

TEMPORAL VARIABILITY OF DISINFECTION BY-PRODUCTS CONCENTRATION IN URBAN PUBLIC WATER SYSTEM

A. SIDDIQUE^{1,*}
S. SAIED²
N. ALAM ZAIGHAM¹
M. MUMTAZ²
G. ALI MAHAR¹
S. MOHIUDDIN²

¹Unit for Groundwater Research and AinZubaida
Rehabilitation, King Abdulaziz University,
Jeddah, Saudi Arabia

²Department of Chemistry, University of Karachi,
75270, Karachi, Pakistan

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*to whom all correspondence should be addressed:
e-mail: amohammad@kau.edu.sa

ABSTRACT

The occurrence of trihalomethanes (THMs) was studied in the drinking water samples from urban water supply network of Karachi city that served more than 18 million people. Drinking water samples were collected from 58 locations in summer (May-August) and winter (November-February) seasons. The major constituent of THMs detected was chloroform in winter (92.34%) and summer (93.07%), while the other THMs determined at lower concentrations. Summer and winter concentrations of total THMs at places exceed the levels regulated by USEPA (80 $\mu\text{g l}^{-1}$) and WHO (100 $\mu\text{g l}^{-1}$). GIS linked temporal variability in two seasons showed significantly higher median concentration (2.5%-23.06%) of THMs compared to winter.

KEYWORDS: trihalomethanes, seasonal variability, chlorination, chloroform, drinking water, WHO, GIS.

INTRODUCTION

Chlorination is the most accepted disinfectant throughout the world because of its economical availability and effectiveness against the waterborne pathogens. Chlorination worked effectively against the microorganisms and provide safeguard against several waterborne diseases (Morris and Levine 1995) on the other hand, it reacts with natural organic matters (NOMs) to form disinfection by-products (DBPs). Studies have shown a relationship between long-term exposure to DBPs and increase risk of cancer and adverse reproductive outcomes (Nieuwenhuijsen *et al.*, 2008). Trihalomethanes (THMs) are the most abundant DBPs (Krasner *et al.*, 1989). THMs constitute a major class of DBPs, including chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), chlorodibromomethane (CHClBr_2) and bromoform (CHBr_3). Since THMs concentration in water is a serious health concern and United States, European Union (EU) and World Health Organization (WHO) regulated THMs in public water supplies (USEPA, 1998; EU, 1998; NHMRC and NRMCC, 2004; Health Canada, 2010; WHO, 2011).

Several factors in addition to NOMs influenced the formation of THMs including the nature of source water, amount and time of contact of chlorine, levels of total organic compounds (TOC), temperature and pH etc (Rodriguez and Serodes, 2001; Hua and Reckhow, 2008; Yamamoto and Mori, 2009). The variation of THMs can also influence temporally and seasonality influenced the THMs formation process. Different studies on seasonality dependency showed variable results in summer and winter (Parvez *et al.*, 2011).

The selected study area, Karachi City with a population of more than 18 million, served by a complex network of canals, conduits, siphons, multi-stage pumping and filtration. 670 million gallon/day (mgd) is the total supply with a loss of 35% and net available supply to the inhabitants is 435.50 mgd. The major supply of the water (about 75%) to Karachi is through Indus River in addition to Hub River

(about 15-20%) and groundwater resources in the city (KWSB, 2011). Present work was aimed to monitor the occurrence of THMs, particularly focused on the geo-spatial distribution of the THMs concentration with emphasis on their seasonal behaviour in a complex water distribution system.

MATERIALS AND METHODS

Water samples were collected from different parts of the city representing main distribution network of water supply to the Karachi City. Sampling locations were shown in Figure 1. Total 58 sampling locations were sampled in summer (May-August) and winter (Nov-Feb). Samples for THMs analysis were collected in headspace-free borosilicate amber glass bottles with Teflon joint screw cap, containing 1.7 mL of 10% sodium thiosulfate as quenching solution to remove any residual chlorine. Sulphuric acid preserved samples for total organic carbon (TOC) were taken in 125 mL bottles. Temperature, pH and free chlorine were measured in the field. Once collected, samples were stored in the dark at 4°C and carried to the laboratory for analytical procedures.

