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THMs assessment in Khuzestan rural water treatment plants

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ABSTRACT

Aims: The trihalomethanes (THMs) concentration was investigated in some of rural water treatment plants in Khuzestan.

Materials and Methods: Fifteen of the water treatment plants with the same drinking water source (Karoon river) were selected for analysis of THMs to assess the levels and the relationship between THMs and total organic carbon (TOC), pH, temperature, chlorination dose, and free chlorine residue.

Results: THMs ranged from 1.8 to 219 mg/l in winter and 1.7 to 98 in summer, where the level in some treatment plants is higher than the Maximum Concentration Level (MCL). The ratio of total THMs levels was significantly correlated with temperature, pH, chlorination dose, and free chlorine residue, but negative correlation with TOC.

Conclusion: Epidemiological studies using total THMs levels should be considered in the analysis of water treatment plant's results, and regulatory check of this parameter with drinking water guidelines.

Key words: Drinking water, Khuzestan, rural water treatment plants, THMs

INTRODUCTION

Although chlorination is most widely used for disinfection of drinking water treatment plants, trihalomethanes (THMs) are formed as a result of chlorination of natural water. Only four THM compounds are normally found: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). Additional chlorination by-products can be formed during the relatively slow organic reactions that occur between free chlorine and naturally occurring organic precursors such as humic and fulvic acids. The formation potentials of these additional by-products can also be determined, but different quenching agents and different analytical procedures may be needed.[1] There are various factors which significantly affect the formation of THMs such as pH, temperature, dissolved organic carbon (DOC), bromide concentrations, and operational factors like chlorine dose and contact time.[2] Many researchers have qualitatively and semi-quantitatively investigated the effects of these factors on THM formation.[3] Since THMs in nation's drinking waters have been related to cancer and reproductive outcomes, the presence of these compounds is of concern from the health-related aspect; epidemiological studies have recommended a probable link between chlorination and chlorination by-products with excess risk of bladder and rectal cancer.[4] Also recent epidemiological studies have also recommended that THMs may have negative acute reproductive effects, as well as spontaneous abortion, birth defects, and stillbirths.[5,6] The most current toxicological and some epidemiological studies have recommended that the

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brominated THMs cause the greatest concern.[7] Therefore, new restrictive rules of surface water and the maximum level of total THM (TTHM) in the distribution systems are being imposed by the Safe Drinking Water Act and its amendments (SDWAA).The recommended maximum contaminant level (MCL) of THM is 80 μg/l.[8] Several studies have been carried out in the USA, Canada, EU, UK, Malaysia, Poland, Spain, and Finland to evaluate the distribution and determinants of THMs and HAAs. They reported that the THMs and HAA_s levels during the chlorination of drinking water were related to disinfection processes and chemicals, water source, pH, temperature, concentration of chlorine residual, residence time, reaction time, humic and fulvic content, total organic carbon (TOC), and bromide content, and that these factors affected the various THMs and HAAs in different ways providing a potentially different mixture of THMs and HAAs in different regions. Also they found that the THMs concentration will increase with enhanced residual time, bromide, residue chlorine, TOC, and specific by-products in water distribution systems.[9-14] Most municipal water supply systems in Khuzestan (southwest of Iran) use chlorination for water disinfections because it is extremely efficient and cost effective. As such the formation of THM during chlorination process is important and need to be monitored with the view to ensure the compliance of the guidelines set. However, little is known about the levels of THMs in drinking water in Khuzestan since to our knowledge no data have been published in the scientific literature. The aim of this study was to measure the THM levels in 15 rural water treatment plants in Khuzestan, Iran.

MATERIALS AND METHODES

Areas of study

Khuzestan Province is one of the 31 provinces of Iran. It is in the southwest of the country, bordering Iraq's Basra Province and the Persian Gulf. Fifteen rural water treatment plants with the same drinking water source (Karoon River) were selected to measure THM_s [Table 1]. Water samples were taken for the analysis of various parameters such as THM_s (μg/l) and its four compounds, TOC (μg/l), pH, temperature (°C), chlorination dose (ppm), free chlorine residue (ppm) in summer and winter of 2009.

