Monitoring of THMs Concentration in Isfahan Water Distribution System and Zoning by GIS, a Case Study in the Center of Iran

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ABSTRACT
Trihalomethanes (THMs) formation in treated water is a consequence of a reaction between the chlorine used for water disinfection and some natural organic matters. The objectives of the present study were monitoring of THMs concentration in Isfahan (A metropolis city in center of Iran) water distribution network (IWDN), evaluation factors that affect the THMs formation potential and identification of critical points by using geographical information system (GIS). The study was performed in summer months of 2014. For sampling point's selection, city divided into 30 zones and water quality parameters such as pH, Electric Conductivity (EC), residual Chlorine, Total Organic Carbon (TOC) and THMs of IWDN measured. Multi regression analysis was used to estimate the correlation between THMs formation and these variables. While the statistical analysis with Spearman non-parametric correlation coefficients showed a positive correlation between distance from treatment plant and THMs concentration(r=0.45, P =0.01) and negative strong correlation(r=-0.95, p>0.001) between THMs and TOC concentrations, there was no strong significant relationship between THMs formation in IWDN and some variables including pH, temperature and residual Chlorine.
The results reveal that the average value of the THMs at sampling points for summer attained 42.56 ppb which was lower than the EPA and WHO standards. It is recommended that the distance from the treatment plant was used as an effective parameter for estimation of THMs formation potential.
Key words: THMs, Drinking water, Chlorine, GIS, Isfahan

INTRODUCTION
The safe drinking water supply is anxiety in the world [1]. Disinfection is the latest step in the water treatment process to prevention of secondary pollution due to regrowth of pathogenic microorganism in the water distribution system. Chlorine is used widely for water disinfection process in developing countries and Iran [2,3].
Trihalomethanes (THMs) formation in treated water is a consequence from the reaction between of chlorine and some natural organic matters, especially humic and fulvic acids [4, 5]. THMs include chloroform ($CHCl_3$) dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform (CHBr3)[6]. Chloroform is the most common by-product produced in water after disinfection by chlorine [7]. In water with high bromide concentrations, chlorination could be caused to brominates THMs formation [8].
THMs are the most important group of chlorinated by products and their production in drinking water can cause bladder, kidney, and liver cancers [1]. The maximum concentration level of THMs in drinking water, the United State environmental protection agency (USEPA), Europe Community and world health organization (WHO) accepted 80µg/L, 100µg/L and ([TTHMs/WHO guideline]≤1)., respectively [6, 9].
THMs production in water is depended on several factors including raw water quality, concentration and nature of the natural organic matter (NOM), disinfection contact time, chlorine dose, bromide concentration, temperature and pH of the water [10]. So, removal of THMs precursors is necessary before water disinfection. As a result, filtration and coagulation processes have an important role in preventing of THMs formation [11, 12].
Some studies survey THMs values on water distribution network in different cities of Iran and other countries. Based on the results of previous studies in Iran, total THMs concentration was less than 200 ppb in Lahijan, Tehran and Ahvaz cities

[13-15]. In similar researches, in Osaka city of Japan and Malaysia, THMs concentration was reported less than 60 ppb and 135 ppb, respectively [16, 17].
This study was aimed to evaluate the relationship between some independent variables and THMs formation in several points of IWDN and identification of critical points by using geographical information system (GIS).

MATERIAL AND METHODS

Study area and water characteristics

Isfahan is one of the largest cities in Iran and located at the central part of Iran. This city has 300 km2 areas. The study was performed in the summer months. For selection of sampling point, city divided into 30 zones as showed in Fig. 1.