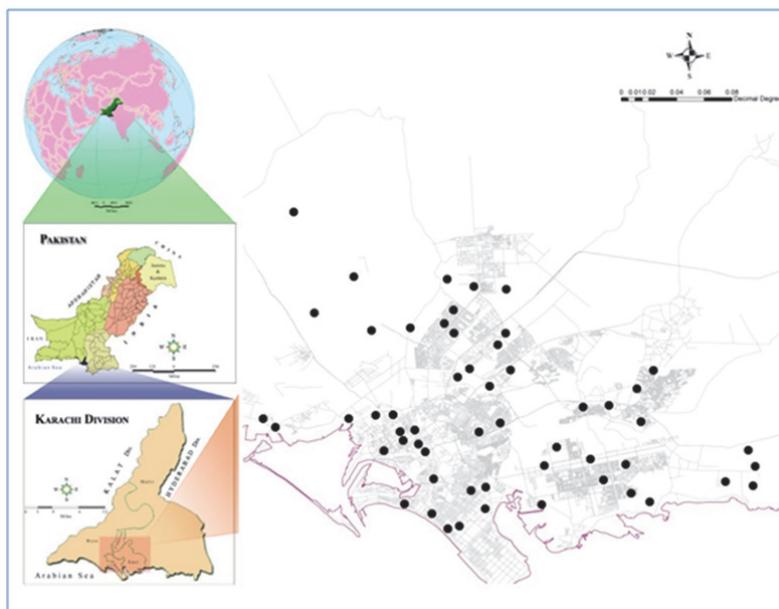


Figure 1. Map showing study area and sampling locations

Measurements of free chlorine were measured in the field using the DPD titrimetric method with a field DR-700 colorimeter (Hach USA). TOC was analyzed in sulfuric acid preserved water samples by Shimadzu TOC analyzer 5000 (Shimadzu corp. Japan). pH and temperature were measured by handylab multi 12 meter (Schott instrument, Germany). A modified EPA method 551.1 was used to determine the THMs (CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3). 2 mL of methyl *ter*-butyl ether (MTBE) was added to 35 mL of sample in 40 mL glass vials. The upper phase layer of MTBE was separated by manual shaking for 1 minute and 1 μg MTBE layer was injected into the HP-5890 II gas chromatograph (GC). The GC was equipped with DB 1 (30 m, 0.32 mm i.d., 0.25 μm film thickness) chromatographic column and the analytical conditions were set as: injection on column volume 0.5 μL ; oven temperature 50 °C for 5 min, 50-150 °C at 6 °C/min; carrier gas Helium 1.3 mL min^{-1} , make-up gas N_2 60 mL min^{-1} ; detector temperature 300 °C. DB-1301 capillary column was used for the confirmation of the. The recoveries of the method were estimated at five concentration levels. Field blanks were used to determine any background contamination. Method blanks and spiked blanks were analyzed and final results were shown after subtracting any contribution of contamination from the laboratory. The recoveries obtained for CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 were 78.1-113.2 (RSD 3.9%), 86.6-109.2 (RSD% 3.1%), 80.3-121 (RSD 4.9%), 89.2-113.7 (RSD 3.4%) and detection limits 0.71 $\mu\text{g l}^{-1}$, 0.34 $\mu\text{g l}^{-1}$, 0.30 $\mu\text{g l}^{-1}$ and 0.25 $\mu\text{g l}^{-1}$ respectively were ensured by the analytical protocol.

