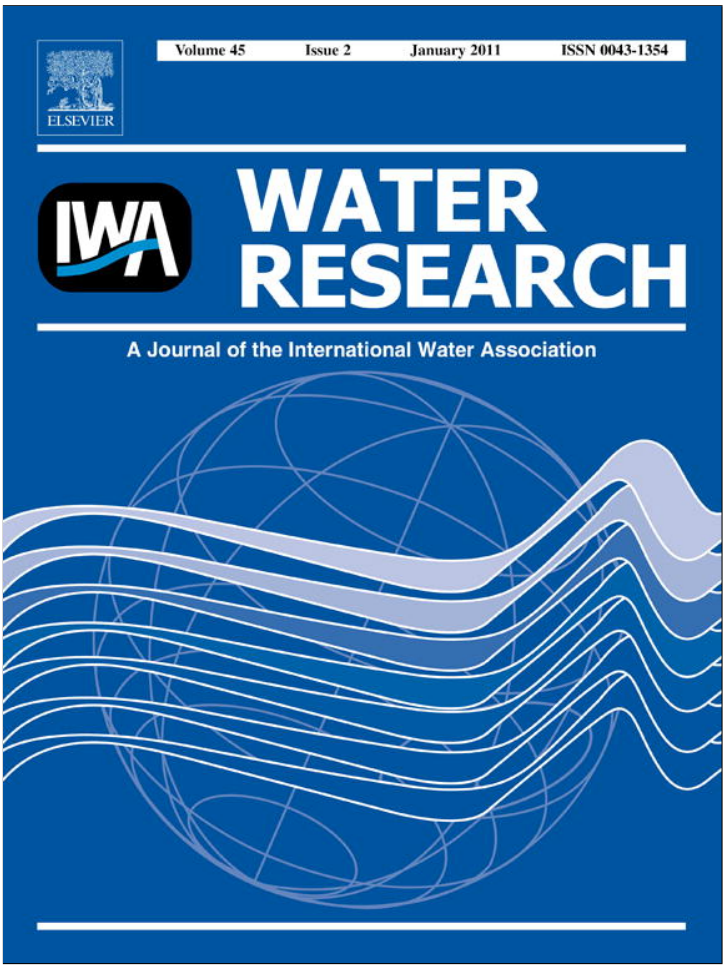

WATER RESEARCH 45 (2011) 926–932

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Formation of disinfection by-products in indoor swimming pool water: The contribution from filling water natural organic matter and swimmer body fluids

*Amer Kanan, Tanju Karanfil**

Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA

ARTICLE INFO

Article history:
Received 4 July 2010
Received in revised form
6 September 2010
Accepted 23 September 2010
Available online 1 October 2010

Keywords:
Disinfection by-products (DBPs)
Body fluid analogs (BFAs)
Natural organic matter (NOM)
Trihalomethanes (THMs)
Haloacetic acid (HAAs)
Halonitromethanes (HNMs)

ABSTRACT

The contribution and role of different precursors in the formation of three class of disinfection by-products (DBPs) [trihalomethanes (THMs), haloacetic acids (HAAs), and halonitromethanes (HNMs)] in swimming pool waters were examined using filling waters obtained from five drinking water treatment plant (WTP) effluents and three body fluid analogs (BFAs). BFAs exerted higher chlorine demands as compared to natural organic matter (NOM) in filling waters. BFAs exhibited higher HAA formation potentials than THM formation potentials, while the opposite was observed for the filling water NOM. There was no appreciable difference in the HNM formation potentials of BFAs and filling water NOM. Different components in the BFAs tested exhibited different degree and type of DBP formation. Citric acid had significantly higher THM and HAA yields than other BFA components. The effect of temperature was greater on THM formation, whereas the effect of contact time had more impact on HAA formation. Experiments with filling waters collected from WTP effluents at three different times showed more variability in HAA than THM formation at the WTPs studied.

1. Introduction

Disinfection is critical for controlling the microbial activity in swimming pools; however it has also important unintended consequences. Chlorine, the most commonly used disinfectant in swimming pools, reacts with the organic matter in swimming pool water producing reaction by-products known as disinfection by-products (DBPs). DBPs have been classified as probable or possible carcinogen, and associated with reproductive and developmental effects. As a result, they are currently regulated in drinking waters around the world (Karanfil et al., 2008), and increasingly stringent regulations have been imposed for them in the United States (US) under the US EPA's D/DBP Rule (US EPA, 2006). DBPs in swimming pools can be ingested, inhaled or absorbed through the skin. It has been shown that there is more risk of DBPs exposure from inhalation and dermal pathways during swimming, showering and bathing than ingestion drinking water (Caro and Gallego, 2007; Villanueva et al., 2007; Kanan, 2010).