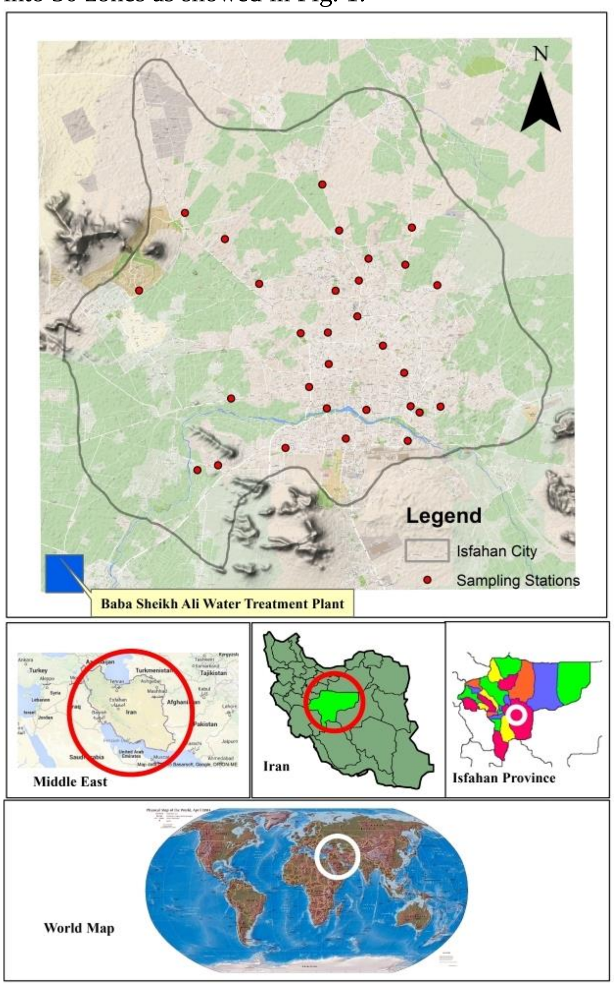

Fig. 1: Sampling points of IWDN

The major resource of drinking water supply in Isfahan city is the surface water of Zayandehroud River and type of water treatment plant (named Babasheikh Ali) is a conventional system. Characteristics of water before and after treatment in Isfahan water treatment plant (IWTP) is shown in Table 1.

Table 1: Characteristics of water before and after treatment in IWTP

parameter	Before treatment	After treatment
TOC, mg/L	2.65- 3.4	2.6- 3.3
Turbidity, NTU	1-3	1>
Alkalinity, mg/L as $CaCO_3$	15-140	13 - 19
pH	8 - 8.5	7.1- 8.4

Preparation of Containers

Before sampling, bottles (300-mL amber glass) washed with detergent – tap water and rinsed by de-ionized water, and then dried in oven at 400 °C for 1 h. Also for removal residual chlorine and prevention of THMs product during sampling, sodium thiosulfate (20 mg/ml) was added to bottles [18].
Sampling procedure and field measurements
Sampling was conducted in the summer season. The temperatures were between 30-40 °C. Water samples were taken from 30 points of IWDN (Fig. 2). Sampling operation was carried out in official and commercial buildings using tap water in the nearest accessible place. During filling bottles, air bubbles entrance were prevented into the samples. After collection samples, bottles were maintained in the dark at 4 °C in the laboratory for THMs detection. Also pH, EC and residual chlorine measured in the field by pH meter 310 AUTECH company and chlorine meter model 58700-12 HACH Company.

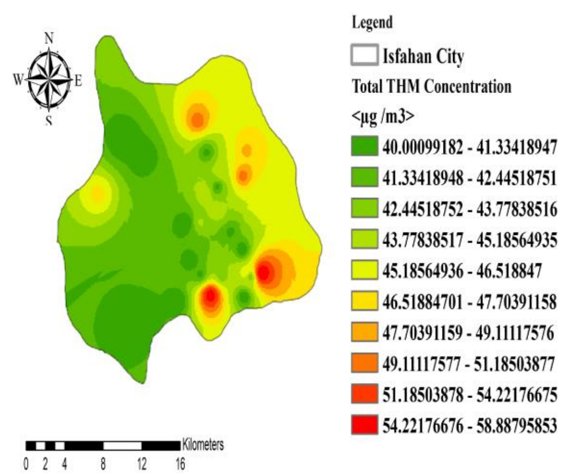

Fig. 2: Zoning of THMs contamination by IDW in IWDN

Determination of THMs and TOC

THMs analyzed based on Method 524.2 (USEPA 1995) by a gas chromatograph-mass spectrometer (GC/MS), Agilent Company 6890 N, and a purge and trap system. Some information about the GC/MS analysis is illustrated in Table 2.

Total organic carbon (TOC) was analyzed, using combustion techniques (method 5310B) by TOC-VCSH analyzer (Shimadzu, Japan).

Table 2: Some information about the GC/MS analysis

Column characteristics	
Model	DB5-MS
Type	Capillary
Length, m	30
Internal diameter, mm	0.25
Injector characteristics	
Injection volume, µL	1500µl HS 10cc Sample
Temperature, ˚C	160
mode injector	Split
injection ratio	2:1
Detector: characteristics	
Type	MS (mass spectrometer)
Carrier gas characteristics	
Type	Helium
Carrier flow, mL/min	1

Spatial analysis method

Two spatial Regression methods, ordinary kriging (OK) and inverse distance weighting (IDW) are used for spatial prediction. Ordinary kriging (OK) is a linear regression model. The non-statistical inverse distance weighting (IDW) method applied for spatial prediction.

