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RESEARCH ARTICLE

Predicting bromide incorporation in a chlorinated indoor swimming pool

Shakhawat Chowdhury¹ · Abu Jafar Mazumder² · Tahir Husain³

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Abstract The water in and air above swimming pools often contain high levels of disinfection byproducts (DBPs) due to chemical reactions between chlorine- or bromine-based disinfectants and organic/inorganic matter in the source water and released from swimmers. Exposure to these DBPs, though inevitable, can pose health threats to humans. In this study, DBPs in tap water (S1), and water from a chlorinated indoor swimming pool before (S2) and after swimming (S3) were measured. The brominated species constituted the majority of DBPs formed in S1, S2, and S3. Trihalomethanes (THMs) in S3 was 6.9 (range 2.9–11.1) and 1.4 (range 0.52–2.9) times those in S1 and S2, respectively; and the haloacetic acids (HAAs) in S3 was 4.2 (range 2.5–7.5) and 1.2 (range 0.6–2.6) times those in S1 and S2, respectively. The mean THMs in air above the swimming pool before (S2-A) and after swimming (S3-A) were 72.2 and 93.0 $\mu\text{g}/\text{m}^3$, respectively, and their ranges were 36.3–105.8 and 44.1–133.6 $\mu\text{g}/\text{m}^3$, respectively. The average percentages of bromide incorporation (BI) into THMs in S1, S2, and S3 were 3.0, 9.3, and 10.6 %, respectively; and the BI into HAAs in S1, S2, and S3 were 6.6, 12.0, and 12.2 %, respectively. Several models were trained

for predicting the BI into THMs and HAAs. The results indicate that additional information is required to develop predictive models for BI in swimming pools.

Keywords Chlorinated swimming pool · Disinfection byproducts · Human exposure · Continuous disinfection · Constant organic loading · Bromide incorporation

Introduction

Swimming pools are disinfected to prevent microbial contamination. The unintended reactions between disinfectants (e.g., chlorine, chloramines (CAs), ozone, or chlorine dioxide) and natural organic matter (NOM), human inputs (e.g., sweat, urine, and skin) and bromide/iodide can form disinfection byproducts (DBPs) (Weisel et al. 2009; Pan and Zhang 2013; Cimetiere and De Laat 2014). The types and concentrations of DBPs depend on several factors, such as the type and amount of disinfectant used, characteristics of the swimming pool, pool water, and users' hygiene (Zwiener et al. 2007; Hansen et al. 2012, 2016). In swimming pools, chlorine-containing compounds are the most commonly used disinfectant (Ford 2007; Chowdhury et al. 2014). Swimming pool water generally has a higher temperature, which leads to higher rates of chlorine decay. To compensate for chlorine demand, swimming pools use relatively high doses of chlorine to ensure free residuals in the pool water (Richardson et al. 2010; Weisel et al. 2009). Higher free residual chlorine (FRC), higher temperature and constant addition of organic loads from swimmers can accelerate DBPs formation in swimming pools (Simard et al. 2013; Hansen et al. 2013).

To date, many DBPs have been identified in swimming pools, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), chloramines (CAs),

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✉ Shakhawat Chowdhury
SChowdhury@kfupm.edu.sa

¹ Department of Civil and Environmental Engineering, Water Research Group, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

² Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

³ Memorial University of Newfoundland, St. John's, NL, Canada A1B 3X5

haloketones, chloral hydrates, haloacids, halodiacids, iodo-THMs, haloaldehydes, halonitriles, halonitromethanes, bromate, haloamides, haloalcohols, nitrosamines, combined available chlorine, dichloromethylamine, cyanogen chloride, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and MX homologues, aromatic halogenated DBPs, halo- and nitro phenols (Richardson et al. 2007, 2010; Kanan and Karanfil 2011; Xiao et al. 2012; Keuten et al. 2012; Pan and Zhang 2013). The most prevalent DBPs in swimming pool are CAs, THMs, and HAAs (Chu and Nieuwenhuijsen 2002). CAs are also an important group of disinfectants, which may themselves form DBPs (e.g., iodinated DBPs, N-nitrosodimethylamine [NDMA]). Given the high nitrogen content of organic matter from swimmers, nitrogenous DBPs, such as HANs and nitrosamines (e.g., NDMA) are also formed in swimming pool water (Soltermann et al. 2013).

