Trihalomethanes Concentration in Different Components of Water Treatment Plant and Water Distribution System in the North of Iran

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ABSTRACT: Since the surface water is one of the main potable water resources, the usage of chlorine as a disinfectant has increased. Consequently the production rate of disinfection by-products (DBPs) such as Trihalomethane (THM) compounds has grown dramatically. In this paper the THM_S concentration changes in the Sangar Water Treatment Plant (SWTP) and Rasht Water Distribution System (RWDS) is presented. The duration of these monitoring tasks were 6 months in 2007 and samples were collected every 2 weeks. Water samples were collected from five locations at SWTP and RWDS. Some independent variables including Total Organic Carbon (TOC), pH, temperature, and residual chlorine were measured by Pearson method to find a relation between THM_S formation and these variables. In the case of TOC, Pearson method showed a correlation of $r = 0.8096$ for SWTP and $r = 0.3696$ for RWDS between THM formation and TOC. Also the relationship for SWTP was $r = 0.239$ and $r = 0.2336$ for RWDS between THM formation and temperature. Correlation between THM formation and pH, Pearson method showed $r = 0.4658$ for SWTP and $r = 0.3232$ for RWDS. In the case of residual chlorine, Pearson method showed a relationship of $r = 0.7354$ for SWTP and $r = 0.5623$ for RWDS. Results proved a direct relation between THM_S concentration and distance of chlorination injection points. The results showed that in SWTP, 42.7 percent of THM compounds were removed after sedimentation and filtration.

Key words: Disinfection by-products, Water distribution system, Chlorination, Guilan province

INTRODUCTION

There is a variety of disinfection methods being utilized world wide for treatment but chlorination is the most common method among these methods. Water disinfection with chlorine improves the hygienic quality of water by eliminating waterborne bacterial pathogens such as dysentery and diarrhea diseases, cholera, typhoid fever, hepatitis A, etc. Residual chlorine can protect water from secondary pollution in the water network; also Chlorine application is simpler than other disinfectants. The usage of chlorine consequences a wide range of organic compounds (DBPs), which occur due to the reaction between chlorine with natural organic compounds, mainly humic substances (Nikolaou, *et al.,* 2001). One of the main groups of DBPs is THM_S compounds. According to Clark et al, more than 500 DBPs have been identified in tap water (Clark, *et al.,* 1996). Chloroform, a DBP was first identified in the finished drinking water in 1974 in the Netherlands

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by Rook (1974) and in the United States by Bellar et al. (1974). As a result of Rook and Bellar findings, a survey was conducted in the United States in 1975 by the national organic reconnaissance for the water supplies of 27 large cities by Symons et al. (1975). This study revealed that four THM_S are widespread in chlorinated drinking waters at trace concentrations: chloroform, bromo-dichloromethane (BDCM), dibromochloro-methane (DBCM) and bromoform. Total THMs (TTHMs) refers to the sum of these four substances (Rodriguez, *et al.,* 2004). International Agency for Research on Cancer (IARC) and some researchers reported that most THM_S are carcinogenic in rodentsand mutagenic in a variety of systems (IARC, 1991; Marimoto *et al.,* 1983; Simpson *et al.,* 1998; Dodds *et al.,* 1999). The United States Environmental Protection Agency (USEPA) classifies THMs compounds into cancer groups including: chloroform ($CHCl_3$), BDCM ($CHBrCl_2$) and bromoform ($CHBr_3$)

belong to cancer group B$_2$ (probable human carcinogens), while DBCM (CHBrC1$_2$) belongs to cancer group C (possible human carcinogens) (Premazzi *et al.,* 1997).Epidemiological studies have demonstrated slightly escalated risks for bladder and colorectal cancer among consumers of chlorinated drinking water in comparison to well water users (IARC, 1991; 2003). Recently, THMs were suspected to cause not only cancer but also liver and kidney damage, retarded fetus growth, birth defects and possibly miscarriage (Wright *et al.,* 2004). A study in California conducted by state health department found that women exposed to high level of chlorine by-products had a 17/5% risk of miscarriage, while women who had little exposure to THMs had a low risk of 9/5% (Elshorbagy *et al.,* 2006). Because of the negative health impacts, THM$_S$ are supposed to be kept below a certain level in finished drinking water. The USEPA requires that TTHM concentration not to exceed 100 µg/L at the consumers tap (USEPA, 1998). Iranian industrial researches and standard institute specify the maximum acceptable concentration (MAC) for chloroform (THM$_S$ index) at 200 µg/L (Samadi *et al.,* 2005). Table 1 shows drinking water regulation of THM$_S$ (µg/L) and CHCL$_3$ (µg/L) in various countries (Yoon, *et al.,* 2001).