Precursors of DBPs in pool water are (i) natural organic matter (NOM) that comes from filling water that is also used as dilution and make-up water, and (ii) human body fluids (BF) that are added to the pool water from swimmers. The filling water is commonly obtained from a drinking water distribution system or a groundwater source. These two types of organics have very different characteristics; therefore, it is hypothesized that they will exhibit different reactivity toward DBP formation and speciation. NOM is present in all natural

* *Corresponding author*. Tel.: +1 864 656 1005; fax: +1 864 656 0672.
E-mail address: tkaranf@clemson.edu (T. Karanfil).
0043-1354/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2010.09.031

waters, and it is a heterogeneous mixture of various organic molecules originating from allochthonous (i.e., biota in a water body) and autochthonous (i.e., soil and terrestrial vegetation) sources. If the filling water is obtained from a water distribution system, it will contain the NOM fraction remaining in water after treatment operations at the drinking water treatment plant. If the filling water is obtained from a groundwater and used without any treatment, it consists of the NOM in the groundwater. In the US, water is disinfected at the effluents of water treatment plants, and the maintenance of a disinfectant residual is required in the distribution systems. As a result, some amount of DBPs is already present in the filling water of swimming pools. However, the DBP formation potential of NOM is not completely exhausted in distribution system because some DBPs are regulated, and chlorine is applied only at sufficient amounts in order to comply with the US EPA's microbial and DBP regulations. Given the fact that high levels of free chlorine residuals are continuously maintained in public swimming pools in US (NSPF, 2006), NOM components will continue to form DBPs in the swimming pool water. A recent survey of twenty-three indoor public pools in the US showed that the median chlorine residual concentration was 3.0 mg/L (Kanan, 2010).

The human body excretions (HBE) are mainly composed of urine, sweat, dirt, saliva, body cells (skin cells, hair), and lotions (synthetic chemicals such as sunscreen, cosmetics, soap residues, etc.). Specifically urine and sweat constituents such as ammonia, urea, various amino acids (e.g., arginine), creatinine, citric acid, uric acid, gluconic acid, and sodium chloride are the major components that are released to water by swimmers (Barbot and Moulin, 2008; Anipsitakis et al., 2008). It is estimated that a bather releases a mixture of 50 mL urine and 200 mL sweat in an average swimming event (Judd and Bullock, 2003). These HBE compounds continuously accumulate and increase in swimming pools with time due to semi-batch nature of swimming pool operations. The survey of twenty-three indoor public pools in the US showed that the total organic carbon (TOC) concentrations ranged from 3.0 to 23.6 mg/L with a median of 7.1 mg/L, which was significantly higher than the TOC levels in the filling waters (Kanan, 2010). In eight indoor swimming pools in London, the dissolved organic carbon (DOC) significantly increased with the number of swimmers, ranging from 3.3 to 12.9 mg/L (Chu and Nieuwenhuijsen, 2002). Thacker and Nitnaware (2003) reported a range of 0.094 to 16 mg/L TOC, which was related to the number of swimmers. Kim et al. (2002) chlorinated materials of human origin (i.e., hair, saliva, skin and urine) separately and together as a mixture in two water sources (surface and groundwater). The formation of five different DBPs (chloroform, bromodichloromethane, chloral hydrate, dichloroacetonitrile, and trichloropropane) from these materials was shown in addition to the amounts formed from the background water used in the experiments.

Since it is not feasible to collect and preserve large amounts of HBEs, different body fluid analog (BFA) recipes have been proposed in the literature to simulate swimmer body excretions (Table 1) (Borgmann-Strahsen, 2003; Judd and Bullock, 2003; Goeres et al., 2004). These recipes were prepared to simulate the release of 50 mL urine and 200 mL sweat during an average swim for one person. They have been used in previous swimming pool research to investigate: (i) the formation and accumulation of THMs (Judd and Bullock, 2003), (ii) the efficiency of disinfection against biofilm formation (Goeres et al., 2004), and (iii) biocidal efficacy of different disinfectants (Borgmann-Strahsen, 2003). To date, no study has compared the formation and speciation of DBPs from these BFAs despite some differences in their compositions.

The objective of this work was to examine the roles and contributions of the two main types of organic precursors (i.e., filling water (NOM) vs. body fluids (BF) components of swimmers) to the formation of three class of DBPs [trihalomethanes (THM_4), haloacetic acids (HAA_9), and halonitromethanes (HNM_9)] in swimming pools. Specifically, we examined and compared the reactivity of (i) three BFAs proposed in literature and some of their components, and (ii) the filling water NOM obtained from distribution systems in the US. Understanding the formation of DBPs from different types of precursors is important for developing strategies to control DBP formation

Table 1 – Body fluid analogs components.