For compartment accuracy of kriging and IDW interpolation approaches was applied to root mean square error (RMSE) as Eq.(1):

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(q_i - \hat{q}_i)^2} \qquad (1)$$

Where n, qi and qiˆ are number of samples, measured value and predicted value, respectively and RMSE larger is better.

RESULTS AND DISCUSSION

THMs values in IWDN

Concentration of TTHMs and the result of water quality parameters measurement in IWDN are presented in Table 3. So, these results confirmed that THMs concentration at sampling points in IWDN were lower than the EPA and WHO standard [6, 9]. According to Table 3, the average value of the THMs at sampling points for summer attained 42.56 ppb which was lower than its standard level. The maximum and minimum values obtained 59 and 40 ppb, respectively. In other recent studies in Iran, THMs concentration in Tehran, Lahijan and Ahvaz cities reported less than 100 ppb. Of course in these cities the main source of water supply is being rivers and dams [13, 14].

Table 3: Concentration of TTHMs and water quality parameters were measured in IWDN

Sample number	**pH (±0.2)**	**EC (µs/cm)**	**Temperature (˚C)**	**Residual Chlorine (ppm)**	**Distance from IWTP (km)**	**TOC (ppm)**	**TTHMs (µg/L)**
1	8.5	419	21	1	17	2.43	57
2	8.4	485	25	1	20	3.41	40
3	8.4	440	22	1.5	22	3.32	41
4	8.1	524	21	1	27	2.95	46
5	8.1	586	27	1	26	2.56	50
6	8.6	564	25	0.8	21	3.12	43
7	8.2	498	21	1	25	2.97	45
8	8.1	490	27	0.7	28	2.68	48
9	8.2	595	22	0.7	25	3.46	41
10	8.1	590	26	0.3	27	2.53	50
11	8.1	560	26	1.2	21	3.48	40
12	8.1	480	28	0.6	22	3.39	40
13	8.2	432	27	3.3	17	2.86	47
14	8.2	446	25	1.7	8	3.49	40
15	8.2	477	25	1.6	10	3.47	40
16	8.5	368	20	0.4	14	3.5	40
17	8.5	475	21	0	17	3.41	41
18	8.5	455	20	0.8	19	3.28	43
19	8.6	446	23	0.3	21	2.91	46
20	8.6	367	23	0.1	23	2.39	59
21	8.5	470	23	1.1	22	3.39	40
22	8.3	436	25	0.6	22	2.99	45
23	8.3	380	26	0.6	20	3.09	44
24	8.3	387	25	1.9	22	3	45
25	8.3	436	26	0.1	23	3.35	41
26	8.3	401	26	0.6	20	3.29	42
27	8.4	375	25	2	19	3.47	40
28	8.3	375	25	1.5	19	3.21	42
29	8.3	355	25	2.8	17	3.43	40
30	8.4	336	25	0.7	13	3.35	42

Distribution levels of THMs in water samples of IWDN by Inverse Distance Weighting and kriging methods are shown in Fig.2, 3 respectively. The highest THMs concentration was found in the east end part of IWDN, because IWTP is located in southwest of Isfahan.

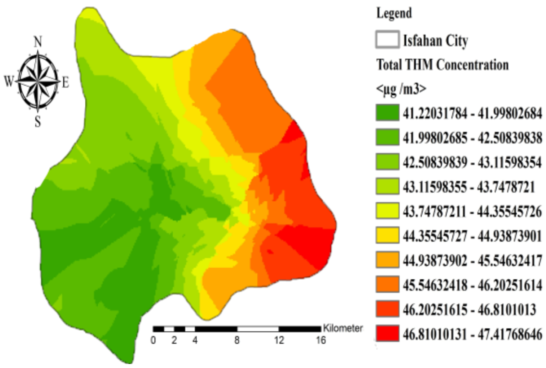

Fig. 3: Zoning of THMs contamination by kriging in IWDN

Effect of residual Chlorine

Figure 4, 5 provide a comparison of residual chlorine concentration zoning in IWDN by IDW and kriging methods respectively. The lowest Chlorine values are measured in eastern part of IWDN. Therefore, THMs formation rose by increasing the distances from IWTP.

In case area study, ranges of measured residual chlorine were between 0.1 to 3.3 ppm. Chlorine in distribution pipes is being necessary agent against secondary pollution. Although, residual chlorine can be one of the main factors in THMs formation; in this study, statistical analysis using Spearman non-parametric correlation coefficients showed no significant relationship between residual chlorine and THMs values. Similar study which was carried out in Sabak Bernam district of Malaysia, showed no correlation between residual chlorine and THMs production. It may be attributed to water quality, temperature or properties of pipes [17].