Table 1. Drinking water regulation for THM$_S$ (µg/L) and CHCL$_3$ (µg/L) in various countries

Country	THM$_S$	CHCL$_3$
Australia	250	-
Canada	350	-
China	-	60
Denmark	10-15 (lowest value)	-
France	-	30
Japan	100	60
Korea	100	-
Taiwan	100	-
UK	100	-
USA	80	-
WHO	-	200

The objective of this study is an overview of THM$_S$ concentration changes in SWTP and its distribution system. By the way the relation between THM$_S$ formation and some of independent variables including TOC, pH, temperature, and residual chlorine were investigated. Previous researches showed that the occurrence of chlorination DBPs in the treated and distributed drinking water varied according to the quality of the water source and operation carried out in the treatment plant (Rodriguez *et al.,* 2004). The areas of this study were SWTP and RWDS which are located in Guilan province, Iran.

Guilan Province is located in the north of Iran and in the south of Caspian Sea. Rasht is the center of this province. Guilan Province has a humid temperate climate with plenty of annual rainfall. SWTP supplies water to the center and east of Guilan, which contain 70% of Guilan population. SWTP, located 20 kilometers from the southeast Rasht, can supply 3 m^3/s treated water for consumers in the first phase. The water source to the plant is Galehroud canal, which receives water from Sefedroud and SherBedjar Rivers. The processes in SWTP involve screening, primary sedimentation, coagulation, flocculation, secondary sedimentation, filtration and disinfection via chlorine. The objective of water treatment process is to produce water of acceptable quality suitable for human consumption complying with established standards. Fig. 1 shows SWTP situation in Rasht city and fig. 2 shows sampling points in the Rasht city.

MATERIALS & METHODS

In SWTP, water samples were collected from five points including: raw water canal, primary sedimentation tank (before coagula-tion units), after secondary sedimentation tank, downstream of filtration and outlet pipe of SWTP after chlorine addition to the treated water. Also five locations were selected at different times for sampling from RWDS. In RWDS, before sample collecting, the faucet was turned on for about 5 minutes, to ensure that water was coming directly from the public distribution system rather than building's plumbing system. Glass bottles with ground-glass stoppers which were washed with phosphate-free detergent and rinsed with de-ionized water and placed in an oven at 400 °C for 1 hr were selected for TTHM sampling. For sampling, bottles were filled to zero head space to prevent THM volatilization. Sampling was undertaken in the afternoon and before sampling, a sodium thiosulfate solution was added to the bottles to remove residual chlorine and to prevent additional chlorination DBPs formation during transportation to the laboratory. Samples were transported in an ice box to the laboratory. This test lasted for 6 months (January to June) and 15 and 27 samples were collected from SWTP and RWDS respectively. The samples were collected every 2 weeks.