BFA(G)		BFA(J)		BFA(B)	
Ingredient	mg/L	Ingredient	mg/L	Ingredient	mg/L
urea	62.6	urea	14800	urea	23000
creatinine	4.3	creatinine	1800	creatinine	1250
uric acid	1.5	uric acid	490	glutamic acid	300
lactic acid	3.3	citric acid	640	aspartic acid	830
albumin	9.7	histidine	1210	glycine	450
glucuronic acid	1.2	hippuric acid	1710	histidine	200
ammonium chloride	7.0	ammonium chloride	2000	Lysine	75
sodium chloride	22.1	sodium phosphate	4300		
sodium sulfate	35.3				
sodium bicarbonate	6.7				
potassium phosphate	11.4				
potassium sulfate	10.1				

BFA(G): BFA proposed by Goeres et al. (2004); BFA(J): BFA proposed by Judd and Bullock (2003); and BFA(B): BFA proposed by Borgmann-Strahsen (2003). The table shows the recipes used in the preparation of BFA stock solutions. The solutions used in the experiments were diluted to the target TOC concentration (1 mg/L) of the experiments.

and speciation in swimming pools and reduce the exposure of swimmers and pool attendants to DBPs, especially in indoor public pools. Furthermore, knowing the differences in the DBP formation and speciation from the proposed BFAs is important to assess their use for studying DBPs in swimming pools.

2. Materials and methods

2.1. BFAs

Three BFAs [BFA(G), BFA(J), and BFA(B)] were prepared using distilled and deionized water (DDW) following their recipes in literature (Judd and Bullock, 2003; Goeres et al., 2004; Borgmann-Strahsen, 2003). Their compositions are provided in Table 1. The BFA solutions used in the experiments had the TOC concentration of 1 mg/L, which were prepared by diluting the stock solution of each BFA to the target TOC concentration. Additional information about their preparation can be found in the Supporting Information and elsewhere (Kanan, 2010).

2.2. Filling water NOM

Filling water NOM samples were collected from five drinking water treatment plants after conventional clarification processes (i.e., after coagulation, flocculation, and sedimentation before any oxidant or disinfectant addition) in South Carolina, US: Spartanburg (SP), Startex–Jackson–Wellford–Duncan (SJWD), Greenville (GV), Myrtle Beach (MB), and Charleston (CH). The only exception was the use of dissolved air flotation at the GV plant instead of sedimentation. Samples were collected before any oxidant and disinfectant addition to determine the overall DBP formation potentials of filling water NOM and compare with BFAs. They were collected at three different times at each location during the study (Table 2). They were filtered with pre-washed 0.2 μm Supor® membrane filters to eliminate the particles and biological activity, and stored in a dark constant temperature room (4 °C) until the experiments, which were usually performed within 2–4 days of storage. For each sample, the TOC, total nitrogen (TN), ultraviolet absorbance at 254 nm (UV_{254}) and bromide concentrations were measured, and specific ultraviolet absorbance ($SUVA_{254} = UV_{254}/DOC$) was determined.

2.3. Formation potential (FP) tests

The DBP reactivity of the precursors in the filling water NOM and BFA samples was investigated by conducting FP tests. These tests, originally developed for drinking water samples, are conducted at excess chlorine concentrations for a long period of time (e.g., 5 and 10 days). Each sample, BFAs or filling water NOM, was initially diluted to bring the organic matter concentration to a constant level of 1 mg/L TOC, except GV samples for which the source water TOC concentrations were consistently slightly lower than 1 mg TOC/L (Table 2). Free chlorine was spiked to each sample at the constant initial dose of 50 mg/L. Therefore, Cl_2/TOC levels were constant for all samples, except slightly higher in GV due to its lower TOC at the source. Chlorinated samples were incubated in headspace free amber glass bottles for 5 and 10 days at 26 and 40 °C using a water bath. The selected temperatures are representative of minimum and maximum water pool temperatures in the US (Kanan, 2010).

2.4. Analytical methods

Analytical methods used in the study and the minimum reporting levels (MRLs) are summarized in Supplemental Information (Table S1) and detailed information can be found elsewhere (Kanan, 2010). In brief, THM_4 and HNM_9 were quantified by liquid/liquid extraction with MtBE followed by gas chromatography with electron capture detection (GC/ECD)

Table 2 – Filling water NOMs collected for the experiments.