RESULTS AND DISCUSSION

Present study revealed considerable seasonal variability in the mean and median THMs concentrations between locations. Table 1 summarises descriptive statistics for individual and total THMs (TTHMs) with physico-chemical parameters in the water samples of Karachi City during winter and summer seasons. The median values were estimated in addition to mean values to demonstrate the central tendency and behaviour of the observed data. Highly variable range of TTHMs concentrations were found (7.03 to 176.24 $\mu\text{g l}^{-1}$) in winter and in summer (4.42 to 147.96 $\mu\text{g l}^{-1}$). The mean TTHMs concentration in winter ($71.80 \pm 34.55 \mu\text{g l}^{-1}$) and in summer ($72.28 \pm 34.46 \mu\text{g l}^{-1}$) corresponds to no significant change (0.66%) compared to a significant change of 18.84% in median levels of winter (62.16 $\mu\text{g l}^{-1}$) and summer (76.60 $\mu\text{g l}^{-1}$) samples. Chloroform concentrations contribute a significant portion to the TTHMs during winter (92.34%) and summer (93.07%) seasons (Figure 2). Chloroform concentrations, similar to TTHMs distributed on a broad scale and ranged between 17.03 $\mu\text{g l}^{-1}$ and 167.32 $\mu\text{g l}^{-1}$, mean concentrations were $67.82 \pm 32.99 \mu\text{g l}^{-1}$ and 71.13 ± 32.36 (%change 4.65), median concentrations 57.60 $\mu\text{g l}^{-1}$ and 74.87 $\mu\text{g l}^{-1}$ (% change 23.06) in winter and summer respectively. The concentrations of two brominated species CHCl_2Br and CHClBr_2 were not varied at large scale and contribute 4.55% & 4% in summer and 2.55% & 2.38% in winter respectively to TTHMs concentrations. Concentrations of CHBr_3 were not taken into consideration in the present study due to few occurrences (n=9 and 13) at low concentration.

Table 1. Seasonal Minimum (min), maximum (max), mean, median and standard deviation (SD) levels of THMs and other water quality parameters in drinking water samples

		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM	pH	TDS	DO	Free Chlo.	TOC	Temp
		$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$		mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	$^{\circ}\text{C}$
WINTER	Min	17.03	1.79	0.63	0.30	7.03	7.20	100	4.50	0.05	0.45	23.6
	Max	167.32	6.22	3.54	0.59	176.24	8.10	480	9.00	0.42	11.69	33.1
	Mean	67.82	3.34	1.87	0.41	71.80	7.44	268	5.96	0.13	3.80	24.4
	Median	57.60	3.02	1.68	0.39	62.16	7.40	269	5.90	0.11	3.63	25.7
	SD	32.99	1.19	0.73	0.08	34.55	0.24	79	0.73	0.07	2.51	5.9
SUMMER	Min	8.39	0.19	0.22	0.34	4.42	6.65	36	3.53	0.04	0.14	28.5
	Max	146.19	5.63	3.32	0.56	147.96	7.81	393	7.09	0.62	12.32	34.2
	Mean	71.13	3.05	1.82	0.42	72.28	7.34	221	5.66	0.17	4.40	31.3
	Median	74.87	3.10	1.84	0.42	76.60	7.37	226	5.75	0.14	4.01	30.7
	SD	32.36	1.19	0.71	0.07	34.46	0.23	89	0.72	0.10	2.53	6.2
% Mean Change		4.65	-9.47	-2.69	2.94	0.66	-1.36	-21	-5.43	23.10	13.70	22.04
% Median Change		23.06	2.51	8.86	4.95	18.84	-0.37	-19	-2.62	22.50	9.46	16.28

