

## Chapter 21

# Occurrence and Formation of Disinfection By-Products in Indoor U.S. Swimming Pools

Amer Kanan,<sup>1</sup> Meric Selbes,<sup>2</sup> and Tanju Karanfil<sup>\*3</sup>

<sup>1</sup>Department of Environmental and Earth Sciences, Al-Quds University, Jerusalem, Palestine

<sup>2</sup>Hazen and Sawyer, Environmental Engineers and Scientists, Fairfax, Virginia 22030, U.S.A.

<sup>3</sup>Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, South Carolina 29625, U.S.A.

\*E-mail: tkaranf@clemson.edu.

Chlorination is commonly used to prevent the spreading of waterborne infectious diseases in swimming pools. This required disinfection practice also results in the formation of undesirable disinfection by-products (DBPs) from the reactions of chlorine with the organic matter (released by swimmers or present in the pool filling water) and inorganics (i.e., bromide). The main objective of this research was to improve our understanding of the occurrence and formation of different classes of DBPs (trihalomethanes [THMs], haloacetic acids [HAAs], halonitromethanes [HNMs], haloacetonitriles [HANs], and nitrosamines) in indoor swimming pools operational conditions in the U.S.. The results showed that the DBPs in the investigated 23 swimming pools were far higher than the drinking water regulation values in the U.S. Average THMs, HAAs, HANs, HNMs, and *N*-nitrosodimethylamine concentrations were 80 µg/L, 1541 µg/L, 19 µg/L, 5.4 µg/L, and 27 ng/L, respectively. An increase in organic matter released by the swimmers and bromide (from the filling water or electrochemical generation of chlorine) levels in the water increased the overall formation of DBPs. Increases in free available chlorine, pH, and water temperature were shown to

enhance the formation of THMs and HAAs. These favorable conditions lead to rapid formation (i.e. 3-6 hours) of THMs and HAAs under swimming pool conditions.

## Introduction

The average swimmer releases several grams of body fluids (BFs) and excretions during an average swim (1-3). The disinfection of this organic and inorganic matter from swimming pool water is essential for deactivating the pathogenic microorganisms that can thrive on the released organic matter. Swimming pool water is continuously circulated, filtered, and disinfected to maintain clear and biologically safe (4). Chlorine is commonly used in swimming pools and is added continuously to maintain free available chlorine (FAC) to prevent microbial growth (5). While deactivating microorganisms, the reaction of chlorine with the organic (e.g., hair, sweat, dead cells, saliva, cosmetics, dust and urine) and inorganic (e.g., urea, nitrates, nitrites and free ammonia) matter can form a wide array of DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloacids, halodiacids, iodo-THMs, haloaldehydes, halonitriles, halo ketones (HKs), halonitromethanes (HNMs), haloamides, haloalcohols, nitrosamines, combined available chlorine, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and MX homologues, etc. (6-11). Furthermore, bromide is introduced to when the pool is being filled and/or as impurities when chlorine is generated electrochemically from sodium chloride. Chlorine oxidizes bromide to HOBr that can react with organic matter to produce brominated DBPs. Although there are currently no federal DBP regulations in swimming pool waters in the U.S., some countries are including THMs within the swimming pool regulations (12, 13).

The overall formation of DBPs is correlated to the amount of precursors such as organic matter. It is also well known that temperature, pH, and chlorine dose influence the formation of DBPs. Therefore, the formation of DBPs in pool waters would be affected by the operation of the swimming pools. The pool operational requirements and regulations in the U.S. are variable among different states and enforced separately by each state department of health and environment. Generally in the U.S., FAC should be maintained in the range of 1 to 5 mg/L in the pool water to prevent microbial growth (5, 8, 14). The pH of swimming pool water is continuously adjusted mainly to assure an acceptable level of disinfection efficiency, comfortable water for swimmers, and elimination of the damage to the swimming pool structures. Typically, the pH of the pool water is maintained between 7.2 and 7.8 range (15). Swimming pool water temperature is maintained constant usually within the range of 26 to 40°C depending on pool type and usage. Finally, the turnover period for the water in swimming pools typically ranges from 4 to 8 hours (3, 5, 16). From a DBP formation perspective, the reaction period corresponds to the time available for chlorine to react with precursors and form DBPs before they are removed through the pool treatment processes. It is well-known that DBPs including THMs and HAAs have fast formation kinetics

at the levels of chlorine dose in drinking waters (17, 18). It is postulated that DBPs will form very rapidly in swimming pools due to much higher free chlorine residual concentrations than in drinking waters.

Although intensive work has been devoted to investigate the formation of regulated THMs and HAAs in drinking waters, there is relatively little known about the formation and occurrence of DBPs in swimming pools. Moreover, the effects of swimming pool operational parameters on the formation and speciation of DBPs in swimming pools have not been systematically investigated. Understanding the effect of operational parameters is essential for developing approaches to control the formation of DBPs in pools and reduce exposure of swimmers and swimming pool attendants to DBPs. Furthermore, to date there is no information regarding the DBP formation kinetics under swimming pool conditions.

The objectives of this study were to (i) investigate the occurrence of regulated DBPs (THMs and HAAs), as well as emerging DBPs including HNMs, HANs, and nitrosamines in 23 indoor swimming pools, (ii) examine the effects of different swimming pool operational parameters such as FAC in pool water, pH, organic carbon, temperature, bromide concentration on the formation and speciation of THMs and HAAs and (iii) determine how fast THMs and HAAs are produced under swimming pool conditions.

## Materials and Methods

### Samples Collection

Indoor swimming pools (n=23) located in South Carolina, Georgia and North Carolina were sampled to investigate the occurrence of five classes of DBPs. Furthermore, three of the swimming pools were monitored over a nine-month period. Grab samples were collected from 30 cm below the water surface of the pool. FAC, pH, and temperature of the swimming pool were obtained from the facilities. A 125-mL amber bottle was used to collect total organic carbon (TOC) and total nitrogen (TN) samples without any preservatives. A 125-mL amber glass was used for the halogenated DBPs analysis (THMs, HAAs, HNMs, HANs), and ammonium chloride was used to quench the free chlorine in these samples. For nitrosamine analysis, a 1L sample was collected in an amber glass bottle and quenched by sodium thiosulfate. All samples were transferred immediately to the lab using an ice box for DBPs analyses, which was conducted either on the same day of sampling or stored at 4°C for the following day.

### Synthetic Swimming Pool Waters

Two synthetic pool waters were prepared using two different filling waters and a body fluids analog (BFA) recipe developed by Goeres and co-workers (19) to simulate the body fluids that are introduced in swimming pool water by swimmers (9). The filling waters were collected from Myrtle Beach (MB) and

Startex-Jackson-Wellford-Duncan (SJWD) drinking water treatment plants in South Carolina prior to the final addition of the disinfectant. These two filling waters served as two different background matrices for the synthetic swimming pool waters. The selected waters had distinct differences in their aromaticity of the organic components determined by their specific ultraviolet absorbances at 254 nm wavelength (SUVA<sub>254</sub>). The MB water had a high aromaticity with a SUVA<sub>254</sub> value of 4-6 mg/L-m, whereas the SJWD had a lower level of aromatic organics with a SUVA<sub>254</sub> of 2-3 mg/L-m. Both waters were diluted to 1 mg/L TOC to provide the same amount of background organic carbon in the synthetic solution. For every experiment 1 mg/L TOC was from the fill water and the remaining TOC was provided by the BFA. Here and after the two synthetic pool waters will be referred to as BFA-MB and BFA-SJWD.