While swimming, swimmers are exposed to DBPs through the inhalation, dermal absorption, and accidental ingestion of pool water (Chowdhury 2015). Many DBPs are known as possible or probable human carcinogens (Richardson et al. 2010; USEPA 2014). Specifically, brominated and nitrogenous DBPs have more genotoxic effects than chlorinated DBPs (Richardson et al. 2010; USEPA 2014). Therefore, it is not surprising that pool water is found to be more genotoxic than tap water (Liviak et al. 2010; Manasfi et al. 2016). Past studies have reported the occurrence of higher levels of THMs in blood after swimming than after oral exposure (Leavens et al. 2007). Attendance at swimming pools has been associated with asthma and other respiratory effects in Olympic swimmers and pool workers and less clearly in recreational adult swimmers and children (Weisel et al. 2009). In a study on 20 indoor swimming pools in the Emilia Romagna region of Italy, Fantuzzi et al. (2010) reported that swimming pool workers with alveolar THMs $>21 \mu\text{g}/\text{m}^3$ were at higher risk of red or itchy eyes, dyspnea/asthma, and blocked nose than workers with lower alveolar THMs. The incidences of red eyes, runny nose, voice loss, and cold symptoms among pool attendants were higher in comparison to employees working in other areas, although Heederik and Jacobs (2013) highlighted several limitations in the reported effects of swimming pool attendance. Epidemiological studies have associated an increased risk of bladder cancer with the use of chlorinated water for drinking and, most recently, swimming (Villanueva et al. 2007). In addition, nitrosamines that are detected in swimming pools are often considered biomarkers of bladder cancer in humans and are highly carcinogenic to bladder tissue (Davis et al. 1991; Moore et al. 1985).

Chowdhury et al. (2014) demonstrated the needs to better understand DBPs occurrences in swimming pools and their effects. Several past studies have reported higher levels of brominated and total DBPs in swimming pools treated with bromine-based disinfectants and/or supplied with seawater

(Chowdhury et al. 2014; Manasfi et al. 2016). In freshwater pools, brominated THMs constituted 7.1–33.3 % of total THMs (Chu and Nieuwenhuijsen 2002), whereas in saline water pools, these represented >95 % (Beech et al. 1980; Lahl et al. 1981; Parinet et al. 2012). If the source water contains bromide and/or is treated with HOBr or electrochemically generated mixed oxidants (EGMO), brominated THMs and HAAs are likely to be formed (Richardson et al. 2010; Lourencetti et al. 2012). However, to our knowledge, no study has yet reported on bromide incorporation factor (BIF) and percentages of bromide incorporation (BI) into DBPs in a swimming pool. In addition, no model is available to predict BI in a swimming pool to date. Availability of these data and model might be useful in controlling brominated DBPs in a swimming pool. In this study, occurrences of DBPs in tap water and an indoor swimming pool before and after swimming were investigated. Correlation analysis was performed for the parameters affecting DBPs formation. For the first time, the BIF and BI were determined for THMs and HAAs in a swimming pool. Contributions of bromide in THMs and HAAs were investigated. Three types of models (linear, non-linear, and neural network [NN] models) were trained to predict the BI into THMs and HAAs in pool water.