Sampling and THM_s measurement

Four THM_s (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were analyzed according to Standard Methods (Method number: 5710).[1] The THM samples were collected in 1-L glass (5710 A) bottles sealed with TFE-lined screw caps. As the sample has been chlorinated previously, they were collected with minimum turbulence and the sample bottles were filled completely and sodium thiosulfate solution (10%) was added to the bottles to avoid loss of THMs already present. A rapid and simple method for THM analysis by Purge and Trap coupled with a capillary column gas chromatograph was used to analyze the THM level in Iran mineral processing research center. The characteristics of GC and its operating conditions were shown in Table 2. The TOC analyzer (Shimadzu, model V_{CSH}) was used to analyze the value of TOC. Standard solution of THM species was purchased from Merck company and used without any purification.

RESULTS

To our knowledge, this is the first published study that has measured THM levels in Khuzestan drinking water. A total of 30 samples were collected for the year 2009. The drinking water quality parameters are shown in Table 3.

Pearson's regression analysis was used to examine the correlation of THM with respect to TOC, pH, and chlorine dosage and residue chlorine [Table 4]. Using Pearson's correlation method, a low but definite with small negative relationship (r = -0.247) was obtained between THM formation and TOC for the drinking water treatment plant. A low correlation, definite with

Table 1: Characteristics of Khuzestan rural water treatment plants

Name	Year of operation	Population served	Nominal capacity (L/S)	Water supply source	Water treatment plant level	
					X	Y
Janat Makan	1997	6510	15	Karoon River	289650	3565500
Chamran	1985	4852	20	"	280708	3566545
Shalili	1983	2380	11	"	300786	3527176
Langar	1995	3705	14	"	297542	3535961
Seyed Enayat	2008	1729	3.50	"	297077	3523525
Arab Hasan	1979	2195	10	"	301250	3523980
Yadvareye Eman	1994	7689	186	"	298354	3498590
Omol gharib	2009	2800	22.2	"	301690	3490550
Sheyban	2009	11240	270	"	289937	3478294
Seviseh ha	1990	4560	60	"	274890	3553328
Shohadaye Jahad	1994	11970	170	"	248996	3443911
Khanafereh	2007	39457	288	"	272576	3393872
Gharbe Karoon	2009	3663	17	"	251659	3420191
Hafar Sharghi	2000	5749	42	"	235782	3372739
Shahid Keshtkar	1993	48500	416	"	223278	3275385

moderate relationship, was obtained between THM formation and pH. Also a significant relationship ($r = 0.815$) was obtained between THM formation and total chlorine dosage in both summer and winter.

DISCUSSION

Statistical analyses were performed using analysis of variance (ANOVA) to check the relation between investigated parameters in winter and summer ($\alpha = 0.05$). The value shows a significant difference between the two seasons. Also the mean value for the total THM_s, $CHBr_2Cl$, $CHBrCl_2$, $CHBr_3$, and $CHCl_3$ was observed to be higher in winter compared to summer. However, $CHBr_3$ was found to be higher in summer compared to winter ($P < 0.05$). This is due to the water quality at different seasonal conditions and environment. As shown in Table 3 and Figure 1, the level of THM_s in the number of water treatment plants in Khuzestan was higher than recommended MCL in both summer and winter, but these levels were set with national standards,[15] although high concentration was more significant in winter compared to summer. The THM_S results were compared with WHO water quality guidelines using a statistical *t*-test. According to the result, there was significant difference between total THM_s in winter and MCL of THM defined by WHO ($P < 0.05$), but no significant difference was observed between total THM_s in summer and MCL of THM defined by WHO ($P > 0.05$). It seems it was due to various compounds of organic matter in winter.[3] . Table 5 was used for compares THM standards in this study with different locales of world.