### DBP FP and Kinetics Tests

THM and HAA formation potential (FP) tests were conducted in the presence of an excess disinfectant. Chlorine stock solutions (500–2,000 mg/L) were prepared by diluting sodium hypochlorite (~5% available free chlorine). The chlorination FP tests were performed in 125 mL amber bottles filled headspace free with the sample and capped with Teflon-lined PTFE caps. After mixing for five minutes with magnetic stir bars, the bottles were stored headspace free in a water bath for 5 days at 26 or 40°C. For the kinetic experiments an initial dose of 100 mg/L chlorine was used. Each solution was chlorinated, and DBPs were determined at different reaction times during 5 days (e.g., 0.5, 1, 3, 5, 7, 10, 15, 24, 48, 72, 96, 120 hours).

### Analytical Methods

Analytical methods used in the study and their respective minimum reporting levels (MRLs) are provided in Table 1. Either standard methods (SM) or USEPA methods were used for DBP analyses with minor modifications. The detailed information about these methods can be found elsewhere (20–23). For TOC, TN and DBP analyses, samples were analyzed in duplicates. Error bars in all the graphs show the variability due to multiple analysis (n=2) under the same conditions.

**Table 1. Analytical Methods and Minimum Reporting Levels**

<i>Parameter</i>	<i>Unit</i>	<i>Measurement Method</i>	<i>Instrument</i>	<i>MRL or Accuracy<sup>a</sup></i>
TOC <sup>b</sup>	mg/L	SM 5310B	TOC-V <sub>CHS</sub> & TNM-1, Shimadzu Corp., Japan	0.1
TN <sup>c</sup>	mg/L	High Temperature Combustion	TOC-V <sub>CHS</sub> & TNM-1, Shimadzu Corp., Japan	0.1
UV Absorbance <sup>d</sup>	cm <sup>-1</sup>	SM 5910	DU 640, Beckman Inst. Inc., USA	±0.005 <sup>d</sup>
Bromide	µg/L	US EPA Method 300	ED 40, Dionex Corp., USA	10
pH	-	SM 4500-H <sup>+</sup>	420A, Orion Corp., USA	±0.01 <sup>e</sup>
THMs & HANs <sup>f</sup>	µg/L	US EPA Method 551.1	6890 GC-ECD, Agilent, USA	1.0
HAAs <sup>g</sup>	µg/L	SM 6251 B <sup>g</sup>	6890 GC- ECD, Agilent, USA	1.0
HNMs <sup>h</sup>	µg/L	US EPA Method 551.1	6850 GC-ECD, Agilent, USA	0.7
Nitrosamines <sup>i</sup>	ng/L	US EPA 521	Varian GC/MS/MS	3.0
FAC	mg/L	SM 4500-Cl F	NA	0.1

<sup>a</sup> MRLs were determined in the lab in previous works (24). Accuracy as reported by the manufacturer. <sup>b</sup> Reagent grade potassium hydrogen phthalate was used to prepare external standards. <sup>c</sup> Reagent grade potassium nitrate was used to prepare external standards. <sup>d</sup> At wavelengths of 254 nm using a 1- or 5-cm cell. Photo-metric accuracy (absorbance units). <sup>e</sup> Accuracy (pH units). <sup>f</sup> THMs and HANs were extracted by liquid-liquid extraction with methyl-tert butyl ether (MtBE) and analyzed by GC-µECD. <sup>g</sup> HAAs were extracted by liquid-liquid extraction with MtBE, derivatized with diazomethane and analyzed by GC-µECD. <sup>h</sup> HNM were extracted by liquid-liquid extraction with MtBE and analyzed by GC-µECD. <sup>i</sup> Nitrosamines were extracted by solid phase extraction, eluted with dichloromethane and analyzed by GC-MS. THM (Trihalomethanes), HAN (Haloacetonitriles), HAA (Haloacetic acids), HNM (halonitromethanes), SM (Standard Methods), EPA (Environmental Protection Agency), GC (Gas Chromatography), MS (Mass Spectrometer), FAC (Free Available Chlorine), NA (Not Applicable).

## Results and Discussion

### Water Characteristics of the Selected Indoor Swimming Pools (n=23)

All of the indoor swimming pools selected in this study used chlorine as disinfectant. Some of the sampled pools used calcium hypochlorite directly, whereas others generated chlorine in situ electrochemically using sodium chloride. Most of the pools were operated at an approximate temperature of 26°C and some at 34°C. Except for a single pool that used groundwater from a local well, all the pools used the local water distribution system for both fill and make-up water. Of the 23 pools under study, sand-filter filtration was used to treat water, and micro-filter filtration used for the other two. The water samples characteristics of all pools under study are shown in Table 2. The FAC in the pools was between <0.1 and 4.0 mg/L, and the pH, TOC and TN ranged between 7.2 to 7.8, 3 to 23.6 mg/L, and 0.8 to 12.3 mg/L, respectively. The TOC was higher than TN except for four of the swimming pools in this study.

### Occurrence of DBPs in Indoor Swimming Pools (n=23)

The occurrence ranges of the five classes of DBPs in the selected twenty three indoor pools are shown in Figure 1. The concentration of each DBP class, along with their speciation for each swimming pool is summarized in Table 3 and Table 4. In general, carbonaceous DBPs concentrations were higher than nitrogenous DBPs. In this survey, the HAAs were the highest measured class of DBPs, followed by the THMs>HANS>HNMs>nitrosamines. The median, maximum, and minimum HAAs were 960, 9005, and 172 µg/L, respectively. Trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA) were the dominant species among the measured HAAs. Bromochloroacetic acid (BCAA) and bromodichloroacetic acid (BDCAA) were also detected in all samples although at much lower levels compared to DCAA and TCAA. In some of the samples dibromoacetic acid (DBAA) and bromoacetic acid (BAA) were detected at concentrations <6 and <25 µg/L, respectively. These exceptionally (compared to drinking water samples) high values of HAAs are attributed to (i) nonvolatile and soluble nature of these compounds resulting in accumulate in the pool waters provided that pool water dilution is not common in U.S., and (ii).human body fluids that have been shown to have a high formation potential of HAAs (7, 9).

The median, maximum, and minimum THMs measured in the pools were 63, 213 and 26 µg/L, respectively, with chloroform the major THM determined in all pools. Although the brominated THM species were at low levels in most cases, there were relatively high in pools that use sodium chloride to generate chlorine electrochemically and in the pool that was filled with groundwater. In 43% of the pools, the total THMs was equal to or higher than 80 µg/L (MCL in U.S. drinking water), while in all the pools, the measured THM was greater than 20 µg/L (the maximum allowed in some European countries for swimming pools).