In this research the following equipment were used:
- GC set Shimadzu model 14A equipped with Electron Capture Detector (ECD) for analysis of different THM compounds according to standard methods for the examination of water and wastewater (APHA, 2003).
- Capillary column (J&W) scientific DB-624, 60 m × 25 mm (ID), Hamilton syringes for extract injection to the GC.
- Teflon lined screw capped vials for sample collection and standard preparation.
- pH meter for measurement of the water pH.
- TOC analyzer set Shimadzu model 5000 for TOC analysis.
- Colorimeter for measurement of free chlorine in the water samples.
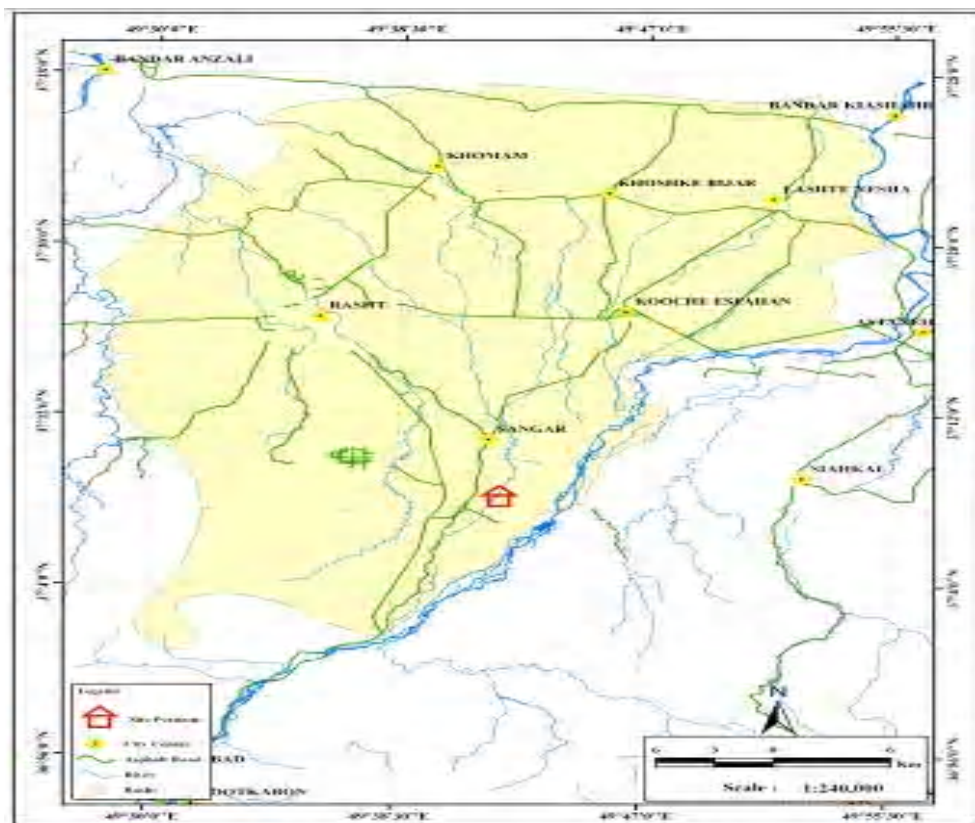
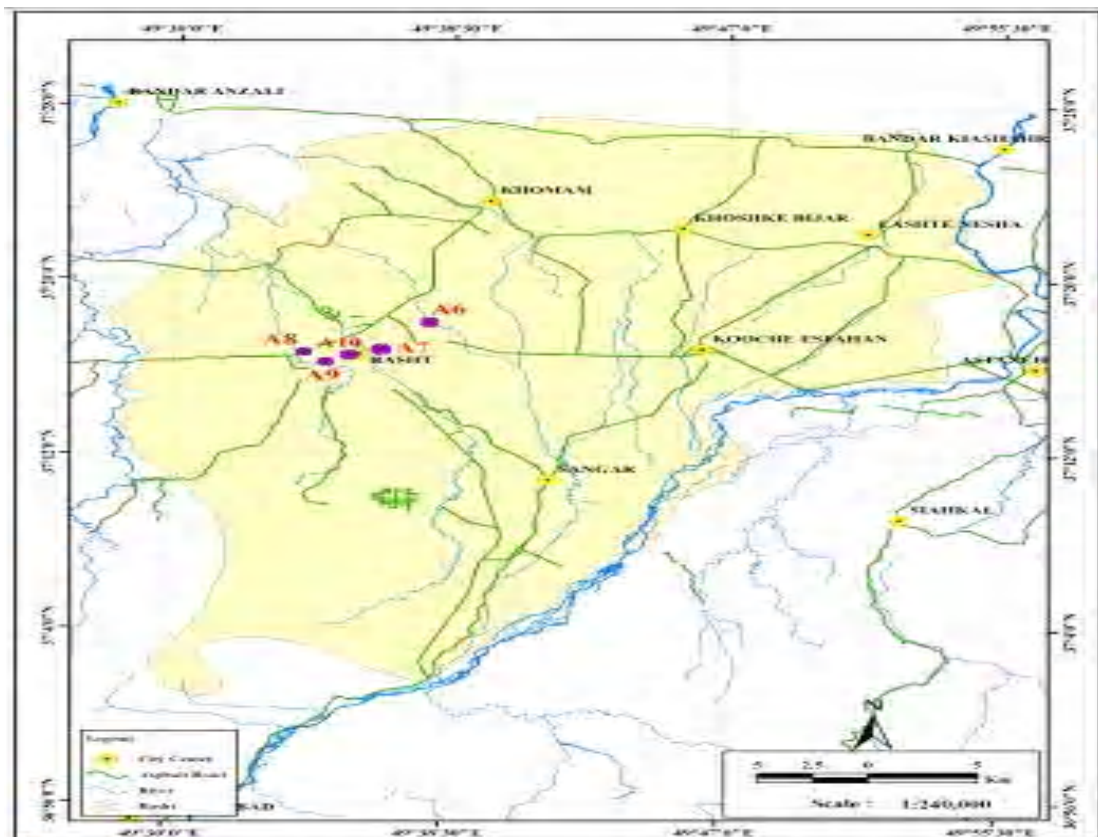**Fig. 1. Rasht City and Sangar Water Treatment Plant location**