WTP	Sampling Date	TOC mg/L	TN mg/L	UV_{254} cm^{-1}	SUVA L/mg-m	Br μg/L
SJWD	November-08	1.7	0.3	0.0300	1.74	31
	March-09	1.4	0.3	0.0237	1.73	19
	September-09	1.7	0.3	0.0287	1.71	19
SP	November-08	1.6	0.2	0.0181	1.11	<MRL
	March-09	1.7	0.2	0.0209	1.25	<MRL
	September-09	1.7	0.2	0.0204	1.17	<MRL
GV	November-08	0.7	0.1	0.0119	1.63	<MRL
	March-09	0.8	0.1	0.0138	1.71	10
	September-09	0.8	0.1	0.0075	0.96	<MRL
CH	November-08	2.5	0.3	0.0535	2.10	110
	March-09	3.1	0.3	0.0586	1.88	79
	September-09	3.1	0.3	0.0583	1.86	75
MB	November-08	6.7	0.3	0.1365	2.05	37
	March-09	6.1	0.3	0.1212	1.98	29
	September-09	5.4	0.3	0.1127	2.08	45

WTP: Water Treatment Plant, TOC (total organic carbon), TN (total nitrogen), SJWD (Startex–Jackson–Wellford–Duncan), SP (Spartanburg), GV (Greenville), MB (Myrtle Beach), CH (Charleston), MRL (minimum reporting level: 10 μg/L).

according to US EPA Method 551.1 with some modifications (Kanan, 2010). HAA_9 were analyzed by liquid/liquid extraction with MtBE followed by derivatization with diazomethane and analysis by GC/ECD. The relative standard deviation of DBP measurements were less than 10%.

3. Results and discussion

3.1. DBP formation potentials of BFAs

The chlorine demands (17–25 mg Cl_2/mg TOC) of BFAs were relatively high, which was attributed to chlorine demands of the nitrogenous and carbonaceous compounds present in their compositions. These demands are consistent with those reported during previous chlorination studies of some of the same BFA components (Hureiki et al., 1994; Li and Blatchley, 2007; Hong et al., 2009). Since there was no detectable bromide present in the DDW used to prepare BFA solutions, formation of only chlorinated DBP species [TCM (chloroform) for THM_4, DCAA and TCAA for HAA_9 and TCNM (chloropicrin) for HNM_9] were observed.

The formation of TCM was always lower than the formation of total HAA (i.e., sum of DCAA and TCAA) during the FP tests (Table 3, Fig. S1). BFA(B) and BFA(J) exhibited comparable but higher total HAA formation potentials than that of BFA(G), mainly due to significantly higher formation of DCAA than TCAA (Fig. S2). DCAA to TCAA mass ratio ranged from 2.5 to 8.0 for BFA(J) and BFA(B), but it was nearly 1:1 for BFA(G). These differences were attributed to the presence of citric acid and two free amino acids (histidine and aspartic acids) in the compositions of BFA(B) and BFA(J). These two amino acids have been reported to exhibit high HAA formation potentials with preferential formation of DCAA in a previous study (Table 4). TCNM formation was at the trace levels from all three BFAs in the range of 0.8–2 μg/L (Table 3). TCM yields increased with contact time and temperature; however, the majority of 10-day yield (55–88%) formed during five days of reaction time. The effect of temperature was more pronounced on TCM than DCAA and TCAA formation.

In order to further examine the reactivity of BFAs, FP tests were conducted with the individual organic components in their mixtures. The results showed that citric acid exhibited significantly higher TCM and DCAA formation than all other individual components despite its lower chlorine consumption than other components except hippuric acid (Table 4). The occurrence of citric acid in tap waters (28–35 μg/L) and natural waters (44–85 μg/L) has been reported (Afghan et al., 1974; Bjork, 1975; Larson and Rockwell, 1979). Citric acid is also introduced continuously to pool waters from metabolic activity of both human body (sweat and urine) and microbial cells. Chlorination of citric acid in a previous study produced a considerable amount of TCM at a very fast rate (within 2 h) at pH 7 (Larson and Rockwell, 1979). After citric acid, albumin showed the second highest TCM yield (Table 4). TCM formation potential from 5 mg/L albumin at 20 °C and pH 7 was previously reported to be 97 μg/L (i.e., 19 μg/mg) (Scully et al., 1988), which was comparable to the yield obtained in this study (23 μg/mg). Other BFA components urea, creatinine, hippuric acid, glucuronic acid, lactic acid and uric acid showed comparable TCM yields. The formation of TCM from the amino acids in the BFA composition was shown to be minimal in previous studies (Hong et al., 2009). The DCAA and TCAA yields from BFA components other than amino acids were similar to the pattern observed for TCM with two major differences: (i) formation of DCAA and TCAA from histidine and aspartic acid were higher or comparable to the yield of albumin, and (ii) DCAA and TCAA yields of urea, creatinine, hippuric acid, glucuronic acid, lactic acid, uric acid were very small. The formation of TCNM was always at the MRL levels of the measurement and did not show any compound specific pattern.

3.2. DBP formation potentials of filling water NOM

The chlorine demands (2–8 mg Cl_2/mg TOC) of filling water NOM samples were much lower than those of the BFAs under the same experimental conditions. Filling water NOM exhibited significantly higher reactivity toward producing THMs than HAAs at 26 °C (Table 5 and Fig. 1) and at 40 °C

Table 3 – THM, HAA and HNM formation from BFAs at pH 7, TOC of 1 mg/L, and initial chlorine dose of 50 mg/L.