**Table 2. Water Characteristics of the Selected Indoor Swimming Pools**

<i>Swimming Pool Code</i>	<i>Temperature (°C)</i>	<i>pH</i>	<i>FAC (mg-/L)</i>	<i>Disinfectant</i>	<i>Filter Type</i>	<i>TOC (mg C/L)</i>	<i>TN (mg N/L)</i>
S1	27	7.5	3.0	Cl <sub>2</sub>	Sand	4.3	1.4
S2C	18	7.4	3.0	Cl <sub>2</sub>	Sand	4.1	1.8
S2W	31	7.4	3.0	Cl <sub>2</sub>	Sand	11.3	4.7
S3S	29	7.4	1.4	Cl <sub>2</sub>	Microfilter	10.3	4.5
S3D	28	7.3	3.1	Cl <sub>2</sub>	Microfilter	5.5	2.8
S4C	27	7.4	4.0	Cl <sub>2</sub> *	Sand	7.1	9.1
S4W	30	7.4	3.0	Cl <sub>2</sub> *	Sand	6.5	3.2
S5	27	7.4	2.0	Cl <sub>2</sub>	Sand	3.0	1.2
S6L	29	7.6	2.0	Cl <sub>2</sub> *	Sand	7.9	4.8
S6T	34	7.4	3.0	Cl <sub>2</sub> *	Sand	7.7	2.5
S7	27	7.2	1.0	Cl <sub>2</sub>	Sand	7.8	4.3
S10	31	7.4	3.0	Cl <sub>2</sub>	Sand	8.4	5.2
S11L	28	7.2	2.0	Cl <sub>2</sub>	Sand	5.2	3.4
S11D	30	7.2	3.0	Cl <sub>2</sub>	Sand	5.3	3.6
S12L	27	7.5	2.7	Cl <sub>2</sub>	Sand	3.7	10.2
S12I	30	7.5	2.4	Cl <sub>2</sub>	Sand	4.3	7.4
S13	29	7.6	1.0	Cl <sub>2</sub>	Sand	3.9	1.2
S14	27	7.8	3.0	Cl <sub>2</sub>	Sand	13.8	12.3
S15L	27	7.7	2.8	Cl <sub>2</sub> *	Sand	3.8	0.8
S15T	32	7.8	1.2	Cl <sub>2</sub> *	Sand	7.5	1.2
S16	27	7.2	<0.1	Cl <sub>2</sub>	Sand	7.5	2.2
S17L	28	7.6	3.5	Cl <sub>2</sub> *	Sand	7.3	4.1
S17T	33	7.4	3.5	Cl <sub>2</sub> *	Sand	23.6	4.4
<b>Median</b>	28	7.4	3.0			7.1	3.6
<b>Maximum</b>	34	7.8	4.0			23.6	12.3
<b>Minimum</b>	18	7.2	<0.0			3.0	0.8

\* Electrochemically generated chlorine. FAC (free available chlorine), TOC (total organic carbon), TN (total nitrogen).

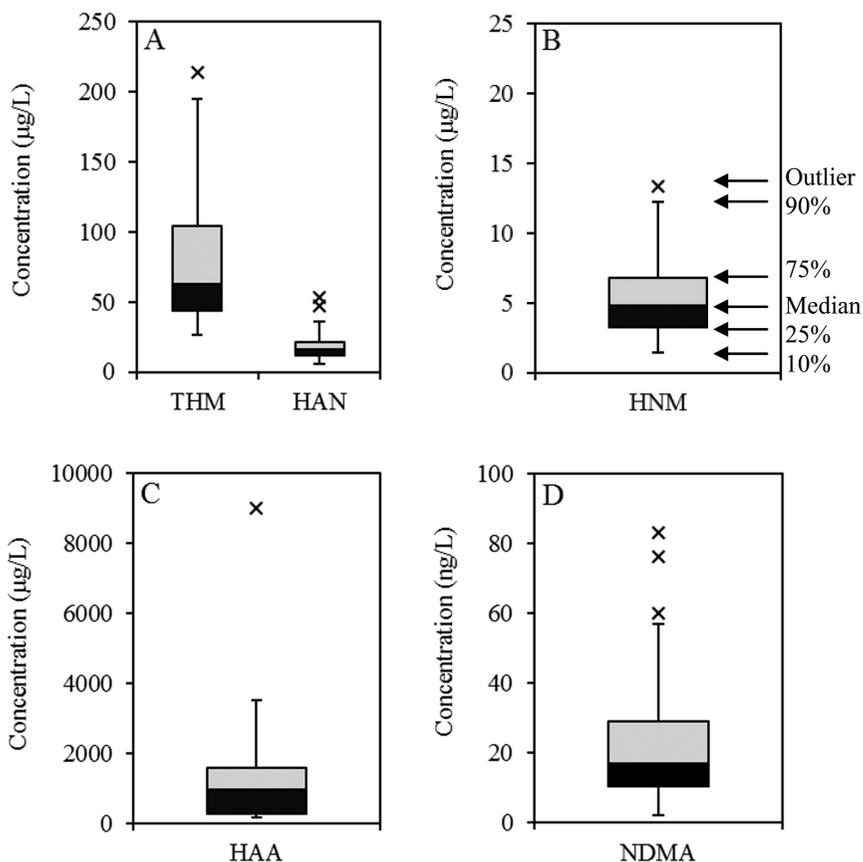


Figure 1. Box and Whisker plots of the occurrence of (A) THMs & HANs, (B) HNMs, (C) HAAs, and (D) NDMA in indoor swimming pools ( $n=23$ ).

The median, maximum and minimum HANs were 16, 53, and 5  $\mu\text{g/L}$ , respectively. The major haloacetonitrile quantified was dichloroacetonitrile (DCAN) among the six measured HANs. In few pools, brominated acetonitriles were detected at low levels (1-3  $\mu\text{g/L}$ ) except in the pool which was filled with groundwater. In general, it was observed that the pool waters with high levels of HAAs had high levels of HANs. Furthermore, when brominated

HAA species were high, the brominated HANs species also increased. Since HANs hydrolyze to HAAs, it is expected to have a positive correlation between these two classes of DBPs (25). Among the nine HNM species, only three HNM species [trichloronitromethane (TCNM), bromonitromethane (BNM), and bromochloronitromethane (BCNM)] were detected in the collected swimming pool samples. Total HNMs were between 1.4 and 13.3  $\mu\text{g/L}$ .

Among the nitrosamines analyzable using the current method (22), NDMA was the only species detected in the selected 23 indoor swimming pool water samples, with NDMA concentrations ranging between 2 and 83  $\text{ng/L}$  with a median of 17  $\text{ng/L}$ . These levels of NDMA are somewhat higher than the drinking water levels, which was consistent with the literature (6), and also indicating that some NDMA precursors are released with body fluids and excretions. Nitrosamines are mainly formed during chloramination of amines (26). Although swimming pools are mostly chlorinated, the ammonia coming from urea would inevitably lead to the formation of chloramines in the pools. Therefore, it is not surprising to see some NDMA formation in swimming pools. Furthermore, there was no correlation between NDMA and the other classes of DBPs, which clearly indicates that their precursors differ from carbonaceous DBPs precursors, a finding consistent with the literature (27, 28). Although the nitrogenous DBPs (HANs, HNMs, NDMA) were detected at lower levels than carbonaceous DBPs, they were still significant regarding their cyto- and geno-toxicity (29).

