.98	20.47	20.47	7.89	8.30	7.57	6.91	0.00	1.20	0.18	1.20
14	6.18	4.02	3.39	3.00	24.56	21.49	21.49	20.98	7.56	8.27	7.93	6.81	0.00	1.05	0.25	1.80
15	5.33	4.73	2.54	1.96	21.49	20.98	20.47	20.47	7.89	8.59	7.54	6.81	0.00	1.06	0.63	1.50
16	5.81	4.34	3.66	3.25	20.47	19.96	19.96	19.96	8.10	8.22	8.13	6.81	0.00	1.03	0.64	2.34
17	5.47	3.46	2.93	2.59	19.96	20.47	20.47	20.47	8.21	8.64	7.43	6.60	0.00	0.52	0.31	1.18
18	5.45	4.16	2.88	3.24	19.44	18.93	18.42	18.93	7.50	8.43	8.21	6.70	0.00	0.75	0.51	1.17
19	4.82	4.09	3.46	3.07	21.49	20.98	24.05	22.51	8.21	8.46	7.35	6.60	0.00	0.97	0.40	1.65
20	5.37	4.12	3.47	2.55	18.93	18.93	19.44	19.44	8.10	8.50	8.21	6.81	0.00	1.00	0.45	2.26
21	5.84	4.02	3.71	3.27	17.40	18.93	17.91	18.42	8.10	8.42	7.44	6.50	0.00	1.03	0.48	1.98
22	5.45	4.12	3.47	3.24	19.44	20.47	20.47	20.98	8.21	8.50	7.78	6.81	0.00	0.66	0.57	1.48
23	4.63	4.34	3.39	2.76	21.49	21.49	25.07	23.54	7.89	8.30	7.22	7.01	0.00	0.60	0.36	1.33
24	5.77	4.91	4.37	3.47	22.00	21.49	24.56	24.05	7.54	7.75	7.49	6.91	0.00	0.67	0.48	1.95

Table 2: Average parameters affecting the formation of THMs in samples

Sampling period		DOC (mg/l)	Temperature (°C)	pH	Residual chlorine (mg/l)
RW	Mean	3.28	21.77	7.89	0.00
	St. Dev	0.3	2.09	0.25	0
CE	Mean	2.50	20.80	7.89	0.61
	St. Dev	0.26	1.153	0.2	0.14
FE	Mean	2.05	21.13	7.89	0.36
	St. Dev	0.253	1.734	0.2	0.13
DE	Mean	1.79	20.75	6.64	1.15
	St. Dev	0.249	1.335	0.17	0.238

the samples were $37.92 \pm 4.82 \mu\text{g/l}$, $51.15 \pm 9.44 \mu\text{g/l}$, and $52.71 \pm 8.37 \mu\text{g/l}$ for CE, FE, and DE, respectively. The maximum values were $47.10 \pm 4.82 \mu\text{g/l}$, $65.22 \pm 9.44 \mu\text{g/l}$, and $64.76 \pm 8.37 \mu\text{g/l}$ for CE, FE, and DE, respectively (Figure 1). None of the mean values met the desirable and allowable standards.

In order to determine the extent of any interference parameters in the form of THMs, by converting data into logarithmic scale, the data were standardized in linear mode and by comparison of the value of Beta, the effect of each parameter in THMs formation was estimated, as presented in Table 3.

As shown in Table 3. THM formation rose with increasing soluble humic material (DOC) in natural occurring water.

Discussion

Due to the distance of 90 km between Minab and Bandar Abbas water treatment plants, and direct interference of parameter of time, the calculated values for THMs of clarifier effluent were less than those of the other two locations. On the other hand, due to the existence of residual chlorine in the disinfection unit, the maximum amount of THMs was calculated in this unit. In order to evaluate the fitness of Rodriguez model on our data, fitness index for multiple regression was prepared (Table 4).