Table 2: Characteristics of GC and operating conditions

Column:Model	DB-1701
Manufacturer	Agilent Technologies (USA)
Type	Fused silica capillary GC column
Length (m)	30
Internal diameter (mm)	0.32
Film thickness (μm)	1
Injector	
Injection time (min)	0.15
Temperature (°C)	200
Detector	
Type	μECD
Temperature (°C)	300
Oven temperature Program	Initial 40°C for 1 min, Ramp 1: 5°C/min to 100°C for 0 min, Ramp 2: 100°C/min to 200°C for 3 min.
Carrier gas	
Type	Nitrogen
Carrier flow (ml/min)	5.6
Make-up gas	
Type	Helium
Make-up flow (ml/min)	60

Effect of TOC

Most investigators reported that THM formation rises with increasing soluble organic material content in natural water. The rate of THM formation will enhance as a result of TOC consumption and the results fitted to first-order reaction. [18, 19] In fact with adequate residue chlorine, the formation of THM will increase by higher available TOC. In comparison to studies previously reported about the positive impact of TOC on THM formation in drinking water, the statistical analysis showed a negative impact of TOC [Table 4]. This result is in accordance with Matamoros *et al*,

Table 3: Water quality parameters in selected Khuzestan rural water treatment plants (2009)

Water quality parameter	Winter		Summer	
	Mean ± SD	Range	Mean ± SD	Range
pH	7.75 ± 0.23	7.45-8.2	7.92 ± 0.13	7.7-8.12
Temperature (°C)	20.75 ± 2.1	17.3- 25	30.24 ± 2.4	24.7-32.8
TOC (mg/l)	3.4 ± 0.29	3.02-4.03	3.6 ± 0.42	2.95-4.49
Chlorine dosage (mg/l)	2.95 ± 0.99	1.5-5	2.62 ± 0.91	1.5-4
Residue chlorine (mg/l)	1.67 ± 0.82	0.5-3	1.5 ± 0.83	0.5-3
Total THMs (μg/l)	64.83 ± 68.83	1.8-219	35.37 ± 40.74	1.7-98
$CHBr_2Cl$ (μg/l)	26.43 ± 24.36	< 2-69	13.53 ± 15.8	< 2-46
$CHBrCl_2$ (μg/l)	15.01 ± 21.02	< 2-62	3.53 ± 2.5	< 2-9
$CHBr_3$ (μg/l)	13.2 ± 10.65	< 2-38	20.13 ± 25.76	< 2-94
$CHCl_3$ (μg/l)	12.6 ± 20.27	< 2-73	2.53 ± 2.06	< 2-10

Table 4: Relationship between THM_s concentration with effective variables

	pH	Temperature (°C)	Residue chlorine (mg/l)	Total THM_s (μg/l)	TOC (mg/l)
Temperature (°C)	-0.589 (0.021)				
Residue chlorine (mg/l)	-0.888 (0.000)	0.536 (0.039)			
Total THM_s (μg/l)	0.556 (0.031)	0.470 (0.077)	0.585 (0.022)		
TOC (mg/l)	0.207 (0.459)	0.332 (0.226)	-0.167 (0.552)	-0.247 (0.074)	
Chlorine dosage (mg/l)	-0.818 (0.000)	0.625 (0.013)	0.855 (0.000)	0.815 (0.000)	0.016 (0.955)

Cell Contents: Pearson's correlation(*P*-Value)

Table 5: Toxicological information and standards/guideline related to THM_s (mg/l) in various locales of the world[15-17]

Compounds	Toxicological information		Regulatory					IRAN (2009)
	Animal	Human	WHO (2011)	USEPA (2012)	Health Canada (2007)	AUS-NZ (2004)	UK (2000)	
CHCl3	Liver Tumor	B2	0.300	0.070*	-	-	-	0.300
CHCl2Br	Kidney Tumor	B2	0.060	0.000*	0.016	-	-	0.060
CHClBr2	Colon Tumor	C	0.100	0.060*	-	-	-	0.100
CHBr3	Liver Tumor	B2	0.100	0.000*	-	-	-	0.100
TTHM	-		(THM/WHO) ≤ 1**	0.080	0.100	0.250	0.100	(THM/WHO) ≤ 1**