Methodology

Data generation

Occurrences of THMs, HAAs, and CAs in tap water (S1), pool water before (S2) and after swimming (S3) were investigated in an indoor swimming pool at King Fahd University of Petroleum and Minerals, Saudi Arabia. The swimming pool is disinfected with chlorine and the source water is a mixture of treated groundwater and desalinated seawater while the fraction of desalinated water was 40–60 % of total water. The size of the swimming pool was approximately $19.2 \times 12.5 \times 1.7$ m and the mean number of daily pool attendants was 32.3 with a range of 14–62. The samples were collected at two times: before swimming (at 4:00 pm, which is the opening time) and after swimming (at 9:00 pm, which is the closing time). Water samples were collected in duplicates through 1-L glass bottles on a bi-weekly basis for a period of 6 months (Jan–Jun 2014). The bottles were filled with water from four corners at a distance of 1 m from the side walls and 6 in. below the water surface. Approximately 100 mg/L of sodium thiosulfate was used to cease further formation of DBPs. Temperature and pH were measured in situ and FRC and total chlorine (TC) were measured with a HACH spectrophotometer (model DR 3900) following HACH methods 8021 and 8167, respectively (HACH 2014). Turbidity was measured with a turbid meter (HACH model 2100 N). The samples were stored in a temperature adjustable refrigerator at

2 ± 0.1 °C and analyzed within 1 week. The total organic carbon (TOC) was measured with a Shimadzu TOC analyzer (Model: TOC-L-CSN) following standard method 5310B (APHA 1995). UV_{254} was measured using a spectrophotometer (Genesys 10 UV VIS model) at 254 nm with a 10-mm optical path quartz cell. Prior to analysis by UV_{254} , the water samples were filtered with 0.45- μ m membrane filter. THMs and HANs in the water were measured by GC–MS by following USEPA method 551.1 and HAAs were measured by following USEPA method 552.2 (USEPA 1995a, b). Measurements of CAs (mono-, di-, and trichloramines) in water were performed by following the DPD method (Richardson et al. 2010). THMs in air before swimming (S2-A) and after swimming (S3-A) were measured by following an approach described in Richardson et al. (2010). Air samples were collected with a pump that was 60 cm above the floor and 1.5 m from the pool border. Air was pumped (7 mL/min) for 20 min through a Tenax TA cartridge. THMs were determined through an automatic thermal desorption unit coupled to a GC–electron capture detector.

Data analysis

Descriptive analysis was performed by using Minitab statistical software, whereas the models were investigated by using JMP statistical software. Correlation analysis was performed for the physical and chemical parameters and DBPs in water and air. Analysis by means of boxplots was performed to assess DBPs variability. Three types of models (linear, nonlinear, and NN) were trained to predict BI into THMs (BI_{THMs}) and HAAs (BI_{HAAs}) in the pool water. In the linear models, both the main factor alone, and the main factor with interactions and higher-order-terms models were investigated. The main factor linear models are the simplest form of multiple linear models (Montgomery and Runger 2007). These models are developed by using significant main factors and ignoring interactions and higher-order terms. The model coefficients and the predictor variables are linear in this model. In the main factor with interactions and higher-order-terms models, the significant main factors, the effect of two factors that vary together (e.g., TOC and FRC), and higher-order terms (e.g., quadratic, cubic) are incorporated. However, the model parameters remain linear. Equations 1 and 2 show the generic form of linear models, which represent the model with main factors, and the model with main factors with interactions and higher-order terms, respectively, wherein y denotes the output, β_0 denotes the model intercept, β denotes the model parameters, x denotes the predictor variables, ε denotes residuals and $i, j = 1, 2, 3 \dots n$. The fitness and performance of the regression models are generally assessed by the coefficient of determination (R^2), F Ratio, root mean square error (RMSE), significance probability, lack of fit test, normal

probability plot of residuals, and residuals versus predicted and data-order plots (Montgomery and Runger 2007). The linear models have been well explained in textbooks (e.g., Montgomery and Runger 2007).