BFA	T (°C)	Incubation (days)	FAC residual (mg/L)	TCM (μg/L)	DCAA (μg/L)	TCAA (μg/L)	THAA (μg/L)	TCNM (μg/L)
BFA(G)	26	5	31	21 ± 0.7	15	19	34 ± 1.5	1.5 ± 0.2
	26	10	30	28 ± 0.9	22	24	46 ± 0.7	1.3 ± 0.2
	40	5	28	29 ± 0.9	20	19	39 ± 2.4	1.1 ± 0.3
	40	10	25	35 ± 0.6	18	18	36 ± 3.0	0.8 ± 0.0
BFA(J)	26	5	33	30 ± 1.1	51	19	70 ± 2.7	1.6 ± 0.1
	26	10	32	38 ± 1.1	54	21	75 ± 6.4	1.1 ± 0.4
	40	5	29	50 ± 0.8	66	15	81 ± 0.6	1.1 ± 0.4
	40	10	28	77 ± 2.8	68	27	95 ± 5.1	0.9 ± 0.0
BFA(B)	26	5	28	16 ± 0.4	63	11	74 ± 4.3	2.0 ± 0.3
	26	10	27	18 ± 1.0	70	12	82 ± 3.3	1.0 ± 0.1
	40	5	26	18 ± 0.6	63	8	71 ± 1.4	1.1 ± 0.1
	40	10	24	33 ± 0.7	66	14	80 ± 1.0	1.0 ± 0.1

T (temperature), FAC (free available chlorine), TCM (chloroform), DCAA (dichloroacetic acid), TCAA (trichloroacetic acid), THAA (total HAA: sum of DCAA and TCAA), TCNM (trichloronitromethane).

Table 4 – Disinfection By-Products formation from 1 mg/L BFA components at 22 °C, pH 7, initial chlorine dose 50 mg/L, and 5-days contact time.

BFA Component	FAC mg/L	TCM μg/L	DCAA μg/L	TCAA μg/L	THAA μg/L	TCNM μg/L
Urea	37	13	4	6	10	0.7
Albumin	43	23	16	23	39	0.8
Creatinine	37	12	2	4	6	0.7
Citric acid	45	307	173	8	181	0.8
Hippuric acid	46	14	2	4	6	0.9
Glucuronic acid	41	13	2	4	6	0.8
Lactic acid	41	14	2	5	7	0.8
Uric acid	39	15	2	4	6	<MRL
Histidine[a]	[b]	1.55 ± 0.5	32.5 ± 0.031	14 ± 0.2	46.5	NM
Aspartic acid[a]	[b]	1.68 ± 0.5	26.9 ± 4.97	3.17 ± 2.12	30	NM
Glycine[a]	[b]	ND	ND	ND		NM
Lysine[a]	[b]	1.09 ± 0.011	3.52 ± 0.12	0.52 ± 0.05	4	NM

FAC (free available chlorine), TCM (chloroform), DCAA (dichloroacetic acid), TCAA (trichloroacetic acid), THAA (total HAA), TCNM (trichloronitromethane). ND: Not Detected; NM: Not Measured); MRL: Minimum Reporting Level.

a Obtained from Hong et al. (2009).

b Experimental condition of the study was Cl_2/DOC = 10, 4- days contact time at 20 °C.

Table 5 – THM_4, HAA_9 and HNM_9 formation potentials of filling water NOM samples at 26 °C, pH 7, TOC[a] of 1 mg/L, and initial chlorine dose 50 mg/L.