Fig. 2. Sampling points in Rasht city (A$_6$: Janbazan square, A$_7$: Heshmat hospital, A$_8$: Sabze meydan, A$_9$: Saadi street, A$_{10}$: Takhti street)

Due to rapid chemical changes that occur in water samples during transit and storage, certain parameters were measured on site, once the samples were collected. These parameters were residual chlorine, temperature and pH. Other parameters including TOC and different THM compounds: chloroform, BDCM, DBCM, and bromoform were measured at the lab. In the laboratory water samples were immediately transferred to Pyrex bottles with Teflon lined screw caps and stored in the refrigerator for determination of THMs. Samples for experiment were extracted by means of hexane and were analyzed within 14 days by the liquid-liquid extraction method. Liquid-liquid extraction was performed according to standard method for the examination of water and wastewater (APHA, 2003). For analyze THMs concentration in the samples, a rapid and simple method by purge and trap coupled with capillary column GC with ECD was used (Pauzi Abdullaha, 2003). For extraction of THM compounds, the inert gas was bubbled through the sample and afterward THMs were trapped in a tube that contains sorbent materials. After completion of extraction, sorbent tuber was heated and back flushed with an inert gas to desorb trapped sample components in a GC column. The temperature characteristics of GC set and flow rate of gases for THMs analysis were as follows: Injector temperature: 150 °C, detector temperature: 250 °C, flow of carrier gas He: 20 cm/s, flow of supportive gas N_2: 40 cm/s, temperature program: 32 °C (5 min), 32-120 °C (107 min) and 120 °C (10 min). TOC was analyzed by means of a TOC analyzer according to standard method for the examination of water and wastewater (APHA, 2003). Water pH and temperature were measured on site by using a solid selective electrode. Free chlorine was measured by the DPD titrimetric method with a colorimeter according to standard method for the examination of water and wastewater (APHA, 1995).

RESULTS & DISCUSSION

The previous researches demonstrated that the major factors which affect TTHM formation are residual chlorine dose, concentration and type of Natural Organic Material (NOM), contact time, pH and temperature of water (Najm *et al.,* 1994). Due to this effect, some characteristics of water quality were measured in this research and Pearson correlation coefficient was used to measure the strength of relation between these variables with formation of THMs compounds Table 2. The water quality characteristics measured in raw and treated water during investigation period are presented in Table 3. Table 4 shows the mean values of chloroform and TTHM at each sampling station.According to this table, the mean value of TTHM and chloroform in water treated at SWTP is between 4.7 to 8.97 µg/L and 2.1 to 6.3 µg/L and in RWDS is from 8.31 to 12.35 µg/L and 5.36 to 8.16 µg/L respectively(Fig. 3).

Table 2. Drinking water quality parameters for SWTP during the investigation period (cool & warm months)

Water quality parameter		Year 2007			
		Cool months		Warm months	
		Mean	Min/Max	Mean	Min/Max
Raw water	pH	7.2	5.8-7.77	7.14	6.94-7.23
	Temperature (°C)	4.4	4.1-6.55	15.8	13.5-17.7
	TOC (mg/L)	6.1	5.1-7.8	8.2	7.16-11.45
	THMs (µg/L)	8.7	7.6-11.8	9.25	10.56-13.56
Treated water	pH	6.9	5.45-7.27	7.05	6.86-7.24
	Temperature (°C)	4.7	7.56-8.87	17.6	16.5-19.3
	TOC (mg/L)	4.4	4.25-6.58	7.42	5.31-9.22
	cl$_2$ residual (mg/L)	1.11	0.86-1.32	1.45	1.25-1.52
	THMs (µg/L)	5.9	4.5-6.1	6.05	5.26-7.69