The nonlinear models are complex relative to the linear models. The parameters of these models are nonlinear. The simplest form of nonlinear model can be developed by using two parameters and a single predictor variable. To construct a nonlinear model, the initial model is defined through observation of data plots (e.g., matrix plot) and the initial values for the parameters are assigned. Iterations are performed on the initially defined parameters until convergence is obtained. The values of the parameters upon convergence are the model parameter values (SAS Inc 2014; Minitab Inc. 2014). Formulation of a three-parameter first-order decay kinetic model is presented in Eq. 3, wherein θ_1 – θ_3 denotes the model parameters. The general form for a four-hidden-node NN model is presented in Eqs. 4 and 5, wherein H_γ denotes the γ th hidden node (here, $\gamma = 1$ –4) and λ denotes the coefficients for the NN model. The hidden node (H_γ) is a hyperbolic tangent function—a sigmoid function whose output ranges from -1 to 1 . For each of the four nodes in these models, H_γ is estimated as the hyperbolic tangent function of the linear combinations of the predictor variables. In Eq. 5, factors α_0 and α_i denote the intercept and coefficients of the predictor variables associated with each hidden node.

$$y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \dots + \varepsilon \quad (1)$$

$$y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i,j=1}^n \beta_{i,i+j} x_i x_{i+j} + \sum_{i=1}^n \beta_{ii} x_i^2 + \dots + \varepsilon \quad (2)$$

$$y = \theta_1 + \theta_2 \text{Exp}(-\theta_3 x) \quad (3)$$

$$y = \lambda_0 + \sum_{\gamma=1}^4 \lambda_\gamma H_\gamma \quad (4)$$

$$H_\gamma = \tanh[0.5 \times (\alpha_0 + \alpha_i x_i)] \quad (5)$$

Further details on the models, their advantages, limitations, and applications can be found elsewhere (Montgomery and Runger 2007; SAS Inc 2014; Minitab Inc. 2014). For the models, statistically significant main factors, interaction terms, and higher-order terms were identified through the screening test module of JMPTM, normal probability plots of residuals, effects analysis, and parameter estimates (SAS Inc 2014). By using the significant factors, models were developed, and the statistical adequacies of the models were tested by means of numerical and graphical techniques.

Results and discussion

Data statistics

The water quality parameters are summarized in Table 1. The TOC in S3 was higher than in S1 and S2 ($S3/S1=1.94$; $S3/S2=1.18$). Higher levels of TOC in S2 and S3 than S1 indicate higher concentrations of organic matter in the pool water (Table 1). The higher UV_{254} of the pool water also indicates higher levels of organic matter. In addition, ammonia–nitrogen (represented by N_2 in this article) was detected in S2 (0.05–0.18 mg/L) and S3 (0.13–0.37 mg/L), but not in S1. In S3, average turbidity was 1.5 and 1.9 times the turbidity in S2 and S1, respectively. Similarly, conductivity was highest in S3 ($893.1 \pm 292.5 \mu\text{S/cm}$), followed by S2 ($575.3 \pm 167.8 \mu\text{S/cm}$) and S1 ($225.8 \pm 71.4 \mu\text{S/cm}$). Concentrations of bromide in S1, S2, and S3 were in the ranges of 0.07–0.67, 0.16–0.81, and 0.21–1.09 mg/L, respectively, with the averages of 0.34, 0.52, and 0.60 mg/L, respectively (Table 1). Bromide concentrations in S1, S2, and S3 were relatively higher than the typical freshwater sourced systems. The seawater from the Arabian Gulf are desalinated to produce the desalinated water. The average concentration of bromide in seawater from the Arabian Gulf was reported to be 64.0 mg/L (Abdel-Wahab et al. 2010). The World Health Organization reported that seawater could contain bromide in the range of 65 to >80 mg/L (WHO 2007, 2010). Despite desalination could remove most of the bromide (>99 %), presence of few hundred micrograms per liter of bromide in water

was anticipated. Further, the groundwater aquifers in the Gulf coast might have been contaminated by saline water intrusion from the Arabian Sea. Past studies have indicated higher levels of bromide in the groundwater in this region. Concentrations of bromide in S3 were 2.5 (range 0.55–8.9) and 1.3 (range 0.46–3.1) times to the bromide in S1 and S2, respectively. Higher concentrations of bromide in the pool water might be partially explained by accumulation of bromide from human inputs and attachment of bromide with the suspended/settled matter in the pool water. Overall, TOC, N_2 , bromide, turbidity, conductivity, and UV_{254} were higher in S3 than S2 and S1, which indicate possible addition of organic and inorganic constituents by the swimmers.