WTP	Date	Incubation days	TCM μg/L	BDCM μg/L	THM_4 μg/L	DCAA μg/L	TCAA μg/L	BDCAA μg/L	HAA_9 μg/L	TCNM μg/L
SJWD	November-08	5	64	5	70 ± 0.8	13	20	3	37 ± 1.2	1.5 ± 0.3
SP		5	70	5	75 ± 1.9	13	22	2	39 ± 1.3	1.7 ± 0.2
GV		5	44	3	48 ± 1.6	7	12	1	20 ± 0.2	1.1 ± 0.0
CH		5	64	12	77 ± 1.4	13	23	8	47 ± 1.7	1.3 ± 0.3
MB		5	80	4	85 ± 0.9	13	27	3	43 ± 0.2	1.1 ± 0.2
SJWD		10	83	7	91 ± 1.4	9	18	3	31 ± 0.8	1.1 ± 0.1
SP		10	94	5	99 ± 0.6	10	21	2	33 ± 1.3	1.2 ± 0.0
GV		10	58	4	63 ± 0.0	10	16	2	28 ± 4.4	1.1 ± 0.1
CH		10	82	14	98 ± 0.7	14	26	9	50 ± 2.4	1.3 ± 0.3
MB		10	100	5	106 ± 2.6	13	30	3	46 ± 1.3	1.0 ± 0.0
SJWD	March-09	5	69	5	75 ± 3.0	NR	14	3	NR	1.1 ± 0.1
SP		5	79	4	84 ± 0.2	NR	22	2	NR	1.3 ± 0.0
GV		5	70	4	75 ± 1.8	NR	11	2	NR	1.1 ± 0.0
CH		5	71	10	82 ± 3.3	NR	14	5	NR	1.0 ± 0.2
MB		5	78	3	81 ± 0.1	NR	16	1	NR	1.1 ± 0.0
SJWD		10	95	6	103 ± 0.9	39	48	7	97 ± 3.8	0.8 ± 0.0
SP		10	99	5	104 ± 0.1	52	59	5	119 ± 2.3	1.0 ± 0.0
GV		10	87	5	92 ± 0.9	29	33	4	68 ± 3.1	<MRL
CH		10	90	11	104 ± 1.2	36	45	12	97 ± 2.0	<MRL
MB		10	94	12	108 ± 1.3	27	43	12	86 ± 4.5	0.7 ± 0.2
SJWD	September-09	5	85	5	91 ± 3.7	NR	18	5	NR	<MRL
SP		5	90	4	95 ± 2.3	NR	20	3	NR	0.7 ± 0.0
GV		5	101	3	106 ± 2.0	NR	31	5	NR	1.0 ± 0.1
CH		5	83	10	96 ± 0.7	NR	29	17	NR	0.7 ± 0.0
MB		5	97	4	103 ± 2.9	NR	24	5	NR	<MRL
SJWD		10	103	6	110 ± 3.7	25	31	8	65 ± 3.7	0.7 ± 0.1
SP		10	110	4	115 ± 1.2	32	49	6	89 ± 2.9	0.8 ± 0.1
GV		10	121	4	126 ± 2.0	48	49	6	105 ± 2.3	1.0 ± 0.1
CH		10	102	12	117 ± 1.8	21	33	18	73 ± 1.1	0.7 ± 0.0
MB		10	117	5	123 ± 2.4	20	39	6	66 ± 2.3	0.7 ± 0.1

WTP: Water Treatment Plant. TCM (chloroform), BDCM (bromdichloromethane), DCAA (dichloroacetic acid), TCAA (trichloroacetic acid), BDCAA (bromodichloroacetic acid), TCNM (trichloronitromethane). The concentrations of dibrochloromethane, bromochloromethanes and dibromochloroacetic acid were lower than 3 μg/L; they were not individually listed in table.

NR: Not Reported; MRL: Minimum Reporting Level.

a GV had TOC concentrations 0.7–0.8 mg/L (Table 2); they were used in the experiments without any dilutions. Other filling water NOMs were diluted to 1 mg/TOC/L.

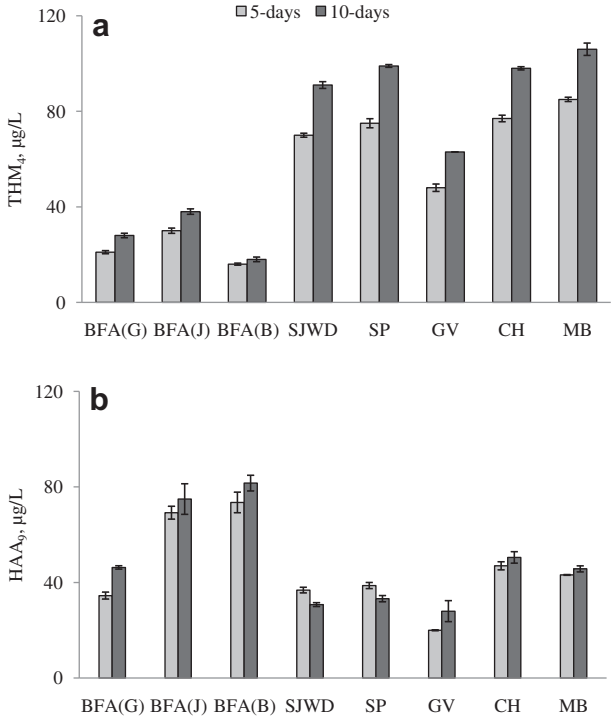

Fig. 1 – THM_4 (a) and HAA_9 (b) yields from BFAs and five filling water NOMs (November 08 samples) after 5 and 10 day FP tests (error bars are standard deviation).

