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Trihalomethanes and Halogenated Organic Formation in Water Treatment Plant

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Formation of trihalomethanes (THMs) and other haloqenated organics is associated with use of chlorine for disinfection of drinking water, (Rook, 1974). THMs are suspected carcinogens and/or mutagenic compounds (Rapson et al., 1980, WHO 1984). A maximum contaminaiton level (MCL) of 0.1 mg/L is recommended by US Environmental protection Agency (EPA 1983) and a 30 ug/L of chloroform as the permissible level for drinking water (WHO 1984).

Conventional water treatment generally includes alum addition, flocculation, sedimentation and rapid sand filteration. Chlorine used as disinfectant, is added to the raw water (pre-chlorination) and to the filtered water (post-chlorination).

The present study aimed to follow the generation and concentration levels of THMs and other halogenated organics liable to be formed during water treatment.

MATERIALS AND METHODS

Water samples were collected to represent the various treatment processes at Al-Giza water works in Cairo. The samples were collected once every week for 6 months to explore possible seasonal changes during winter and summer conditions. The standard methods (1985) were applied for analyses of water sampels with respect to bacterial counts, chlorophyll a (chl. (a)), pH, chemical oxygen demand (COD) and residual chlorine. For total trihalomethanes (TTHMs) and halogenated organics, collection, dechlorination, liquid - liquid extraction of samples were carried out as given by standard methods (1985).

For identification and quantification of THMs and halogenated organics, a Perkin Elmer GLC, model 8320 was used. The GLC was equipped with an electron capture detector (Ni 63), data station and a conventional stainless steel column (packed with 4% Ov-101 and 6%-OV-210 on chromosorb W). The injector and detector temperatures were 230°C and 250°C, respectively. The column temperature was programmed as follows: isothermal for 7 minutes for THMs and unknown volatile chlorinated organics (UVOC), isothermal at 100°C for 5

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Table 1. Range and mean Values of biological and physicochemical parameters of water (1989)

Sampling site	Total bacterial count/mL				pH		Chl. (a)		COD		Residual	
	22°C		37°C				mg/L		mg/L		Cl2 mg/L	
	Range	Mean	Range	Mean	Range	Mean	Renge	Mean	Range	Mean	Range	Mean
Raw	1800 7900	3500	900-3700	3500	7.2-8.4	8.0	13.5-66.9	47.1	14.0-40.8	24.5	0.0	0.0
Flocculator	0.0-3.0	1.0	0.0-3.0	2.0	6.6 7.8	7.4	0.0-6.3	0.6	10.3-7.6	20.5	0.7-3.5	1.9
Sedimentation basin	0.0-4.0	0.6	0.0-9.0	2.0	7.0-7.7	7.3	0.0-1.4	0.1	0.6-29.6	14.6	0.1-3.2	1.1
Filters	0.0-14.0	2.0	0.0-3.0	1.0	6.5-7.6	7.2	0.0-4.0	0.4	10.1 28.0	16.8	0.4-2.9	1.4
clear well	0.0 2.0	0.6	0.0-4.0	1.0	6.6-7.5	7.1	0.0-3.0	0.3	5.5-18.4	15.8	0.3-3.5	1.4

minutes to elute semivolatile halogenatic organics (SVOC) and finally the temperature was raised to 180°C and kept isothermal for separation of non-volatile halogenated compounds (NVOC). Nitrogen was used as a carrier gas at a flow rate of 30 mL/minute. No attempt was done to identify the nature of halogenated organics other than THMs.

At Al-Giza water works, alum is applied at dose of 25-30mg/L, prechlorination is affected by a chlorine dose of 5 mg/l whereas for post-chlorination of filtered water 2 mg/L chlorine is added.

To assess the formation potential of THMs (THMFP) after a contact time of 3 hours, water samples were collected to represent each of the treatment processes. The samples were incubated at 25°C for 3 hours in the dark. Thereafter the total THMs were measured.

Chioroform (CHCl3), dichlorobromomethane (CHCl2Br), chlorodibromomethane (CHClBr2), and bromoform (CHBr3), were used as external standards. Other halogenated organics were measured in terms of chloroform. Percentage recoveries of standard aqueous solutions of CHCl3 , CHCl2Br, CHClBr2 and CHBr3 amounted to 92.9, 88.2, 88.1 and 97.7, respectively.

RESULTS AND DISCUSSION

Biological and chemical charactersitcs of the raw water are given in Table I and show the wide variation in the values of bacterial counts, Chl.a, pH and COD. However, the applied treatment processes were effective in the removal of bacteria and algae. Residual chlorine was always present and the pH of water tends to be in the alkaline range. COD values decreased following flocculation, whereas the water after passing through settling basins (3 hours detention time) and filters was still loaded with organic matter as indicated by the COD values. Such results are in agreement with that reported by Otson et al. (1982) where organic carbon values, upon treatment of raw water, slightly decreased or remained the same. According to Sinsbaugh et al. (1986), and Knocke et al. (1986), ion metal coagulation was efficient for removing high molecular weight organic compounds whereas low molecular weight organic species (< 1000) were not effectively removed. Consequently, the latter compounds would contribute to the increasing percentage of THMs as the retention time is extended during the course of water treatment.

The presence of halogenated organics in raw water is most probably due to the discharge of chlorinated waste water.

The so formed CHCl3 , THMs and halogenated organics exhibited a wide range of concentration levels (Table 2). The concentration of CHCl3 , THMs and UVOC progressively increased as the water passes though the various treatment processes. Aggozzotti and Predceri (1986) reported that THMs contributed the main fraction of volatile halogenated organics. Available results tended to show that UVOC could reach significant concentration approaching that of CHCl3 . SVOC reached their maximum values after flocculation. NVOC, however, decreased after flocculation and restored their high concentration level after sedimentation. A

Table 2. Variation in trihalomethanes and organo-halide concentrations during water treatment (µg/L).