### **DBPs Measured in the Selected Indoor Pools (n=3) for 9-Months**

Three indoor swimming pools were further monitored for a 9-month sampling period. The operational conditions, water quality and DBPs occurrences in these pools are summarized in Table 5. The average FAC fell within the range of 3  $\text{mg/L}$ , which is well within the state guidelines in place regarding adequate pool chlorination. Although the TN varied over a narrower range, between 2.0 and 5.0  $\text{mg/L}$  in the three pools under study, the temperature and pH remained relatively constant and the TOC fell within a wide range of 5.3 to 25.4  $\text{mg/L}$ .

During the nine-month monitoring period for these three pools, a narrow variation in the DBPs occurrence was observed in each (Table 5). The THM concentrations in all of them ranged from 29 to 259  $\mu\text{g/L}$  with an average of 108  $\mu\text{g/L}$ . The highest THMs measured were in the warmest pool (S17T), which also had the highest TOC measurements. Of the THM levels measured in the three pools, chloroform was the most predominant (data not shown). The authors also found higher levels of measured BDCM in pools S17L and S17T because sodium chloride was used in both to generate chlorine electrochemically. The range of the BDCM in these three pools was 0 to 29  $\mu\text{g/L}$ . The HAAs in all three pools was also higher than the THMs, which fell within a range between 667 to 11695  $\mu\text{g/L}$ , with an average of 2820  $\mu\text{g/L}$  DCAA. The TCAA were the dominant species, and BDCAA was the major brominated HAA species. The maximum amount of BDCAA was 151  $\mu\text{g/L}$  and the minimum was 9  $\mu\text{g/L}$  with an average of 57  $\mu\text{g/L}$ . The levels of all of the dibrominated species were much lower ( $<20$   $\mu\text{g/L}$ ), however.

**Table 3. Carbonaceous-DBPs Occurrence in Indoor Swimming Pools Water (n=23)**

<i>Swimming Pool Code</i>	<i>Trihalomethanes (µg/L)</i>					<i>Halocetic Acids (µg/L)</i>							
	<i>TCM</i>	<i>BDCM</i>	<i>DBCM</i>	<i>TBM</i>	<i>Total</i>	<i>BAA</i>	<i>DCAA</i>	<i>BCAA</i>	<i>TCAA</i>	<i>DBAA</i>	<i>BDCAA</i>	<i>DBCAA</i>	<i>Total</i>
<b>S1</b>	41	1	<MRL	ND	42	<MRL	100	1	87	<MRL	8	1	198
<b>S2C</b>	49	1	<MRL	ND	51	<MRL	314	3	224	<MRL	13	1	555
<b>S2W</b>	119	3	<MRL	ND	122	1	896	14	718	<MRL	36	<MRL	1665
<b>S3S</b>	77	2	<MRL	ND	80	<MRL	712	5	1537	<MRL	21	<MRL	2276
<b>S3D</b>	62	1	<MRL	ND	63	<MRL	937	7	776	<MRL	16	1	1738
<b>S4C</b>	37	1	<MRL	ND	38	<MRL	688	10	789	1	27	3	1518
<b>S4W</b>	49	3	<MRL	ND	53	1	81	4	241	<MRL	60	5	392
<b>S5</b>	26	1	<MRL	ND	28	<MRL	82	3	141	<MRL	22	2	251
<b>S6L</b>	72	3	<MRL	ND	76	1	928	30	552	2	48	3	1563
<b>S6T</b>	72	12	4	1	90	1	1033	36	351	4	36	7	1468
<b>S7</b>	113	1	<MRL	ND	114	<MRL	1139	5	418	<MRL	22	<MRL	1585
<b>S10</b>	89	2	<MRL	ND	91	<MRL	1297	4	416	<MRL	13	<MRL	1731
<b>S11L</b>	29	2	<MRL	ND	31	<MRL	123	2	76	<MRL	15	<MRL	216
<b>S11D</b>	111	2	<MRL	ND	113	<MRL	360	3	149	<MRL	11	<MRL	523
<b>S12L</b>	25	1	<MRL	ND	26	<MRL	162	1	95	<MRL	8	3	269
<b>S12I</b>	32	1	<MRL	ND	34	<MRL	242	2	216	<MRL	22	2	484
<b>S13</b>	74	28	10	1	114	1	73	13	100	2	55	15	260

<i>Swimming Pool Code</i>	<i>Trihalomethanes (µg/L)</i>					<i>Haloacetic Acids (µg/L)</i>							
	<i>TCM</i>	<i>BDCM</i>	<i>DBCM</i>	<i>TBM</i>	<i>Total</i>	<i>BAA</i>	<i>DCAA</i>	<i>BCAA</i>	<i>TCAA</i>	<i>DBAA</i>	<i>BDCAA</i>	<i>DBCAA</i>	<i>Total</i>
<b>S14</b>	47	3	<MRL	ND	50	<MRL	52	2	92	<MRL	25	2	172
<b>S15L</b>	38	6	1	ND	45	2	115	21	102	5	47	14	306
<b>S15T</b>	121	5	1	ND	127	2	690	31	183	6	45	2	960
<b>S16</b>	61	2	<MRL	ND	63	<MRL	549	5	568	<MRL	20	1	1143
<b>S17L</b>	82	11	2	ND	95	5	504	106	288	25	110	32	1070
<b>S17T</b>	207	6	<MRL	ND	213	4	6787	176	1925	16	93	4	9005
<b>Median</b>					63								960
<b>Maximum</b>					213								9005
<b>Minimum</b>					26								172

TCM (Trichloromethane), BDCM (bromodichloromethane), DBCM (dibromochloromethane), TBM (tribromomethane), CAA (chloroacetic acid), BAA (bromoacetic acid), DCAA (dichloroacetic acid), BCAA (bromochloroacetic acid), TCAA (trichloroacetic acid), DBAA (dibromoacetic acid), DBCAA (dibromoacetic acid), TBAA (tribromoacetic acid), MRL (Minimum Reporting Level), ND (Not Detected).

**Table 4. Nitrogenous-DBPs occurrence in indoor swimming pools water (n=23).**

<i>Swimming Pool Code</i>	<i>Haloacetonitriles (µg/L)</i>							<i>Halonitromethanes (µg/L)</i>				<i>Nitrosamines (ng/L)</i>
	<i>CAN</i>	<i>TCAN</i>	<i>DCAN</i>	<i>BAN</i>	<i>BCAN</i>	<i>DBAN</i>	<i>Total</i>	<i>TCNM</i>	<i>BNM</i>	<i>BCNM</i>	<i>Total</i>	<i>NDMA</i>
<b>S1</b>	1	ND	8	ND	ND	ND	9	<MRL	<MRL	2.4	2.9	30
<b>S2C</b>	ND	ND	4	ND	ND	ND	5	0.8	<MRL	7.5	8.3	9
<b>S2W</b>	1	ND	22	ND	1	ND	25	<MRL	<MRL	1.3	1.9	83
<b>S3S</b>	1	ND	27	ND	1	ND	30	0.7	<MRL	6.3	7.0	28
<b>S3D</b>	1	ND	7	ND	ND	ND	8	0.9	<MRL	3.9	4.8	14
<b>S4C</b>	1	ND	15	ND	1	ND	16	<MRL	<MRL	2.5	3.0	16
<b>S4W</b>	1	ND	21	ND	2	ND	24	<MRL	<MRL	1.1	1.7	18
<b>S5</b>	1	ND	14	ND	1	ND	15	<MRL	<MRL	3.2	3.7	28
<b>S6L</b>	1	ND	12	ND	1	ND	15	0.8	<MRL	2.6	3.6	9
<b>S6T</b>	1	ND	13	ND	4	2	21	<MRL	2.2	3.8	6.5	60
<b>S7</b>	1	ND	14	ND	ND	ND	15	2	<MRL	3.4	5.4	9
<b>S10</b>	2	ND	16	ND	ND	1	18	2.3	<MRL	11	13.3	3
<b>S11L</b>	1	ND	11	ND	ND	ND	13	<MRL	<MRL	3.6	4.1	12
<b>S11D</b>	1	ND	7	ND	ND	1	9	0.9	<MRL	4.6	5.5	17
<b>S12L</b>	1	ND	15	ND	ND	ND	16	1	<MRL	4.3	5.4	2
<b>S12I</b>	1	ND	17	ND	ND	ND	18	1.1	<MRL	5.5	6.6	6
<b>S13</b>	1	ND	27	1	13	5	47	<MRL	2.0	4.7	7.3	13

