Factors Influencing the Formation of Trihalomethanes in Drinking Water Supplies

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Abstract Presence of Trihalomethanes (THMs) in drinking water has become a major concern worldwide because of their adverse health impacts. These THMs are formed due to reaction of chlorine with natural organic matter and other precursors found in water. This study aims at establishing the concentration range of THMs in drinking water supplies. The concentrations of THMs (274-511 µg/l) found to be much higher than the prescribed USEPA standards and WHO guidelines. The study also revealed that amongst various THMs, contribution of chloroform was highest (93.07-98.9%) followed by other THMs. Correlation study delineated that TOC, DOC and UV_{254} are the main organic precursors responsible for the formation of THMs in drinking water. Bromoform was not detected in the water which can be attributed to the absence of bromide in raw water. Pearson correlation matrix revealed that pH and temperature have also significant and definite correlation ($r = 0.767$ and 0.945, respectively) with the THMs.

Keywords: Drinking water, Chloroform, Trihalomethanes, UV_{254}, SUVA, NOM

1. INTRODUCTION

The disinfection of water using chlorine is most commonly used practice all over the world because of its low cost, easy to use, efficient against a broad spectrum of microorganisms and enables the maintenance of a residual protection. Disinfection of water using chlorine has a strong drawback, which is the generation of several Disinfection By-products (DBPs) as reported by researchers long back in 1970's (1; 2; 3). During chlorination, chlorine reacts with the residual natural organic compounds in water to form DBPs, which have been reported to be potent carcinogens (4; 5). The most common form of DBPs is the trihalomethanes (THMs) which include trichloromethane ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and tribromomethane ($CHBr_3$). Amongst the various DBPs, THMs are of major concern today because of their presence in greatest concentration in the drinking water and are sometime used as indicators of total disinfection by-product formation (6).

The formation of DBPs depends primarily on source water quality characteristics and on the location in the treatment process where disinfectants are added. The most important water quality parameters that influence the formation of DBPs include the nature and concentration of organic precursor materials, water temperature, pH, and conditions under which the disinfectant is used, such as the disinfectant dose, point of addition, contact time, and residual disinfectant concentration. In the presence of bromide, free chlorine (hypochlorous acid) rapidly oxidizes bromide to hypobromous acid which then along with the residual hypochlorous acid, reacts with the precursor materials to produce mixed chloro-bromo substitution products. (7).

Natural organic matter (NOM) e.g., humic and non-humic substances, which are present to various degrees in all water supplies and constitute the major component of the total organic carbon (TOC) concentration in most waters, have also been identified as the principal precursors in the formation of THMs and Haloacetic acids (HAAs) (8). Halogenated DBP formation increases with the "activated (defined as electron-rich) aromatic" content of NOM (9). Many efforts have been made to correlate various fundamental characteristics of NOM (e.g. size, structure, functionality) to DBP formation, among which SUVA (specific ultraviolet absorbance, defined as ultraviolet absorbance at 254 nm (UV254) times 100 divided by the dissolved organic carbon concentration) demonstrated to be a good predictor of the aromatic carbon content of the NOM and the DBP formation potential of the water (10).

Considering the severe health impacts of THMs, regulations have been formulated and reaffirmed time to time in almost all the countries across the world for controlling and regulating concentration of THMs in drinking water supplies. However, in India, recently standards/guideline values for controlling these THMs in drinking water supplies has been incorporated as per IS 10500 (11). However, there are very few studies on THM levels and its control are reported for Indian conditions. In the light of above, the present study was undertaken to establish the concentration of THMs in drinking water in Eastern part of the India and assess the major influencing factors responsible for the formation of THM in drinking water.

2. MATERIALS AND METHODS

The water samples were collected from five major water treatment plants, situated in the Eastern part of India. All the plants follow the conventional method of treatment comprising coagulation-flocculation, sedimentation, filtration, and chlorination. Two main rivers in this region of India i.e. Ganga and Damodar rivers are the source of raw waters. The analysis of various parameters like pH, Temperature, TOC, DOC, SUVA, UV_{254}, Bromide ion and residual chlorine were carried out as per the standard methods (12). Liquid–liquid extraction method, followed by qualitative and quantitative estimation by gas chromatograph (GC) equipped with electron capture detector (ECD), had been used for the determination of THMs in aqueous samples. TOC and DOC were analyzed by high-temperature combustion-infrared method.