Table 3. Mean values of concentration of THMs (µg/L) and $CHCL_3$ (µg/L) at SWTP and RWDS during study

Sampling point	TTHM (µg/L)		$CHCL_3$ (µg/L)	
	Mean	Min/max	Mean	Min/max
A$_1$- raw water	8.97	7.6-11.8	6.3	5.3-8.5
A$_2$- before coagulation	8.2	6.9-10.6	5.9	4.5-8.8
A$_3$- after sedimentation	7.5	4.2-8.8	4.6	2.1-5.3
A$_4$- after filtration	4.7	3.3-6.4	2.1	1.3-4.6
A$_5$- treated water	5.97	4.5-6.1	2.6	2.1-3.5
A$_6$- Janbazan square	8.31	7.22-11.5	5.36	3.62-6.81
A$_7$- Heshmat hospital	11.23	9.45-13.1	7.21	5.26-8.39
A$_8$- Sabze meydan	10.83	8.33-12.05	6.03	4.86-8.08
A$_9$- Saadi street	12.35	9.26-14.53	8.16	5.16-10.21
A$_{10}$- Takhti street	11.3	8.66-13.95	7.02	5.11-9.23

Table 4 . Relation between THMs formation with independent variables in SWTP and RWDS

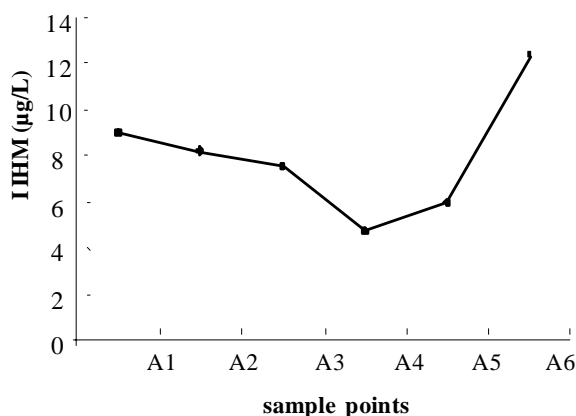| THM formation with independent variable	SWTP	RWDS
	Pearson *r*	Pearson *r*
residual chlorine	0.7354	0.5623
pH	0.4658	0.3232
Temperature	0.2390	0.2336
TOC	0.8096	0.3696

Fig. 3. THMs concentration in SWTP and RWDS (A1 to A5 points presented in Table 3 and A6 corresponds to maximum value of RWDS)

CONCLUSION

Results of this study point out that maximum decrease of THMs concentration in SWTP is after coagulation & flocculation and filtration units. A combination of alum ($Al_2(SO_4)_3, 14H_2O$) and polyelectrolyte is mostly used for coagulation process in SWTP. Coagulation process of improving the removal of DBP precursors in a conventional water treatment plant could be an effective method for organic matter removal (Marhaba *et al.,* 2000).

Previous researches have shown that enhanced coagulation by combination of alum and polymer technique could be used to improve THM precursor removal (Bolto *et al.,* 1999; Hubel *et al.,* 1987). THMs concentration increased in the outlet pipe upon addition of chlorine into treated water. Results showed that higher value of THMs concentration was in distribution system that proved relation between resident time and chlorination DBP formation. Although the four components of the THM_s observed in total samples and chloroform was the major component in the water sample, but $CHCl_3$ and TTHM concentrations did not exceed the maximum permissible value of 100 µg/L for TTHM of the USEPA standard and 200 µg/L for chloroform (THMs index) of the Iranian industrial researches and standard institute standard in all samples. *Effective Parameters (TOC, Temperature, pH, Residual chlorine, Distance from chlorination)* In the case of TOC, THMs formation rose by increasing

soluble humic material content in natural water. The rate of THM formation was equal to the TOC consumption. Indeed in the higher available TOC more THM was occurred (Babcock *et al.,* 1979). Using Pearson correlation method, r = 0.8096 was obtained between THM formation and TOC for SWTP and r = 0.3696 for RWDS.