<i>Swimming Pool Code</i>	<i>Haloacetonitriles (µg/L)</i>							<i>Halonitromethanes (µg/L)</i>				<i>Nitrosamines (ng/L)</i>
	<i>CAN</i>	<i>TCAN</i>	<i>DCAN</i>	<i>BAN</i>	<i>BCAN</i>	<i>DBAN</i>	<i>Total</i>	<i>TCNM</i>	<i>BNM</i>	<i>BCNM</i>	<i>Total</i>	<i>NDMA</i>
<b>S14</b>	1	ND	13	ND	1	ND	15	0.9	<MRL	3.7	4.7	18
<b>S15L</b>	1	ND	7	ND	2	1	11	<MRL	0.7	1.5	2.7	15
<b>S15T</b>	1	ND	4	ND	ND	ND	6	<MRL	<MRL	0.8	1.4	76
<b>S16</b>	1	ND	15	ND	ND	ND	16	0.8	<MRL	2.6	3.4	53
<b>S17L</b>	1	ND	16	1	3	1	22	0.7	1.6	5.8	8.1	17
<b>S17T</b>	3	1	47	ND	2	ND	53	1.4	1	6.8	9.2	42
<b>Median</b>							16				4.8	17
<b>Maximum</b>							53				13.3	83
<b>Minimum</b>							5				1.4	2

CAN (chloroacetonitrile), TCAN (trichloroacetonitrile), DCAN (dichloroacetonitrile), BAN (bromoacetonitrile), BCAN (bromochloroacetonitrile), DBAN (dibromoacetonitrile), TCNM (trichloronitromethane), BNM (bromonitromethane), BCNM (bromochloronitromethane), NDMA (*N*-nitrosodimethylamine), MRL (Minimum Reporting Level), ND (Not Detected).

**Table 5. Characteristics of the Three Selected Indoor Swimming Pools Waters Monitored for 9-Months**

<i>Swimming Pool/ Sampling date</i>	<i>TOC mg/L</i>	<i>TN mg/L</i>	<i>FAC mg/L</i>	<i>Temp. °C</i>	<i>pH</i>	<i>THMs µg/L</i>	<i>HAAs µg/L</i>	
<b>S16</b>	22/05/2009	5.6	2.1	2.6	28	7.8	60	2039
	24/05/2009	5.6	2.1	3.9	28	7.3	52	1648
	30/05/2009	6.2	2.1	4.6	28	6.7	53	1725
	02/06/2009	6.4	2.1	3.2	28	7.0	56	1691
	06/06/2009	6.3	2.1	0.7	26	7.0	48	1708
	09/06/2009	6.6	2.1	2.1	27	7.6	40	1674
	18/10/2009	5.3	2.0	2.3	28	7.5	81	1804
	25/10/2009	5.5	2.0	0.6	27	7.5	38	1673
	22/12/2009	NM	NM	NM	NM	NM	NM	NM
	10/01/2010	6.9	2.4	1.6	27	7.7	29	1479
	17/01/2010	7.3	2.4	2.9	27	7.6	54	1005
	17/02/2010	7.5	2.2	0.1	27	7.2	63	1143

<i>Swimming Pool/ Sampling date</i>	<i>TOC mg/L</i>	<i>TN mg/L</i>	<i>FAC mg/L</i>	<i>Temp. °C</i>	<i>pH</i>	<i>THMs µg/L</i>	<i>HAAs µg/L</i>
S17L 22/05/2009	6.8	3.4	3	28	7.6	92	NM
24/05/2009	6.1	3.4	3.5	28	7.6	91	1437
30/05/2009	6.5	3.5	3	28	7.6	83	1392
02/06/2009	7.0	3.5	1.5	28	7.6	77	1377
06/06/2009	7.4	3.6	4	28	7.6	77	1434
09/06/2009	7.2	3.6	3	28	7.6	84	1470
18/10/2009	6.6	4.3	3.5	27	7.2	79	1174
25/10/2009	6.6	4.2	3	28	7.2	79	1196
22/12/2009	5.8	4.2	3	27	7.6	64	955
10/01/2010	6.3	4.3	4.5	26	7.5	72	793
17/01/2010	6.4	4.4	3.5	29	7.6	91	667
17/02/2010	7.3	4.1	3	27	7.6	95	1070

*Continued on next page.*

**Table 5. (Continued). Characteristics of the Three Selected Indoor Swimming Pools Waters Monitored for 9-Months**

<i>Swimming Pool/ Sampling date</i>	<i>TOC mg/L</i>	<i>TN mg/L</i>	<i>FAC mg/L</i>	<i>Temp. °C</i>	<i>pH</i>	<i>THMs µg/L</i>	<i>HAAs µg/L</i>	
S17T	22/05/2009	14.5	2.1	3	33	7.6	163	NM
	24/05/2009	14.8	2.2	2	33	7.6	161	2244
	30/05/2009	15.5	2.3	4	33	7.6	199	2397
	02/06/2009	16.5	2.1	3	33	7.6	192	2427
	06/06/2009	16.9	2.3	4	33	7.6	137	2869
	09/06/2009	16.9	2.2	2	33	7.6	160	2884
	18/10/2009	21.7	3.1	3.5	34	7.8	259	9691
	25/10/2009	20.9	3.2	6	33	7.2	249	9348
	22/12/2009	22.3	4.7	3.5	34	7.6	176	11695
	10/01/2010	25.2	5.0	3	34	7.6	182	7392
	17/01/2010	25.4	5.0	3.5	32	7.4	188	6291
17/02/2010	23.6	4.4	3	33	7.5	213	9005	

FAC (free available chlorine), TOC (total organic carbon), TN (total nitrogen), THM (Trihalomethanes), HAA (Haloacetic acids), NM (Not measured).