The THMs and HAAs in S1, S2, S3, S2-A, and S3-A are summarized in Fig. 1. Averages of THMs in S1, S2, and S3 were 10.1, 52.5, and 68.3 $\mu\text{g/L}$, respectively, and their corresponding ranges were 7.4–14.5, 28.6–74.1, and 28.7–95.5 $\mu\text{g/L}$, respectively. THMs in S3 were 6.9 (range 2.9–11.1) and 1.4 (range 0.52–2.9) times to the THMs in S1 and S2, respectively. In swimming pool air, THMs in S2-A and S3-A were 72.2 (range 36.3–105.8) and 93 (range 44.1–133.6) $\mu\text{g/m}^3$, respectively (Fig. 1). Concentrations of HAAs in S1, S2, and S3 were 24.1, 86.9, and 100.2 $\mu\text{g/L}$, respectively, and their ranges were 17.9–31.7, 55.9–125.1, and 68.9–158.9 $\mu\text{g/L}$, respectively. In S3, HAAs were 4.2 (range 2.5–7.5) and 1.2 (range 0.6–2.6) times to the HAAs in S1 and S2, respectively.

Figure 2 shows the component-wise summary of THMs in S1, S2, S3, S2-A, and S3-A. In S1, S2, and S3, average CHBr_3

Table 1 Physical and operational parameters for the swimming pool

	S1		S2		S3	
	Average	Range	Average	Range	Average	Range
TOC (mg/L)	1.19 (0.28)	0.66–1.71	1.95 (0.45)	1.34–3.26	2.31 (0.58)	1.29–3.87
DOC (mg/L)	0.91 (0.3)	0.52–1.42	1.71 (0.36)	1.01–2.87	1.99 (0.43)	1.1–3.62
N_2 (mg/L)	0.00	0.00	0.11 (0.03)	0.05–0.18	0.22 (0.05)	0.13–0.37
TC (mg/L)	0.3 (0.06)	0.2–0.46	1.1 (0.23)	0.69–1.54	0.69 (0.13)	0.41–0.98
FRC (mg/L)	0.21 (0.05)	0.11–0.31	0.82 (0.23)	0.07–1.29	0.43 (0.12)	0.18–0.74
Comb-C (mg/L)	0.094 (0.063)	0.05–0.246	0.27 (0.14)	0.06–0.72	0.26 (0.11)	0.08–0.58
Br^- (mg/L)	0.34 (0.17)	0.07–0.67	0.52 (0.15)	0.16–0.81	0.60 (0.19)	0.28–1.09
T_w ($^{\circ}\text{C}$)	29.3 (3.8)	22–33	30.9 (1.4)	28–33	30.9 (1.4)	28–33
T_a ($^{\circ}\text{C}$)			32.2 (1.3)	29.5–34.9	32.2 (1.3)	29.5–34.9
pH	7.14 (0.49)	6.5–8.81	7.53 (0.62)	6.2–8.86	7.5 (0.61)	6.2–8.86
TURB (NTU)	0.29 (0.09)	0.13–0.48	0.37 (0.15)	0.14–0.68	0.55 (0.2)	0.2–0.99
UV_{254} (/cm)	0.02 (0.01)	0.01–0.04	0.03 (0.01)	0.02–0.06	0.04 (0.01)	0.02–0.08
COND: ($\mu\text{S/cm}$)	225.8 (71.4)	96–364	575.3 (167.8)	198.4–862	893.1 (292.5)	207.8–1679.2

S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session

TOC total organic carbon, DOC dissolved organic carbon, N_2 ammonia nitrogen, TC total chlorine, FRC free residual chlorine, Comb-C combined chlorine, Br^- bromide, T_w water temperature, T_a air temperature, TURB turbidity, UV_{254} UV absorbance at 254 nm, COND conductivity