As shown in the above Table, the Rodriguez model has good fitness on the data. Based on the information in Table 3, the strongest coefficient between DOC and THMs formation was found in effluent of disinfection unit ($\beta=0.774$). It means that a higher available DOC

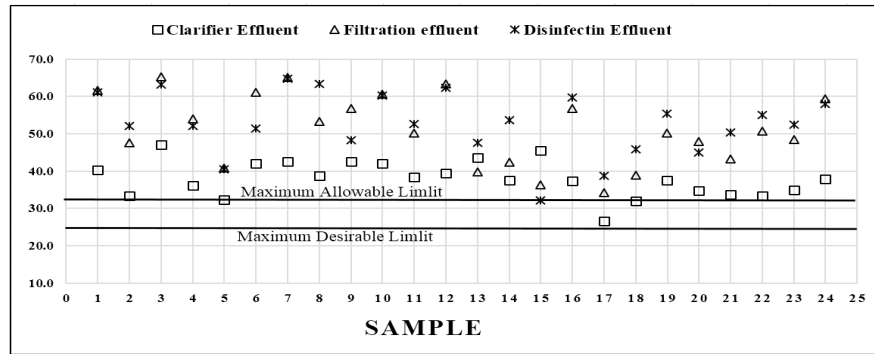


Figure 1: Calculated THMs ($\mu\text{g/l}$) and thresholds of maximum desirable and allowable limits.

Table 3: Coefficients of multiple regression model in different sampling locations

Location	Parameter	Unstandardized Coefficients		Standardized Coefficients	t	P value
		B	Std. Error	Beta		
CE	DOC	1.014	0.025	0.586	40.179	<0.001
	temperature	0.970	0.030	0.428	32.657	<0.001
	pH	1.159	0.075	0.221	15.387	<0.001
	Residual Chlorine	0.282	0.007	0.533	39.649	<0.001
FE	DOC	1.031	0.011	0.572	92.909	<0.001
	temperature	0.978	0.015	0.418	65.341	<0.001
	pH	1.159	0.027	0.274	43.627	<0.001
	Residual Chlorine	0.278	0.003	0.571	94.325	<0.001
DE	DOC	1.034	0.010	0.774	98.756	<0.001
	temperature	0.965	0.021	0.367	46.857	<0.001
	pH	1.030	0.053	0.158	19.515	<0.001
	Residual Chlorine	0.276	0.007	0.343	42.077	<0.001

Table 4: Fitness index for multiple regression in different locations

Location	R	R ²	Adjusted R ²	Std. Err of the Estimate
CE	0.998a	0.997	0.996	0.00796
FE	1.000a	0.999	0.999	0.00553
DE	0.999a	0.999	0.999	0.00627

a. Predictors: (Constant), residual Cl, PH, temp, DOC

will provide more THM if enough residue chlorine is available. This finding was in accordance with a large number of the previous studies.^{9,12,28-33}

Among the measured parameter, the lowest effectiveness was related to pH (Beta=0.158). Higher temperatures may promote chlorination reaction rates, leading to higher production of THMs.

In Bandar Abbas, temperature conditions (hot weather), the presence of organic matter in the raw water, long contact time (due to the distance between consumers and water source) and in some of cases excessive injected chlorine into the raw water have created suitable conditions for the THMFP in drinking water. Based on these results, given that most of the THMFP effect is related to DOC, to control THMs we need to reduce the organic matters' content in the raw water sources. So the construction of activated carbon site in BA water treatment plant is necessary to remove the organic matter in the raw water. In addition, in the presence of zero-valent iron, organic

matters are involved in a de-halogenation reaction, so their concentration in water decreases. Thus its use can be effective in control of organic matters in water.³⁴ According to the results, the calculated THMs concentration in all locations except for raw water was higher than EPA standard (30-40 $\mu\text{g/l}$).³⁵

Conclusion

Considering health risks and particularly carcinogenic potential related to THMs in drinking water, measurement of these compounds in water is very important but due to expensive and time consuming nature of these tests, routine examination for THMs is not performed in many water supply systems, so mathematical modeling is an alternative approach to complex experimental procedures for determining THMs concentrations in drinking water. Existing THMs prediction models have a number of advantages, as well as limitations. According to the results, the calculated THMs concentration in all locations except for raw water was higher than EPA

standard (30-40µg/l).

It found high effectiveness of DOC in THMPF which can be a key for control of THMs in these types of water resources.

Due to the fact that very little data about THM is currently available for distribution system in Iran, the generation of data using a modeling approach can be useful. However, with given complexity of water quality, evolution in distribution system, modeling results must be interpreted with caution and experimental studies should be conducted to validate the results of such studies.

As a general interpretation of the study results, the long distance between pre-chlorinated water and consumers, hot climate of Bandar Abbas, and particularly existence of organic matters in raw water have created a good condition for THMs formation in the drinking water system; therefore, more detailed studies should be done to resolve the consumers' concerns in this regard.

Conflict of Interest: None declared

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