## The Effects of Swimming Pool Operational Conditions on DBPs

The swimming pool operational parameters that affect both the THM and HAA formation is presented in Figure 2. An overall comparison of the results between the filling background waters (MB and SJWD) showed that formation of THMs and HAAs was approximately 10% higher in BFA-MB than in BFA-SJWD water. Although both synthetic pool waters had the same TOC concentration (1 mg/L from the filling water and 5 mg TOC from BFA), there was a slightly higher rate of THM and HAA formation in the MB than in the SJWD water, which was due to the aromatic nature of the MB source water. Specifically, the MB water exhibited a somewhat higher SUVA<sub>254</sub> (~2.0 L/mg-m) compared to the SJWD water (~1.7 L/mg-m), indicating it's slightly higher aromatic character over SJWD. An analysis of each parameter, except the filling waters is provided below.

### *Effect of FAC*

FAC levels 1, 3, and 5 mg/L were tested in this study. It was determined that an increase in FAC concentrations resulted in a slight increase in THM formation: 5% for BFA-MB and 14% for BFA-SJWD (Figure 2). There was, however, a distinct increase in HAA formation observed, which was caused when the chlorine dose was increased from 1 mg/L to 5 mg/L. Specifically, the HAA formation increased 25% and 27%, respectively for the BFA-MB and BFA-SJWD (Figure 2).

This dependence was attributed to the reaction(s) of chlorine with albumin in BFA. An increase in dosage in turn increased the rate of albumin decomposition (hydrolysis), which in turn generated more HAA precursors (free amino acids). The lesser effect of the chlorine concentrations on the THM than HAA was due to the effect of the chlorine dose on the formation of different DBPs. After satisfying the demand, a linear relationship has been previously established between the demand for chlorine demand and THM formation (30), and a weak correlation between the chlorine levels and chloroform formation (31). Consistent with these observations, the results indicate that once the chlorine demand was satisfied, there was no effect of the chlorine dose on the THM formation.

### *Effect of Temperature*

To examine the effect of temperature on DBP formation, the two synthetic swimming pool waters were also chlorinated at 40°C, the highest possible temperature allowable in therapeutic swimming pools, hot tubs, and whirlpool spas. Although this increase in temperature from 26°C to 40°C nearly doubled the formation of THMs in synthetic pool waters, there was only a 60% increase in HAA formation (Figure 2). These results clear indicate that exposure to DBPs in hot tubs or any other type of elevated temperature indoor swimming pools will

be higher. The increase in DBP formation with temperature can be explained by reaction of un-reacted DBPs precursors with chlorine and increase in the reactivity of chlorine with precursors (35, 36).

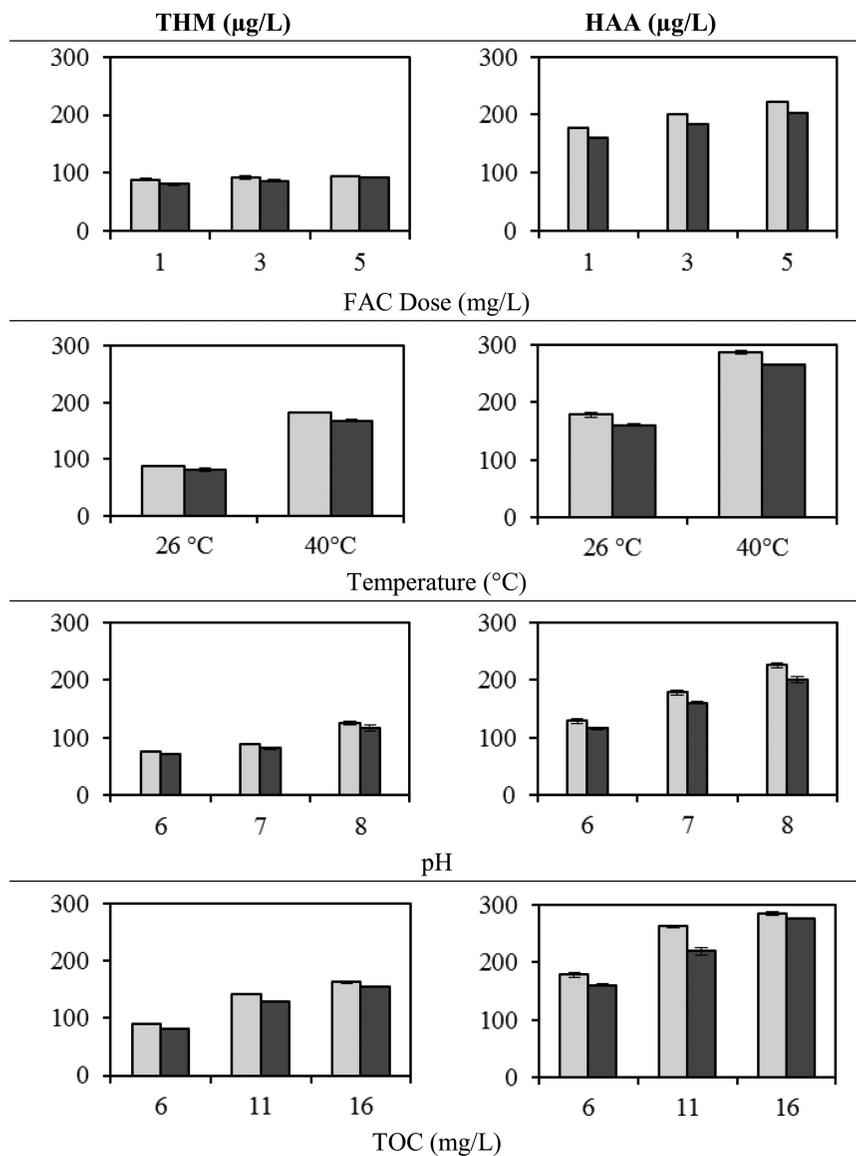


Figure 2. The effect of operational parameters on DBPs formation in swimming pools waters. □ BFA-MB, ■ BFA-SJWD

### *Effect of pH*

The results show that the formation of THMs and HAAs increased with an increase in pH (Figure 2). It is also known that THM formation increases with an increase in pH, while the trend is the opposite for HAA formation (32). However, in this study, an increase in pH resulted in both an increase in both THM and HAA formation. The opposite behavior that was observed for pH dependence of HAAs in synthetic swimming water solution was once again attributed to the hydrolysis of albumin, one of the main components of the BFA, and its reactivity with chlorine. The observed pH trends for HAAs also indicated that the filling water NOM was not a major contributor to HAA formation in synthetic pool waters because in drinking waters, the HAA concentration decreased with an increase in pH, as mentioned above. Finally, the results clearly indicate that the reduction of pH from 8.0 to 6.0 would result in a decrease in both THM and HAA formation by 40-60%. This decrease in pH would also result in a corresponding decrease in the disinfection efficiency of chlorine, particularly below the  $pK_a$  of chlorine where HOCl is a more effective disinfectant agent than  $OCl^-$  (33, 34).

### *Effect of Bather Load*

Although TOC cannot be controlled directly by the facility, there is a correlation to the number of bathers and their BFs in a swimming pool. Thus, pool managers can control the TOC level by controlling the number of bathers using the pool at a given time. As predicted, the formation of both THMs and HAAs increased with an increase in the concentration of BFAs. This dependence on TOC concentration confirms a substantial correlation between the DBPs formation in swimming pools with the population of swimmers (the main TOC source).