UK: United Kingdom; Aus-NZ: Australia-New Zealand; B2: Probable human carcinogen (sufficient laboratory evidence); C: Possible human carcinogen. *Maximum contaminant level goals (MCLG). **The sum of the ratios of the THM level to the WHO guideline values should not exceed 1

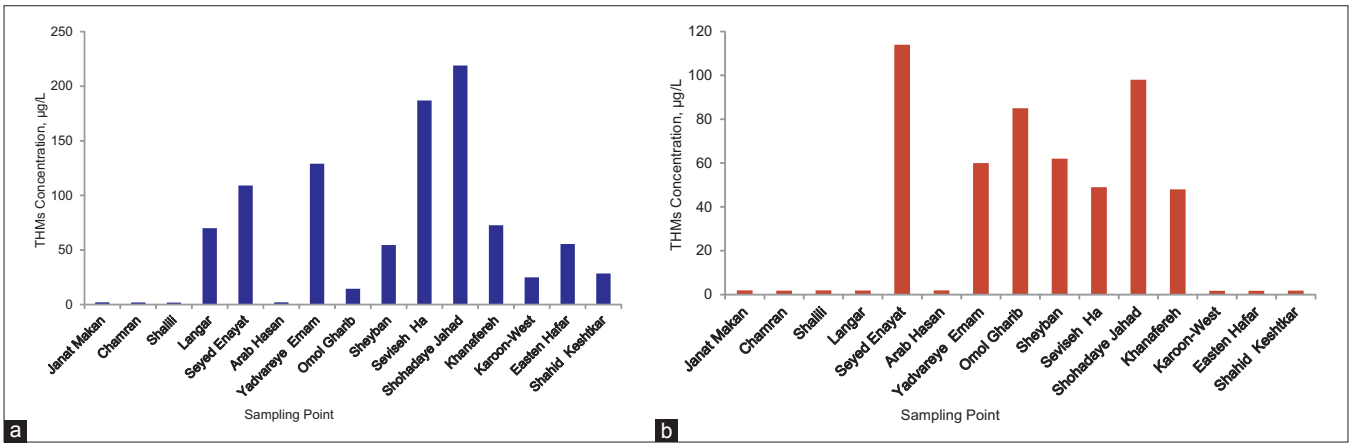

Figure 1: Average of THMs concentration in various rural water treatment plants in (a) winter and (b) summer

who investigated THM formation in wastewater treatment plants in NE Spain. As they reported that while various factors can effect TOC on TTHM formation potential, it is noticeable that the differences in the type and concentrations of the TOC present in drinking water are significant to its formation too.[20]

Effect of pH

According to the findings, the rate of THM construction increases with pH.[21] As Adin *et al*, reported,[22] pH has two effects: decreasing THM formation as a consequence of low pH and correspondingly increasing THM formation as a consequence of high pH.[22] This is due to the reality that the initial reaction is dependent on HClO concentration, which is associated with pH. The lower the pH, the higher the HClO concentration resulting in alters to higher concentration of humics. The formation of THM chiefly depends on the last step of THM attack, which is the base-catalyst as with the THM reaction. Other investigators also pointed this effect,[23] who reported decreased THM formation as a result of lowering the pH.

Effect of chlorine dosage and residue chlorine

According to the finding of Gallard and Gunten, long-term chlorine demand and the formation of THM have a significant relationship and could be described by second-order kinetics.[24] As Malliarou *et al*, reported, many investigators confirm the fact that the ratio between total THM and total HAA levels was significantly correlated with temperature, pH, free, and total chlorine. Because of various parameters' influence on the formation of THMs and HAAs, the correlation was commonly moderate to weak.[9]

CONCLUSIONS

The level of THM in a number of water treatment plants in Khuzestan is higher than MCL in both summer and winter, although high concentration was more significant in winter compared to summer. Based on the validation results obtained, it would appear that using Pearson's method of correlation, the organic matter measured as TOC showed a negative correlation with the formation of THM. A positive correlation was obtained for pH, temperature, chlorination dose, and free chlorine residue. Due to the fact that very little data about THM are currently available for the drinking water treatment plant in Khuzestan, Iran, this study is extremely useful for people to care more for their water drinking quality.

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