Sampling site and date	CHCl3		THM's		UVOC		SVOC		NVOC	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Raw River Water +										
1.	2.2-14.7	7.9	3.1-15.5	9.3	7.9-41.9	22.4	ND*-28.7	24.4	451.8-2215.0	958.3
2.	0.9- 3.8	2.1	4.0-15.8	8.6	2.8- 5.6	4.4	0.4- 29.9	10.4	605.0-1406.0	965.3
Flocculator										
1.	10.7-48.2	27.0	26.7-97.6	51.4	8.0-47.9	29.1	ND-59.9	27.7	318.6-1081.4	625.9
2.	1.8-12.6	7.4	4.0- 30.5	18.2	1.6- 9.4	5.7	ND- 1.90	0.6	407.0- 714.0	643.0
Settling basin										
1.	4.3-48.9	23.0	24.8-108.7	56.5	ND-177.1	56.8	ND-78.0	22.3	440.0-1053.7	719.4
2.	5.2-13.4	10.6	16.7- 39.5	33.0	6.1- 26.5	14.1	ND- 3.1	1.0	660.0-1790.0	1067.4
Filters										
1.	10.5-39.5	27.8	43.5-112.6	64.8	13.2-116.9	45.5	1.4-37.1	14.9	326.8- 133.5	588.0
2.	26.3-30.6	28.6	61.7- 67.0	63.8	8.8- 32.1	16.7	ND -16.6	5.5	866.5-1024.0	947.4
Clear Well										
1.	17.9-78.2	13.0	41.8-247.1	94.2	2.6- 73.9	26.6	ND-161.9	41.7	321- 1032	646.8
2.	6.0-27.8	18.7	18.1- 80.1	53.9	6.5- 9.2	7.6	ND- 0.8	0.5	866- 998	880.9

* ND = non-detectable.

\+ 1. Samples collected at 10/1987 - 2/1988
2. Samples collected at 7/1988 - 8/1988

Table 3 Trihalomethane formation during treatment processes (Winter time*).

Sampling site and retention time	Concentration µg/L				
	CHCl3	CHCl2Br	CHClBr2	CHBr3	TTHMs
Flocculator					
t = 0	14.7	10.5	0.6	0.9	26.7
t = 3 hr	20.8	28.7	0.7	1.0	51.2 (48%)
Settling basin					
t = 0	22.5	45.9	1.3	0.4	70.1
t = 3 hr	37.9	64.3	2.6	1.0	105.8 (33%)
Filter					
t = 0	25.6	45.6	1.6	0.5	73.3
t = 3 hr	30.3	78.7	2.3	1.0	112.3 (34%)
Clear well					
t = 0	27.0	55.9	1.9	3.1	87.9
t = 3 hr	29.0	57.4	1.9	2.1	90.4 (3%)

* ( ) % increase in THMs after 3 hours contact time.

Table 4 Trihalomethane formation potential during treatment processes (Summer time) *.

Sampling site and retention time	Concentration µg/L			
	CHCl3	CHCl2Br	CHClBr2	TTHMs
Flocculator				
t = 0	1.8	2.2	0.2	4.2
t = 3 hr	9.9	12.8	3.2	25.9(83%)
Settling basin				
t = 0	13.5	22.0	7.5	43.0
t = 3 hr	26.0	34.4	7.0	67.9(36%)
Filter				
t = 0	28.8	30.2	4.0	63.0
t = 3 hr	21.6	56.7	10.5	98.8(36%)
Clear well				
t = 0	27.8	50.4	2.0	80.0
t = 3 hr	34.1	61.5	5.2	100.8(20%)

* ( ) % increase in THMs after 3 hours contact time.

decrease of 11% to 18% in the NVOC concentration was recorded after filteration. Storage of filtered water in the clear well usually enhanced the formtion of THMs which reflects the effects of post-chlorination and extended contact time with chlorine. NVOC were always present in treated water at high concentration compared to TTHMs (Table 2). Such findings are in support with that reported by Johnson and Jensen (1986). Formation of NVOC should receive the same concern as THMs since Kool (1982) was able to show that the majority of organic mutagens present in water were non-volatile.

Samples collected in winter showed that the concentration of TTHMs in the effluents after flocculation, sedimentation and filteration amounted to 54%, 60% and 69% of the finished water, respectively (Table 2). In summer samples, values of TTHMs of filtered water increased to represent 116% of that of the finished water. This may be attributed to an increase in dissolved organic precursors carried over to the filters and/or inproper backwash. According to Oliver and Lawrence (1979) filteration is not expected to reduce the haloform formation levels. Meanwhile, Singer et al., (1982) showed that the concentration of THMs in settled water was on the averge, 57% of that of the finished water. In addition, coagulation and sedimentation were effective in removing 42% of the THMFP in the raw water.

The increase in values of THMs attained after a contact time of 3 hours with chlorine (Tables 3 and 4) represents a measure of THM precursors to be found in water after each specific treatment process. Effluents passing through the flocculator, settling basin, filters and reaching the clear well exhibted an increase in THMs which amounted to 48%, 33%, 34% and 3% of that of the corresponding TTHMs values, respectively (Table 3). In case of water samples collected in summer (Table 4) the clear well water showed higher THMs precursors which resulted in an increase of 20% in TTHMs. Available results clearly show the role of pre-chlorination together with the extended contact time in the settling basins and clear well in the formation of THMs. Sand filters may also act as a source of THMs precursors if excessive metabolites are released by the retained microbial life.

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