In the case of temperature, the seasonal variations of THMs compounds in the case study location were significant and THMs concentration was higher in warm water in comparison to cold water. By increasing the temperature in the warmer months, reactions were faster and a higher chlorine dose was required for disinfection, leading a higher formation of THMs. Subsequently, THM concentrations were expected to be higher in summer rather than winter (Fayad, 1993). The seasonal difference in THMs were considerably higher than those found in other temperate environment in recent studies in the US and Europe (Rodriguez *et al.,* 2004; Chen *et al.,* 1998). Pearson correlation method, showed a low relationship r = 0.239 for SWTP and r = 0.2336 for RWDS between THMs formation and water temperature.

In the case of pH, as shown in table 4, Pearson correlation method, showed a low relationship between THM formation and pH. Indeed the correlation coefficient was r = 0.4658 for SWTP and r = 0.3232 for RWDS. Results of other investigations show that decrease in pH leads to low THM formation and similarly increase of pH results in high THM formation (Peters *et al.,* 1980; Adin *et al.,* 1991). In the case of residual chlorine, Pearson correlation method, showed a relationship r = 0.7354 for SWTP and r = 0.5623 for RWDS between THM formation and residual chlorine. Addition of chlorine to the water leads to the formation of hypochlorous acid (HOCl) and hypochloride ion (OCl^-). The formation of these compounds depends on the pH. In acidic solution HOCl is dominant, whereas in the alkaline solution formation of OCl^- dominates (Abdullaha *et al.,* 2003). In RWDS, water pH value is from 5.5 to 8, and HOCl causes THM formation as dominant. Levels of TTHM can increase while the chlorinated water discharges from water treatment plant through water distribution system, due to continued presences of residual chlorine (Golfinopoulos *et al.,* 2000). According to Abdullaha et al. (2003) there is a relationship between level of TTHM and distance from treatment plant in the distribution system. Results of this study confirmed a direct relation between THM_s compounds and distance of chlorination point. Treated water in SWTP had a several hours of retention time in a storage tank with a capacity of 50,000 m^3 and then it was injected to the RWDS. This residence time in the storage tank had a remarkable effect on THMs occurrence (Rodriguez *et al.,* 2004). Subsequently, THMs concentration was expected to be higher in the downstream of RWDS rather than SWTP outlet pipe.

REFERENCES

Abdullaha, Md.P., Yewa C.H., and bin Ramlib, M.S. (2003). Formation, modeling and validation of trihalometha nes in Malaysian drinking water: a case study in the districts of Tampin, Negeri Sembilan and Sabak Bernam, Selangor, Malaysia. Water Research, **37**, 4637–4644.

Adin, A., Katzhendler, J., Alkaslassy, D. and Rav, A.C. (1991). Trihalomethanes formation in chlorinated drinking water: a kinetic model. Water Res., **25**, 797–805.

Al Omrani, A., Fayyad, M. and Abdel Qader, A. (2004). Modeling trihalomethane formation for jabal amman water supply in Jordan. Environment Modeling and Assessment, **9**, 245-252.

APHA, (2003). Standard Methods for the Examination of Water and Wastewater Ed. American Public Health Association, Washington DC.

APHA, AWWA and WPCF., (1995). Standard Methods for the Examination of Water and Wastewater, 19th ed. APHA, AWWA and WPCF, Washington, DC.

Babcock, D. and Singer, P. (1979). Chlorination and coagulation of humic and fulvic acids. AWWA, **71**, 149–52.

Bellar, T., Lichtenberg, J. and Kroner, R. (1974). The Occurrence of organohalides in chlorinated waters. AWWA., **66 (12)**, 703-706.

Bolto, B., Abbt-Braun, G., Dixon, D., Eldridge, R., Frimmel, F., Hesse, S., King, S. and Toifl, M. (1999). Experimental evaluation of cationic polyelectrolytes for removing natural organic matter from Water. Water Science Technology, **40 (9)**, 71-79.

Chen, W.J. and Weisel, C.P. (1998). Halogenated DBP concentrations in a distribution system. AWWA., **90 (4)**, 151–163.

Clark, R., Pourmoghaddas, H., Wymer, L. and Dressman, R. (1996). Modeling the kinetics of chlorination by-products formation: the effects of bromides. SRT-aqua., **45 (3)**, 112-119.