(Table S2). THM yields were twice and sometimes higher than those of HAAs. This trend is opposite to the observations with BFAs that produced higher amounts of HAAs than THMs (Table 3). The higher THM formation potential of NOM than proteins and free amino acids was also observed in early DBP studies when proteins, free amino acids and humic acid were chlorinated and compared under the same conditions (Morris et al., 1980; Scully et al., 1988). These opposing trends of THM and HAA formation from filling water NOMs and BFAs can explain the occurrence of very high HAA concentrations in US indoor swimming pools and their potential precursors. In a recent monitoring study of 23 indoor pools in the US showed that the ranges and average of THM and HAA concentrations were 26–213 μg/L (ave. 80 μg/L) and 173–9005 μg/L (ave. 1541 μg/L), respectively (Kanan, 2010). Therefore, very high concentrations of HAAs in US indoor pool waters are likely due to a combination of factors: (i) the BF components that are continuously added from bathers to swimming pools waters and reacting with chlorine, (ii) the pool waters in the US are not diluted systematically and not periodically replaced, resulting in very long water ages (>1–2 years), and (iii) HAAs are highly soluble in water and do not degrade in the presence of high chlorine residual.

In terms of DBP speciation, TCAA concentrations were always higher than those of DCAA which was attributed to high chlorine to TOC ratios of the FP tests (Miller and Uden, 1983; Zhuo et al., 2001; Hua and Reckhow, 2008). Hua and Reckhow (2008) explained the decrease in DCAA formation at high Cl_2/NOM ratios by the differences in the reactivity of the precursors as a function of chlorine doses and different pathways of DCAA and TCAA formation. Few brominated THM and HAA species were observed due to low bromide levels in filling water tested and high Cl_2/Br ratio of the FP experiments. Increasing the contact time and the temperature increased both THM and HAA formation. The time effect was more apparent on HAA than THM formation; THM yields at 26 °C ranged from 70 to 123 μg/L and from 91 to 103 μg/L for 5- and 10-days reaction periods, respectively, while the HAA yields were 18–50 μg/L and 31–119 μg/L during the same periods. The increase in temperature resulted in higher THM than HAA yields. TCNM concentrations, most of the time, ranged between 0.7 and 1.7 μg/L. The lower concentrations and narrow ranges of TCNM measured indicate low reactivity of the filling water NOMs to produce HNMs, as compared to THMs and HAAs. This was consistent with low degree of HNM formation potentials reported in chlorinated drinking waters (Hu et al., 2010).

THM, HAA, and HNM formation of the filling water NOMs were tested at three different times and under the same experimental conditions (Table 5 and SI Table S2). For THM, although samples were obtained after conventional clarification processes from five water treatment plants using source waters with significantly different characteristics (Table 2), THM FP yields at the treatment plant effluents showed relatively low range of variability (10-days yield from 91 to 123 μg/L) independent of the time and location, except GV water sample. However, HAAs FPs exhibited more variability as function of time and location. This suggested that the removal of HAA precursors during conventional treatment processes was more variable than THM precursors in the treatment plants monitored in this study. The temporal variability of HAAs formation was also reported by others when chlorination of different water types was carried out at the same conditions but at different sampling dates or seasons (Rodriguez et al., 2007).

4. Conclusions

The following conclusions were obtained from the comparative analysis of DBP formation potentials of BFAs and filling water NOM in this study:

- BFAs were more reactive toward chlorine than filling water NOM.
- BFAs formed more HAAs than THMs, while filling water NOM produced more THMs than HAAs. On the other hand, both NOMs and BFAs produced a similar amount of HNMs, which was significantly lower as compared to THM and HAA formation.
- Analysis of individual BFA components demonstrated that citric acid had significantly higher reactivity toward THM and HAA formation than other components. Individual reactivity of BFA components is important to consider and will determine the DBP formation and speciation of a particular BFA mixture.
- Filling waters collected from five different treatment plants in three different sampling events during a one year period exhibited comparable THM formation relatively independent of time and location, whereas HAA yields exhibited more time and spatial dependent variability.

- Increasing temperature and incubation time increased DBP formation. Higher THM and
- HAA yields were observed at 40 °C than at 26 °C. The effect of temperature was more pronounced on TCM than DCAA and TCAA formation, while incubation time had more impact on HAA than THM formation.

Acknowledgment

During this research, Amer Kanan was sponsored by Ford Foundation International Fellowships Program and received a partial financial support from Al-Quds University. The manuscript has not been subjected to the peer and policy review of these agencies and therefore does not necessarily reflect their views.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2010.09.031.

REFERENCES

Afghan, B.K., Leung, R., Ryan, J.F., 1974. Automated fluorometric method for determination of citric acid in sewage and sewage effluents. Water Research 8, 789–795.

Anipsitakis, G.P., Tufano, T.P., Dionysiou, D.D., 2008. Chemical and microbial decontamination of pool water using activated potassium peroxymonosulfate. Water Research 42, 2899–2910.

Barbot, E., Moulin, P., 2008. Swimming pool water treatment by ultrafiltration–adsorption process. Journal of Membrane Science 314, 50–57.