### *Effect of Bromide*

Bromide was spiked at three levels in addition to the ambient fill waters concentration. The change in THMs and HAAs speciation with the increasing bromide concentrations is shown in Figure 3. This increase in bromide concentrations yielded a corresponding increase in both THM and HAA concentration, which was expected since the brominated species increased while the chlorinated species decreased. However, bromide caused a greater increase in THM than HAA formation. The overall mass of THM concentration increased by 65-72%, 106-116%, and 162-167% in synthetic pool waters at 100, 300, and 600  $\mu\text{g/L}$  bromide concentrations, respectively compared to the ambient fill waters THM formation. However, during these same experiments the increase in HAA concentration was only within a fairly limited range of 22 and 39%. Bromine incorporation factor (BIF) “n” is the molar amount of bromine in the

halogenated compound (THM or HAA) divided by the molar total of that halogen (37). That is to say when  $n = 0$  only chlorinated compounds form whereas when  $n > 0$  brominated species begin to appear. Subsequent BIF analysis determined that the presence of bromide increased the formation of brominated THM over HAA formation (data not shown).

Specifically, the incorporation factor a synthetic swimming water sample for a bromide level of 600  $\mu\text{g/L}$  was 1.3 for THMs but only 0.8 for HAAs. This difference in bromide incorporation is also consistent with higher bromine incorporation of THMs than HAAs in sample testing (38). These results clearly demonstrate that the use of water with low bromide levels to either fill swimming pools and as make up water is critical to reduce DBP formation, especially THMs. Thus, bromide impurities should be minimized, if possible, when generating chlorine from sodium chloride. Furthermore, the use of seawater or saline water as either make-up or filling water should be avoided to reduce the DBPs formation in swimming pools.

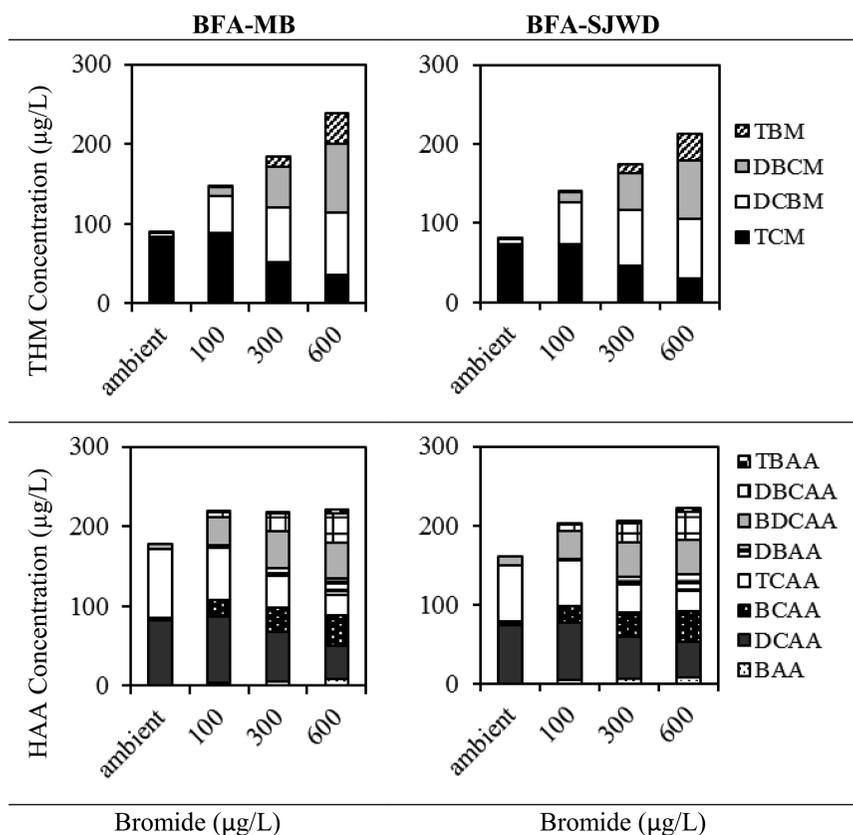


Figure 3. The effect of bromide on the formation and speciation of THMs and HAAs during chlorination of BFA-MB and BFA-SJWD synthetic pool water.

## DBPs Formation as Function of Time

DBP formation as function of time are presented in Figure 4 for three synthetic pool waters: (i) a pool water at 6 mg-C/L (5 mg-C/L from BFA and 1 mg-C/L from MB as the background filling water), (ii) 5 mg-C/L BFA, and (iii) 1 mg-C/L BFA. The last two samples were used to investigate the formation kinetics from BFAs alone and the formation kinetics at two  $\text{Cl}_2/\text{TOC}$  ratios. Results indicate that THM formation (within a range of 53% to 68%) occurred during the first five hours of a five-day formation cycle in the absence and the presence of bromide for synthetic pool water (BFA-MB) and BFA (Figure 4).

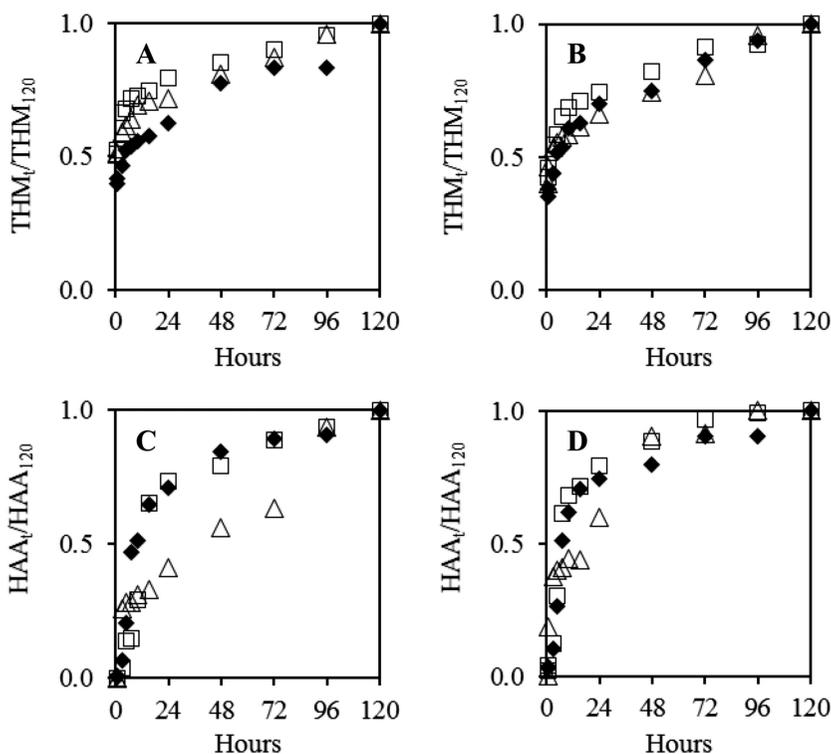


Figure 4. THM formation fraction during five days (A) without bromide and (B) with bromide (200  $\mu\text{g/L}$ ), HAA formation fraction during five days (C) without bromide and (D) with bromide (200  $\mu\text{g/L}$ ).  $\text{THM}_t$  (THM formed at time  $t$ ),  $\text{THM}_{120}$  (THM formed at 120 hours),  $\text{HAA}_t$  (HAA formed at time  $t$ ),  $\text{HAA}_{120}$  (HAA formed at 120 hours).  $\blacklozenge$  BFA-MB (5+1 mg-C/L),  $\square$  BFA (5 mg-C/L),  $\blacktriangle$  BFA (1 mg-C/L)

This is a faster rate of THMs production at early contact times compared to previous studies using several chlorination scenarios, which produced only 15-30% of THMs after at least five hours after treatment (17, 18). Although the fast

formation of THMs observed in this study indicates that a significant portion of THMs formed in the pool prior to treatment, only 15% to 30% of the five-day HAA formation occurred during the first 5 hours under the same experimental conditions (Figure 4). This rate was lower as compared to the formation rate of THMs. The slower rate of HAA formation indicates that there is more opportunity to remove their precursors through swimming pool water treatment processes during pool water turnover.