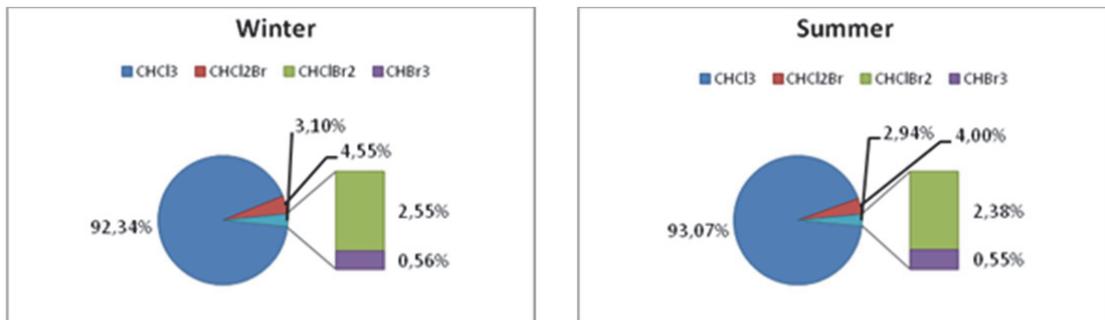


Figure 2. Mean concentration distribution of TTHMs in the water samples

TTHMs and CHCl_3 levels at some locations in winter and summer were found higher than the guideline values regulated in different parts of the world (Figure 3) including United Kingdom, Japan (100 $\mu\text{g l}^{-1}$), USA (80 $\mu\text{g l}^{-1}$) France (30 $\mu\text{g l}^{-1}$) and Germany (10 $\mu\text{g l}^{-1}$) (Rizzo *et al.*, 2005). Median

and mean concentrations were generally higher than the concentrations found in TTHM regulated countries (Krasner *et al.*, 1989; Keegan *et al.*, 2001). In present study, substantial seasonal variation in Median levels of TTHMS were found in the chlorinated water of Karachi City, with generally higher concentrations in summer and lower concentrations in winter (Figure 4).

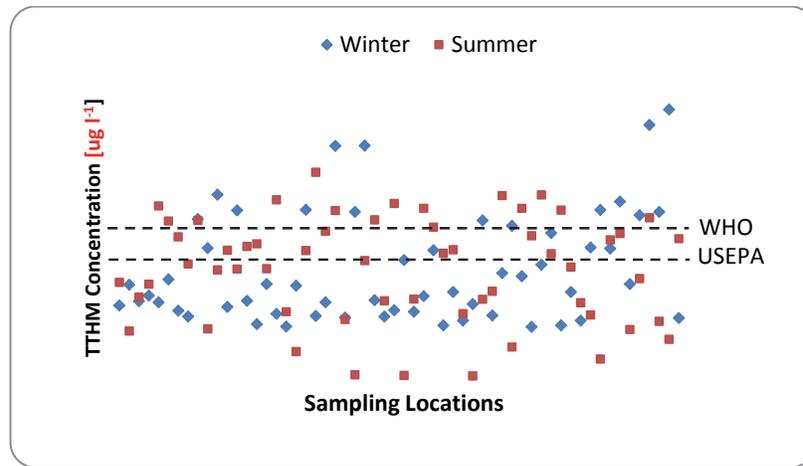


Figure 3. Distribution of TTHMS showing samples exceeding USEPA and WHO regulatory levels