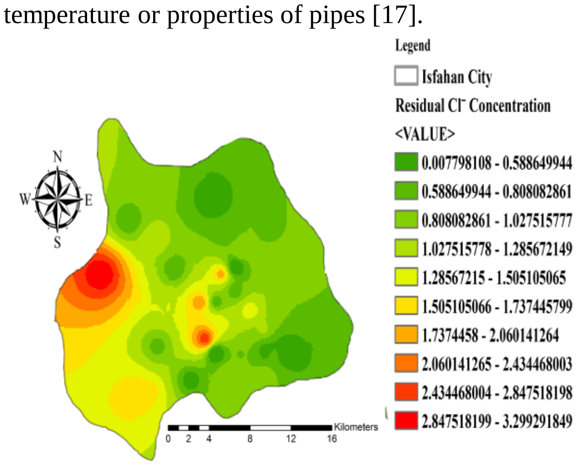

Fig. 4: Zoning of residual chlorine concentration by IDW in IWDN

Effect of pH

In IWDN, water pH value was from 8.1 to 8.6 and its variations was less than 1 unit and negligible. Generally High pH level result is increasing THMs formation [17]. Researchers reported, rate of THM production three-time increase in per unit pH [19].

On the other hand, disinfection efficiency and residual Chlorine in water are pH dependent. While THMs value increases, the concentration of hypochlorous acid (HOCl) decreases and hypochloride (OCl-) increased. So, pH is very important parameter in controlling of THM formation [19]. As can be seen in Table 3, pH value of Isfahan treated water is higher than 8 thus OCl- is the dominant species. Garcia-Villanova et al. reported a strong linear relationship between pH and THMs formation[20], but in this study a significant correlation among pH and THMs formation was not found. It may be due to negligible Variations of pH.

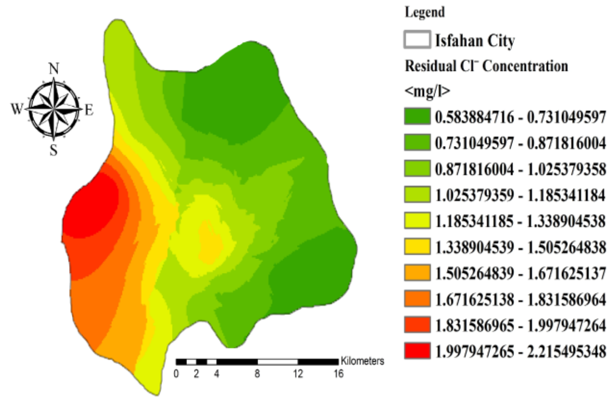

Fig. 5: Zoning of residual chlorine concentration by kriging in IWDN

Effect of temperature

As showed in Table 3, the temperature of water in IWDN was 20 to 28$^{\circ C}$. Water temperature related to the production of THMs. Uyak et al. indicated that THMs formation potential in 22$^{\circ C}$ is 60-70% more than at 2$^{\circ C}$ [19]. Therefore, high temperature (>20$^{\circ C}$) is an important factor for THMs formation. In the present study, water temperature was optimum for THMs formation but no correlation obtained between THMs production and temperature. The reason may be mixing ground water for IWDN and water quality or other confounders. Garcia-Villanova *et al.* obtained the critical temperature value (Tc) for THMs formation 18.97$^{\circ C}$. THM level was reduced severely when the temperature was above Tc value [20]. Also in consistent of our findings, there was no significant relation between temperature and THMs formation in their study.

Effect of Distance from IWTP

As mentioned earlier, THMs values increased with distance of water treatment plant and highest THMs concentration was observed at the end of IWDN (Fig. 2, 3). According to statistical analysis using Spearman non-parametric correlation method, there was a good positive correlation between distance from treatment plant and production of THMs (r =0.45, P=0.01). This direct relation is because of enough contact time for reaction between chlorine and TOC. In another study, in Madras city of India, a direct distance-THMs correlation has been reported [21]. However, Pauzi et al. showed that there is a small relationship between THMs formation and distance of water treatment plant [17]and interestingly, Badawy reported an inverse distance-THMs correlation [22], this different results may be due to volatilization.

Effect of TOC

Table 1 illustrates characteristics of sampled water before and after treatment in IWTP. As can be seen, water supply was of acceptable quality, with its pH, turbidity and alkalinity. It is known that THM production is a multi-stage process including the initial fast reaction followed by secondary slow reaction of chlorine (e.g. water distribution conditions) with remaining NOM to form disinfection byproducts such as THMs in distribution systems.

NOM surrogate parameter, namely TOC concentration of water samples from the distribution network ranged from 2.6 to 3.3mg/L. The average concentration of residual chlorine was 1.07 ppm.