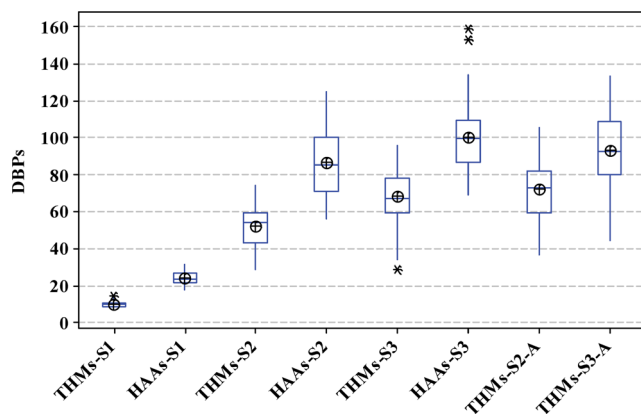


Fig. 1 Summary of THMs and HAAs in the swimming pool water. S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session; S2-A: Air samples from the pool area before the swim session begins; S3-A: Air samples from the pool area at the end of the swim session. Concentrations of THMs in water and air are in micrograms per liter and micrograms per cubic meter, respectively. *Bottom* of the box represents the first quartile (Q1)—25 % of the data value; *top* of the box represents the third quartile (Q3)—75 % of the data value; the *upper whisker* extends up: $Q3 + 1.5 \cdot (Q3 - Q1)$; the *lower whisker* extends to: $Q1 - 1.5 \cdot (Q3 - Q1)$; data outside of the range of *whisker* represent the outliers; the *horizontal bar* in the middle of box represents the median value, and the *round symbol* inside the box represents the mean value

levels were 4.8, 42.7, and 57.6 $\mu\text{g/L}$, respectively (Fig. 2). The average concentrations of CHCl_3 , BDCM, and DBCM were $<5 \mu\text{g/L}$ in all samples (Fig. 2). Brominated species comprised the majority of total THMs in S1, S2, and S3 with average percentages of 86.2, 94.1, and 95.2 %, respectively. In S1, CHBr_3 was 47.2 % of total THMs, whereas in S2 and S3, these percentages were 80.8 and 83.7 %, respectively. For the swimming pool air, CHBr_3 in S2-A and S3-A were 55.6 and 75 $\mu\text{g/m}^3$, respectively, which were 77.1 and 80.6 % of total THMs in air, respectively. HAAs and CAs are summarized in Table 2. The concentrations of brominated HAAs were much higher than the chlorinated HAAs. In S1, averages of DBAA, CDBAA, and TBAA were 7.5, 4.8, and 6.7 $\mu\text{g/L}$, respectively, representing 31.1, 19.9, and 27.8 % of total HAAs, respectively. In S2, DBAA, CDBAA, and TBAA were 15.4, 22.7, and 33.2 $\mu\text{g/L}$, representing 17.7, 26.1, and 38.2 % of total HAAs, respectively. In S3, these DBPs were 16.8 (16.7 %), 27.6 (27.5 %), and 38.6 $\mu\text{g/L}$ (38.5 %), respectively. In case of CAs, none was detected in S1. The samples from S2 and S3 had measurable quantities of mono-, di- and trichloramines (Table 2). Concentrations of CAs were higher in S3 than S2. HANs were not detected in S1, S2, or S3.

Overall, brominated DBPs comprised the majority of DBPs in this pool, due possibly to relatively higher concentrations of bromide in the source and pool water.