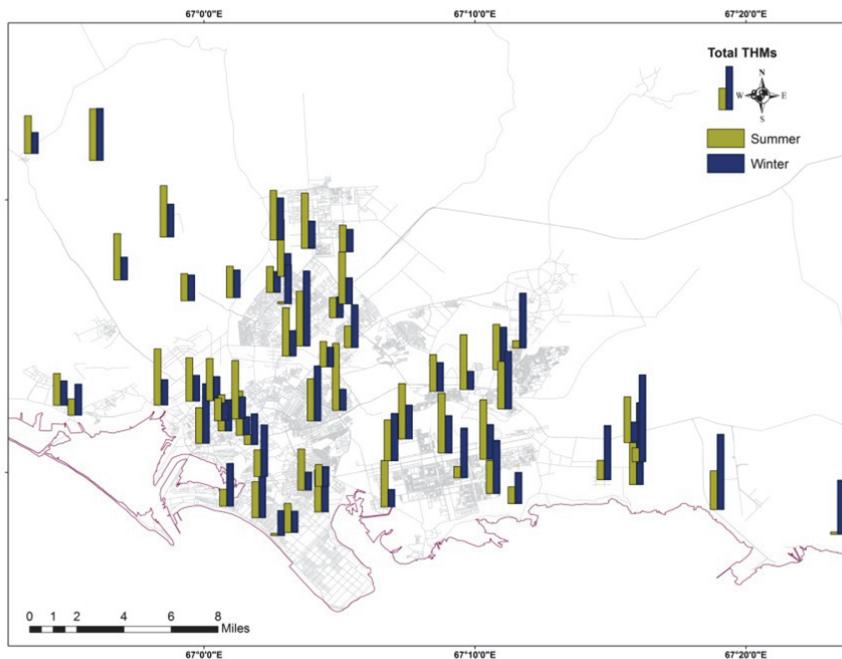


Figure 4. Spatio-temporal distribution of TTHMs in winter and summer seasons

The THM formation generally favoured by high temperature, chlorine residue and source water natural organic matters composition (NOMs) (Nikolaou *et al.*, 1999). The observed seasonal variation of THMs was consistent with earlier studies reported maximum THM formation in summer (Summerhayes *et al.*, 2011; Rodriguez *et al.*, 2004; Toroz and Uyak, 2005). CHCl_2Br and CHClBr_2 exhibit inconsistent higher mean seasonal variations in winter than summer (Figure 5). These higher mean values in winter can be attributed to characteristics of natural organic matter and changes in the nature of THMs precursors in the source water (Ates *et al.*, 2007; Whitaker, 2003).

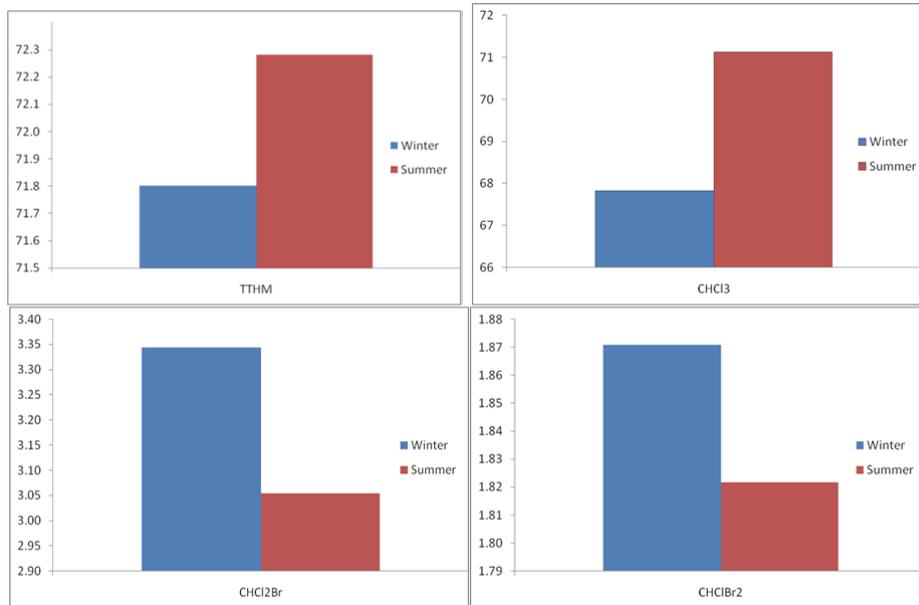


Figure 5. Mean seasonal variations of individual and total THMs ($\mu\text{g l}^{-1}$) in water samples

CONCLUSION

Present study found considerable variation in THM concentration between the winters and summer seasons. Some locations experiencing elevated concentrations above WHO and UEPA's TTHMs regulations and require a systematic monitoring program to carefully observe the THM's level. The TTHMs level followed the general trend of higher concentrations in summer compared to winter with large variations in the concentration level. It is difficult to identify the principal parameter(s) driving the TTHMs formation for all the seasons in the presence of complex nature of source water NOMs matrix. A comprehensive monitoring program of the THMs in the urban water supply is recommended to facilitate the evaluation of principal factor(s) causing elevated levels of THMs, which may cause adverse health effects.

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