Bjork, R.G., 1975. GLC determination of PPB levels of citrate by conversion to bromoform. Analytical Biochemistry 63, 80–86.

Borgmann-Strahsen, R., 2003. Comparative assessment of different biocides in swimming pool water. International Biodeterioration & Biodegradation 51, 291–297.

Caro, J., Gallego, M., 2007. Assessment of exposure of workers and swimmers to trihalomethanes in an indoor swimming pool. Environmental Science and Technology 41, 4793–4798.

Chu, H., Nieuwenhuijsen, M.J., 2002. Distribution and determinants of trihalomethanes concentrations in indoor swimming pools. Occupational and Environmental Medicine 59, 243–247.

Goeres, D.M., Palys, T., Sandel, B.B., Geiger, J., 2004. Evaluation of disinfectant efficacy against biofilm and suspended bacteria in a laboratory swimming pool model. Water Research 38, 3103–3109.

Hong, H.C., Wong, M.H., Liang, Y., 2009. Amino acids as precursors of trihalomethanes and haloacetic acids formation during chlorination. Archives of Environmental Contamination and Toxicology 56 (4), 638–645.

Hu, J., Song, H., Karanfil, T., 2010. Comparative analysis of halonitromethane and trihalomethane formation and speciation in drinking water: the effects of disinfectants, pH, bromide, and nitrite. Environmental Science and Technology 44 (2), 794–799.

Hua, G., Reckhow, D.A., 2008. DBP formation during chlorination: effect of reaction time, pH, dosage, and temperature. Journal of the American Water Works Association 100 (8), 82–89.

Hureiki, L., Croue, J.P., Legube, B., 1994. Chlorination studies of free and combined amino acids. Water Research 28 (12), 2521–2531.

Judd, S.J., Bullock, G., 2003. The fate of chlorine and organic materials in swimming pools. Chemosphere 5 (19), 869–879.

Kanan, A., 2010. Occurrence and Formation of Disinfection By-Products in Indoor Swimming Pools Water. Clemson University, Clemson, SC, USA, PhD dissertation.

Karanfil, T., Krasner, S.W., Westerhoff, P., Xie, Y., 2008. Recent advances in disinfection byproduct formation, occurrence, control, health effects, and regulations. In: Karanfil, T., Krasner, S.W., Westerhoff, P., Xie, Y. (Eds.), Disinfection By-Products in Drinking Water: Occurrence, Formation, Health Effects, and Control. American Chemical Society, Washington, D.C.

Kim, H., Shim, J., Lee, S., 2002. Formation of disinfection by-products in chlorinated swimming pool water. Chemosphere 46, 123–130.

Larson, R.A., Rockwell, A.L., 1979. Chloroform and chlorophenol production by decarboxylation of natural acids during aqueous chlorination. Environmental Science and Technology 13 (3), 325–329.

Li, J., Blatchley III, E.R., 2007. Volatile disinfection byproduct formation resulting from chlorination of organic-nitrogen precursors in swimming pools. Environmental Science and Technology 41 (19), 6732–6739.

Miller, J.W., Uden, P.C., 1983. Characterization of nonvolatile aqueous chlorination products of humic substances. Environmental Science and Technology 17 (3), 150–157.

Morris, J.C., Ram, N.M., Baum, B., Wajon, E., 1980. Formation and Significance of N-chloro Compounds in Water Supplies. U.S. Government Printing Office, Washington, DC. EPA 600/2-80-031. 1980.

NSPF, 2006. Certified Pool-Spa Operator Handbook. National swimming pool Foundation. Colorado Springs, CO.

Rodriguez, M.J., Serodesb, J., Royc, D., 2007. Formation and fate of haloacetic acids (HAAs) within the water treatment plant. Water Research 41, 4222–4232.

Scully, F.E., Howell, G.D., Kravltz, R., Jewel, J.T., 1988. Proteins in natural waters and their relation to the formation of chlorinated organics during water disinfection. Environmental Science and Technology 22 (5), 537–542.

Thacker, N.P., Nitnaware, V., 2003. Factors influencing formation of trihalomethanes in swimming pool water. Bulletin of Environmental Contamination and Toxicology 71 (3), 633–640.

US EPA, 2006. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule. http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-04/w03.pdf.

Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia, C.R., Serra, C., Carrato, A., Castano-Vinyals, G., Marcos, R., Rothman, N., Real, F.X., Dosemeci, M., Kogevinas, M., 2007. Bladder cancer and exposure to water disinfection by products through ingestion, bathing, showering and swimming in pools. American Journal of Epidemiology 165 (2), 148–156.

Zhuo, C., Chengyong, Y., Junhe, L., Huixian, Z., Jinqi, Z., 2001. Factors on the formation by-products MX, DCA and TCA by chlorination of fulvic acid from lake sediments. Chemosphere 45, 379–385.