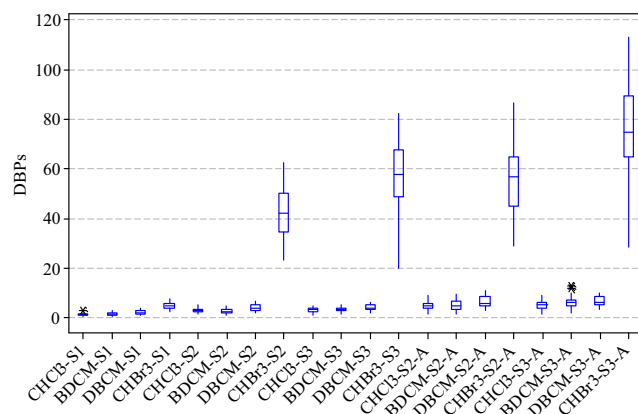


Fig. 2 Summary of CHCl_3 , BDCM, DBCM, and CHBr_3 in the swimming pool water and air. S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session; S2-A: Air samples from the pool area before the swim session begins; S3-A: Air samples from the pool area at the end of swim session. Concentrations in water and air are in micrograms per liter and micrograms per cubic meter, respectively. *Bottom* of the box represents the first quartile (Q1)—25 % of the data value; *top* of the box represents the third quartile (Q3)—75 % of the data value; the *upper whisker* extends up: $Q3 + 1.5 \cdot (Q3 - Q1)$; the *lower whisker* extends to: $Q1 - 1.5 \cdot (Q3 - Q1)$; data outside of the range of *whisker* represent the outliers; the *horizontal bar* in the middle of box represents the median value

Past studies have documented higher fractions of brominated DBPs in swimming pools fed with seawater and/or treated with bromide-based disinfectants (Richardson et al. 2010; Parinet et al. 2012; Chowdhury et al. 2014). The concentrations of DBPs in water and air after swimming were higher than those before swimming. This increase can be partially explained by the higher concentrations of organic and inorganic matter in swimming pool (e.g., higher TOC, N_2 , UV_{254} , Br^-) owing to swimmers, higher water temperatures and higher concentrations of FRC.

Pairwise correlation

A correlation analysis was performed for all parameters from all sources (e.g., S1, S2, S3, S2-A, and S3-A). The parameters representing NOM in S1, S2, and S3 (e.g., TOC and UV_{254}) were strongly correlated ($r=0.65\text{--}0.82$). The TC and FRC showed moderate to strong correlations ($r=0.32\text{--}0.91$ for S1–S3, respectively). TOC and turbidity (Turb) had low correlation ($r<0.1$) in S1 and S2, which was increased to 0.3 in S3. A subset of correlations representing the number of swimmers, TOC, THMs, and HAAs is presented in Table 3. The number of swimmers was strongly correlated with HAAs in S3 ($r=0.72$), whereas no correlation was observed between THMs and number of swimmers. THMs are volatile and might have partitioned significantly into the indoor air. The remaining THMs could not explain the effects of the number

Table 2 Summary of component-wise haloacetic acids and chloramines in tap water and pool water before and after swimming

	S1		S2		S3	
	Average	Range	Average	Range	Average	Range
MCAA	0.52 (0.22)	0.15–0.97	1.06 (0.45)	0.04–1.91	1.44 (0.44)	0.58–2.23
DCAA	0.31 (0.12)	0.06–0.54	1.66 (0.47)	0.81–2.55	1.67 (0.44)	0.76–2.61
TCAA	0.32 (0.11)	0.09–0.56	2.42 (0.85)	0.47–4.19	2.7 (0.9)	1.2–4.7
MBAA	1.34 (0.34)	0.66–2.05	3.7 (1.02)	1.5–5.9	3.8 (1.3)	1.4–6.9
DBAA	7.5 (2.45)	2.2–13.9	15.4 (4.5)	6.8–25.6	16.8 (4.9)	5.9–27.7
BCAA	2.1 (0.93)	0.6–4.2	5.1 (1.85)	1.5–8.7	5.3 (1.4)	2.8–8.3
BDCAA	0.5 (0.22)	0.04–0.92	1.7 (0.92)	0.29–3.5	2.36 (0.91)	0.7–4.4
CDBAA	4.8 (1.6)	1.4–8.3	22.7 (8.4)	7.4–39.8	27.6 (11.3)	7.3–48.2
TBAA	6.7 (1.7)	3.4–10.6	33.2 (16.5)	5.8–72.9	38.6 (10.9)	19.5–73.3
HAAs	24.1 (3.2)	17.9–31.7	86.9 (18.8)	55.9–125.1	100.2 (19.0)	68.9–158.9
MCA (mg/L)			0.17 (0.06)	0.07–0.31	0.27 (0.1)	0.07–0.45
DCA (mg/L)			0.16 (0.08)	0.01–0.31	0.28 (0.11)	0.04–0.49
TCA (mg/L)			0.05 (0.02)	0.0–0.10	0.08 (0.03)	0.01–0.11