Dodds, L., King, W., Woolcott, C. and Pole, J. (1999). Trihalomethanes in public water supplies and adverse birth outcomes. Epidemiology, **10 (3)**, 233-237.

Elshorbagy, W. (2006). Kinetics of THM species in finished water. Water Resources Planning and Management., **126 (1)**, 21-28.

Fayad, N.M. (1993). Seasonal variations of THMs in Saudi Arabian drinking water. AWWA, **85**, 46-50.

Golfinopoulos, S. K. (2000). The occurrence of trihalomethanes in the drinking water in Greece. Chemosphere., **41 (11)**, 1761-1767.

Garcia-Villanova, R.J., Garcia, C., Gomez, J.A., Garcia, M.P. and Ardanuy, R. (1997). Formation, evolution and modeling of trihalomethanes in the drinking water of a town: II, in the distribution system. Water Res., **31 (6)**, 1405-1413.

Hubel, R.E. and Edzwald, J.K. (1987). Removing trihalometh ane precursors by coagulation. AWWA., July, 98-106.

IARC (1991). Chlorinated drinking water chlorination by-product: some other halogenated compounds cobalt and cobalt compounds, IARC Monographs on Evaluation of Carcinogenic Risks in Humans, vol. **52**.

IARC (2003). Some drinking water disinfectants and contaminants, including arsenic, IARC Monographs on Evaluation of Carcinogenic Risks in Humans, vol. **84**.

Marhaba, T.F. and Pipada, N.J. (2000). Coagulation: Effectiveness in Removing Dissolved Organic Matter Fractions. Environ. Eng. Sci., **17(2)**, 107-115.

Marimoto, K.. and Koizumi, A. (1983). Trihalomethanes induce sister chromatid exchange in human lymphocytes in vitro and mouse bone marrow cells in vivo. Environ. Res., **32**, 72-79.

Najm, I., Patania, N.L., Jacangelo, J.G. and Krasner, S.W. (1994). Evaluating surrogates for disinfection by-products. AWWA., **86**, 98-106.

Nikolaou, A. and Lekkas, T. (2001). The role of natural organic materials during formation of chlorination by-products: a review. Acta Hydrochimica et Hydrobiologica **29**, 63-77.

Peters, C.J., Young, R.J. and Perry, R. (1980). Factors influencing the formation of Haloforms in the chlorination of humic materials. Environ. Sci. Technol., **14**, 1391–1395.

Premazzi, G., Cardoso, C., Conio, O., Palumbo, F., Ziglio, G., Meucci, L. and Borgioli, A. (1997). Standards and strategies in the European Union to control trihalomethanes in drinking water; Environment Institute. European Commission Joint Research Centre and Techware. Italy.

Rodriguez, M.J., Serodes, J.B. and Levallois, P. (2004). Behavior of trihalomethanes and haloacitic acids in a drinking water distribution system. Water Research, **38**, 4367-4382.

Rook, J.J. (1974). Formation of haloforms during chlorination of natural waters. Water Treat., Examiners **23 (2)**, 234-243.

Samadi, M.T., Nasseri, S., Mesdaghinia, A. and Alizadefard, M.R. (2006). A comparative study on THM_S removal efficiencies from drinking water through nanofiltration and air stripping packed-column. Iranian Journal of Water and Wastewater., **57**, 14-21.

Simpson, K.L. and Hayes, K.P. (1998). Drinking water disinfection by-products: An Australian perspective. Water Resour., **32** (5), 1522-1528.

Symons, J., Bellar, T., Carswell, J., DeMarco, J., Kropp, K., Robeck, G., Seeger, D., Slucom, C., Smith, B., and Stevens,A. (1975). National organic reconnaissance survey for halogenated organics. AWWA., **67 (11)**, 634-648.

USEPA (1998). National primary drinking water regulations: disinfectants and disinfection by products; Final rule. Federal Register **63** (241), 69390-69476.

Wright, J.M., Schwartz, J. and Dockery, D.W. (2004). The effect of disinfection by products and mutagenic activity on birth weight and gestational duration. Environ. Health Persp., **112**, 920-925.

Yoon, J., Choia, Y., Chob, S. and Lee, D. (2003). Low trihalomethane formation in Korean drinking water. The Science of the Total Environment, **302**,157-166.