3. RESULT & DISCUSSION

Concentration range of THMs in treated water

Total THMs concentration in treated water from different water treatment plants varied from 274 to 511µg/l (Table 3). Amongst various WTPs, THMs in Maithon WTP (511 ppb) was highest followed by MADA WTP (509 ppb), Indira Gandhi WTP (480 ppb), Swarnrekha WTP (281ppb) and ADDA WTP (274 ppb). The variation in TTHM concentration among the selected WTPs (MWTP> MADA > IGWTP > SWTP >ADDA) can be attributed to varying concentrations of TOC, DOC, and UV$_{254}$, found in treated water of different WTPs. It can also be seen that amongst the various THMs, the concentration of chloroform (236 to 503µg/l) was maximum in the finished waters which is very high compared to the permissible USEPA standards (80µg/l). The concentration of dichlorobromomethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$) were however found to be very less as compared to the prescribed USEPA standards. The bromoform was not detected in any of the water samples. This can be attributed to the fact that bromide ion concentration in the water sample was found below detection level. It is also reported that chloroform is the most frequently detected compound among various THMs (13). Many researchers (14; 15) indicated that in the absence of bromide, the chlorinated THMs are predominant than brominated THMs. In fact, the formation of DBPs is affected by several factors including water temperature and pH, nature and concentration of the natural organic matter (NOM), bromide ions, disinfectant type and dose, and residence time of water in the distribution system.

Table 1 Water quality status of various Water Treatment Plants

Parameters	**Name of water treatment plants (WTPs)**				
	IGWTP	**ADDA**	**MADA**	**MWTP**	**SWTP**
pH	7.0±0.2	7.30±0.29	7.69±0.2	7.7±0.23	7.58±0.21
Temperature(°C)	20.9±0.21	18.5±0.21	24.5±0.23	24.5±0.21	13.3±0.11
Turbidity(NTU)	0.14±0.02	0.7±0.01	4.5±0.27	4.8±0.19	5±0.15
Bromide ion(mg Br/L)	< 0.1	< 0.1	< 0.1	<0.1	< 0.1
Dissolved Oxygen(mg/L)	7.4±0.2	7.6±0.19	7.24±0.18	8±0.11	8±0.10
Free Residual Chlorine(Cl_2/L)	0.2±0.012	0.2±0.012	0.14±0.01	0.18±0.01	0.22±0.01
Total Organic Carbon (TOC)	4.431±0.035	2.1±0.05	4.35±0.05	4.43±0.06	2.42±0.02
Dissolved Organic Carbon (DOC)	3.501±0.036	1.95±0.04	3.67±0.04	4.37±0.058	2.20±0.01
UV 254(/cm)	0.157±0.013	0.115±0.01	0.123±0.01	0.2±0.012	0.105±0.001
SUVA (L/mg/m)	4.4±0.03	5.47±0.032	3.351±0.03	4.5±0.031	4.77±0.17
Chloroform (µg/L)	466±22	255±11.5	503±23	501±24	236±11
Dibromochloromethane (µg/L)	2±0.1	11±0.5	2±0.1	2±0.1	31±1.5

Dichlorobromomethane (µg/L)	12±0.5	8±0.4	4±0.18	8±0.39	14±0.5
Bromoform (µg/L)	ND	ND	ND	ND	ND
Total THMs(µg/L)	480±24	274±13.5	509±23.5	511±24	281±12

4. EFFECT OF VARIOUS PARAMETERS ON THMS FORMATION

The Person Correlation Matrix showing the correlation of various water quality parameters on THM formation is given in Table 2.

Table 2 The pearson correlation matrix between water quality parameters and THMs

		pH	Temp	DO	Turbidity	Cl_2	TOC	DOC	UV_{254}	SUVA	$CHCl_3$	TTHM
pH	r	1	.847**	.611	.506	-.444	.502	.671*	.460	-.061	.710*	.767**
Temp	r		1	.460	.454	-.325	.832**	.913**	.738*	.254	.924**	.945**
DO	r			1	.700*	.172	.060	.245	.218	-.028	.236	.324
Turbidity	r				1	-.061	.201	.487	.403	-.143	.132	.203
Cl_2	r					1	-.197	-.345	-.025	.309	.371	.331
TOC	r						1	.898**	.692*	.295	.886**	.880**
DOC	r							1	.808**	.276	.849**	.860**
UV_{254}	r								1	.726*	.658*	.636*
SUVA	r									1	.338	.269
$CHCl_3$	r										1	.989**
TTHM	r											1
** Correlation is significant at the 0.01 level (2-tailed).												
* Correlation is significant at the 0.05 level (2-tailed).												