Two BFA solutions at 1 and 5 mg TOC/L showed similar THM formation patterns indicating very little effect of the  $\text{Cl}_2/\text{TOC}$  ratio (100 vs. 20) on the THM formation rate (Figure 4). Thus, the formation rates observed in this study are representative of THM formation in swimming pools. There was, however, some difference between the trends of the BFA solutions at 1 and 5 mg-C/L, indicating that the decrease in  $\text{Cl}_2/\text{TOC}$  ratio from 100 to 20 increased the HAA formation rate. This difference was attributed to the changes in the formation rates of di-halogenated HAAs vs. tri-halogenated HAAs (data not shown). Since there is always a high FAC concentration in the pool water, the HAA formation rates in swimming pools are likely to be rapid for HAAs. This is especially true for swimming pools in the U.S. where the dilution of pool water with the filling water is not regularly practiced and the pool water is not replaced for long time. Therefore, chlorine demand of filling water is exhausted at the very early period of operation after filling the pool. Afterwards, the BF components serve as the primary catalyst for THM and HAA formation.

The presence of NOM (i.e., BFA-MB synthetic pool water) (BFA = 5 mg-C/L) reduced the formation rate of THMs by ~20% during the first 24 hours as compared to the absence of NOM. This behavior is due to the higher reactivity of NOM compared to BFA with chlorine to form THM but which occurs at a slower rate, as compared to BFA. Concurrently, the presence of NOM (i.e., BFA-MB) did not affect the formation rate of HAAs, indicating that while the filling water NOM can affect the THM formation, the formation rate of HAAs remains constant.

There were small differences in the formation rates under ambient bromide levels for both THMs and HAAs. In the presence of bromide, the difference in the formation rates of both DBPs diminished. Since halogenation reactions are faster with bromide than chloride (39–41), higher formation rates observed in this study is attributed to the formation of brominated DBP species from NOM at high bromide levels.

The overall formation rate of THMs was higher than that of HAAs in swimming pools Figure 5. THMs were formed almost instantaneously when chlorine reacted with BFs, whereas HAA formation occurred at a slower rate. Practically, these results indicate that within the typical turnover time of swimming pools most HAA precursors can be removed by the treatment system whereas THM precursors cannot. Thus, precursors control (i.e., the release of human BFs) will be critical in reducing the formation of THMs in swimming pools. The precursor control requires improving the practices and behavior of swimmers, and implementing more strict hygienic conditions by swimming pools utilities. Better hygienic conditions include showering immediately before swimming and not releasing urine intentionally during swimming.

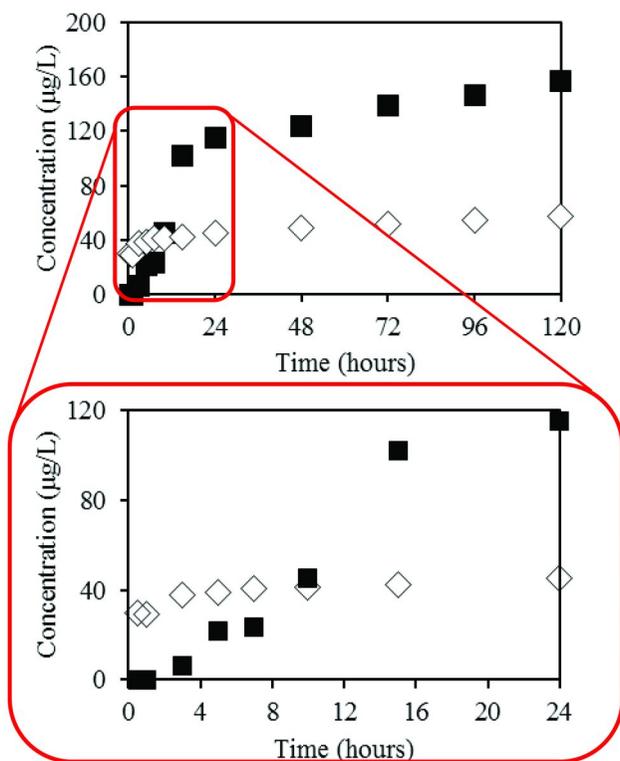


Figure 5.  $\diamond$  THMs and  $\blacksquare$  HAAs formation during 5-day reaction from BFA.

## Conclusions

The DBPs in the 23 swimming pools that were the subject of this study were far higher than the drinking water regulation values in the U.S., with THM levels ranging between 26 and 213  $\mu\text{g/L}$  with an average of 80  $\mu\text{g/L}$ . The HAAs ranged between 173 and 9005  $\mu\text{g/L}$  with an average of 1541  $\mu\text{g/L}$ . HNMs ranged between 1.4 and 13.3  $\mu\text{g/L}$  with an average of 5.4  $\mu\text{g/L}$ . HANs ranged between 5 and 53  $\mu\text{g/L}$  with an average of 19  $\mu\text{g/L}$ . The NDMA ranged between 2 and 83  $\text{ng/L}$  with an average of 26.5  $\text{ng/L}$ . The electrochemically generation of chlorine increased the brominated species of halogenated DBPs (THMs, HAAs, HNMs, HANs). Furthermore, during the sampling period for nine months, the water quality (TOC, TN, pH, FAC) and DBPs concentrations (THMs, HAAs) in the swimming pools remained relatively constant. However, some fluctuation was observed likely due to time of the year and the specific pool events/activities on the time of sampling.

The formation and speciation of THMs and HAAs were also investigated under various disinfection and operation conditions typically used in U.S. swimming pools. Although the increases in free available chlorine, pH, TOC, water temperature, and bromide levels in the water increased overall DBP formation, these factors affected the different classes of DBPs at different

magnitudes. Higher levels of free available chlorine increased the HAA levels more than the THMs. The temperature effect was greater on the formation of THMs than for HAAs whereas contact time increased HAAs more than THMs. The authors also determined that under swimming pool related conditions, DPB formation was quite rapid, with an appreciable percentage of the increase occurring in the first 3-6 hours, which is the typical turnover time for the pool water. Moreover, THM formation was faster than HAA formation, with 53 to 68% of five-day THMs formed within the first 3-6 hours and 15 to 30% of five-day HAAs formed during the first six hours. Although it is possible to reduce DBP formation by the controlling operational parameters (pH, free available chlorine, bather load, the number of swimmers in a pool in a 24 hour period- or dilution), these fast formation rates imply that DBP control strategies in swimming pools should mainly focus on control the DBP precursors at the source (i.e., swimmers).

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