Some of the previous researches have shown an apparent positive correlation between water TOC and THMs concentrations. As reported by Hassani et al. using Pearson correlation method, a significant direct correlation (r=0.36) was obtained between THM formation and water TOC levels for Rasht water distribution system [23]. In the present study Spearman correlation coefficients showed a strong negative correlation (r =-0.95, p<0.001) between TOC and THMs formation. Similarly, Ahmadi *et al.* based on the results of their investigation carried out in Khuzestan province of Iran, showed a negative impact of TOC on THMs formation [24]. Possible reasons for negative correlations are including: not all of the organic compounds necessarily result in the formation of disinfection byproducts. TOC does not differentiate between the various chemical compounds that make up the precursor compounds.

THMs formation and EC in IWDN

The electrical conductivity (EC) of water is a good indicator of the total amount of dissolved solids in water. The main source of IWDN supply is surface water, Zayandehrud River and several deep wells. So the values of water conductivity were low than 590 µs/cm in all analyzed samples.

Although, the major factors for THMs formation are being TOC, Cl_2, pH, contact time and temperature[10], in the present study due to non-apparent correlation among THMs by some of these factors, EC values were evaluated in water samples as a additional factor. Table 3 indicates that the samples with high EC levels have low THMs because pumping ground water in network and dilution Chlorine.

THMs formation modeling in IWDN

Statistical analyses for THMs formation modeling were carried out using SPSS software, version 16(Multi regression method). In this model according to the equation 2, amount of THMs formation estimated from TOC, residual Chlorine, pH, temperature and distance from IWDN values. Also regression model accuracy shows statistically significant (R Square = 0.93).

$$\mathbf{THMs = 69.205 + (-0.093 \times Cl) + (2.771 \times pH) + (-0.098 \times T) + (-0.059 \times L) + (-14.216 \times TOC)} \quad (2)$$

Table 4 illustrates the level of significant regression model. This model could be used for prediction of THMs formation potential in IWDN.

Table 4: Regression model coefficients and their level of significance

Variables	β	Standard errors	t-values	*p*-level
(Constant)	69.205	15.849	4.366	0.000
Cl_2	-0.093	0.405	-0.230	0.820
pH	2.771	1.601	1.731	0.096
Time	-0.098	0.077	-1.269	0.217
Distance from WTP	-0.059	0.081	-0.727	0.474
TOC	-14.216	1.031	-13.791	0.000

Spatial analysis of THMs

Spatial analysis of THMs and residual Chlorine concentration in water IWDN is given in Table 5. Root means square error (RMSE) was used to be choice the best prediction approach. kriging (RMSECl =0. 8, RMSETHM =4.9) and IDW (RMSECl =0.798, RMSETHM=5) methods estimated for values of THMs and Residual Chlorine, but the kriging method was more accurate for Residual Chlorine and IDW for THMs. It is apparent that the IDW method is better for zoning of parameters in water distribution network [25].

Table 5: Spatial analysis of THMs and residual Chlorine concentration in IWDN

RMSE	Name of parameter	Type of model
0.798	residual Chlorine	IDW
5.067	THMs	IDW
0.806	residual Chlorine	OK
4.955	THMs	OK

CONCLUSION

The results of this study revealed that all of the samples which were taken from Isfahan water distribution network, showed THMs concentration less than EPA and WHO guideline values. Based on the findings, no significant relationship was found among THMs formation in IWDN and effective parameters such as pH, temperature and residual Chlorine, probably due to mixing ground water for IWDN or other confounders. Also, it was evident that distance from the treatment plant is an important parameter for THMs production in a water distribution network. By increasing distance from IWTP higher THMs concentration was found. Multi regression model was used for estimation of THMs formation from TOC, residual Chlorine, pH, temperature and distance from IWDN values. Since, regression model accuracy showed statistically significant (R Square =0.93), this model could be used for prediction of THMs formation potential in IWDN. Finally, IDW method was chosen as the best prediction approach for zoning of parameters in a water distribution network by Arc GIS software.

ETHICAL ISSUES

Ethical issues such as plagiarism have been observed by authors.

CONFLICT OF INTERESTS

Authors of this manuscript declare that we have no significant competing interests that might have influenced the performance of the work described in this manuscript.

AUTHORS' CONTRIBUTIONS

The study was directed by A.E. A.M (first author) performed all the experiments and drafted the manuscript. SN (Corresponding author) edited the manuscript. M.M was participated in Spatial and statistical analysis and H.KH was involved in discussion of the results. All authors have read and approved the final manuscript.

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