Effect of TOC, DOC, UV_{254} and SUVA. Total organic carbon (TOC) and dissolved organic carbon (DOC) are direct measurements of organic content. Increases in TOC generally lead to increase in THMs formation (17). It is reported that the rate of THMs formation is equal to that of the TOC consumption (18). The Pearson correlation matrix shows a strong correlation (r = 0.880) between TTHM formation and TOC (Table 4). Comparatively a stronger correlation (r = 0.886) was obtained between TOC and chloroform. Similar observations were made by many researchers (19; 20). Besides, it was also observed that the rate of THM formation is equal to that of TOC consumption, and a first-order reaction was reported with respect to TOC (21). Due to slow reaction between THM precursors with chlorine, THM formation with respect to TOC is of second-order reaction especially for long-term formation of THM. THM production can thus be explained as a multi-stage process involving an initial fast reaction of chlorine with the TOC to produce chlorinated intermediates, which may then undergo further slow reaction by several possible pathways to produce THM and other products.

The DOC and UV254 can provide insight into the nature of the organics present and the potential for DBP formation. Dissolved organic carbon is generally more representative of the soluble organic carbon fraction than TOC and increase in DOC generally led to increase in THMs formation. UV254 has been widely used to predict natural dissolved organic carbon (DOC) in water or its reactivity in forming disinfection by-products during the chlorination process. Because of easy measurement, UV254 offers potentially simple and reliable methods to quantify the contribution of organic carbon in water leading to the formation of various DBPs during chlorination. Strong and significant correlation was obtained between DOC with chloroform and THM (r = 0.849 & 0.860). Similarly, strong & significant relationship was found between UV254 with chloroform and TTHMs however the correlation coefficients (r= 0.658 & 0.636) were slightly lower than TOC and DOC. These findings support in favor of some previously published literature (19; 9). They revealed that the natural waters with high UV_{254} values have been shown to have relatively high hydrophobic and aromatic content with high molecular weight DOM fractions, such as humic and fulvic acids. Higher values of UV_{254} (> 0.1 cm^{-1}) found in the present study indicated that humic contents in the natural organic matter are very high as compared to the non-humic fraction of organic matter

Specific UV absorbance (SUVA), a ratio between UV absorbance and DOC, is a good indicator of NOM in water. The values of SUVA (3.35-5.47 L/mg/m) found in the present study also indicates higher hydrophobic content in the natural than hydrophilic fraction. It can also be seen that comparatively higher correlation of SUVA (r = 0.338) with chloroform than THMs (r = 0.269) in the present study. This can be attributed to the fact that SUVA has better correlation with chloroform than TTHM. A strong correlation between SUVA and the aromatic-carbon content of NOM in natural waters were reported by several researchers (9; 10). Because the hydrophobic fraction usually contains more aromatic carbon and higher-molecular-weight material than the corresponding hydrophilic fraction, the SUVA of the hydrophobic fraction is consistently higher than that of the hydrophilic fraction.

Effect of pH & Temp The formation of THMs depend mainly on the last step of THM reaction pathway, which is base-catalyst as with the haloform reaction. Under alkaline conditions, base-catalyzed hydrolysis prevails, yielding more THMs while in acidic environments, trihaloacetic acids will be formed. Temperature provides the activation energy required for the reaction of organic matter with the residual disinfectant. A strong and significant correlation of temperature with $CHCl_3$ (r = 0.924) and TTHMs (r = 0.945) indicates that temperature is one of the crucial parameters that is responsible for formation of TTHMs. The studies reported higher THMs formation during the summer months than during the winter months, as the increase in reaction rate yields a higher rate of THMs formation (22,23).

Effect of bromide ion The presence of bromide ion in water can lead to the formation of brominated by-products. During chlorination, the bromide ions are oxidized to hypobromous acid (HOBr), which reacts more readily with organic precursors than chlorine, forming brominated THMs. In this study, level of bromide was found below detection limit (<0.1 mg/l) hence no correlation could be established amongst the bromide and THMs.

5. CONCLUSIONS

The analysis of THMs in drinking water revealed the presence of very high concentration of THMs (274 to 511µg/l) which is much higher than the USEPA standards and WHO guidelines. The study depicted that amongst various THMs, the contribution of chloroform was highest (93.07-98.9%) followed by DBCM & CBDM (1.2-6.93%). The study revealed a significant correlation of temperature followed by, TOC, DOC and pH with the formation of TTHMs. A strong correlation of UV_{254} with THMs & TOC also indicate the predominance of aromatic content of organic matter in the water which are normally not removed from the conventional treatment processes and lead to the formation of THMs in drinking water.

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