S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session

MCAA monochloroacetic acid, DCAA dichloroacetic acid, TCAA trichloroacetic acid, MBAA monobromoacetic acid, DBAA dibromoacetic acid, TBAA tribromoacetic acid, BCAA bromochloroacetic acid, BDCAA bromodichloroacetic acid, CDBAA chlorodibromoacetic acid, MCA monochloramine, DCA dichloramine, and TCA trichloramine

of swimmers on THMs in S3. In contrast, HAAs are non-volatile and accumulated in the water; they might better explain the effects of number of swimmers. Correlations between THMs in the pool water and air were moderate. In S2 and S3, the correlation coefficients between THMs in water and air were 0.61 and 0.54, respectively. Some past studies have reported poor correlations between THMs in water and air of swimming pools (Aggazzotti et al. 1995). The absence of strong correlations between THMs in pool water and pool air might be due to the effects of air recirculation, pool hall volume to water volume ratio, and water temperature

(Chowdhury et al. 2014). One important aspect is air circulation through the windows and mechanical ventilation. The pool air is warmer than the outside air, which results in the windows being the coldest point in the pool hall. The relatively colder air from outside pushes the warmer pool air in the upper layer. However, the air directly above the pool water, which is warmer (in this study, 32.2 °C in pool air and 30.9 °C in pool water) and very humid, tends to rise in the upper layer as well. As such, a cold and warm air circulation pattern develops in the pool environment, which is unique to each pool based on wind speed, flow direction, percent air change, and

Table 3 Correlation coefficients for number of swimmers, TOC, total THMs, and total HAAs in pool water and air above swimming pool

	Swimmers	TOC-S1	THMs-S1	HAAs-S1	TOC-S2	THMs-S2	HAAs-S2	TOC-S3	THMs-S3	HAAs-S3	THMs-S2-A
TOC-S1	0.05										
THMs-S1	−0.01	0.16									
HAAs-S1	−0.01	0.04	−0.12								
TOC-S2	−0.24	−0.09	−0.27	−0.14							
THMs-S2	−0.09	−0.04	−0.01	−0.13	0.03						
HAAs-S2	0.00	−0.03	0.14	−0.16	0.46	−0.01					
TOC-S3	0.12	−0.19	−0.28	−0.17	0.02	−0.07	0.17				
THMs-S3	−0.01	0.03	−0.01	0.04	−0.09	0.04	−0.16	−0.21			
HAAs-S3	0.72	0.07	−0.07	0.08	−0.05	−0.17	0.05	−0.16	−0.10		
THMs-S2-A	−0.09	0.06	0.06	−0.06	0.00	0.61	0.02	−0.11	0.03	−0.15	
THMs-S3-A	0.03	0.11	0.07	0.10	−0.11	0.07	−0.11	−0.25	0.54	−0.07	0.13

Table 4 Bromide incorporation (BI) in swimming pool water before and after swimming

	BI _{THMs} (%)		BI _{HAA_s} (%)	
	Average	Range	Average	Range
S1	2.96 (2.29)	0.84–10.74	6.55 (4.98)	2.32–21.28
S2	9.34 (3.36)	3.99–19.75	12.01 (4.54)	5.05–24.36
S3	10.64 (3.74)	4.78–19.57	12.2 (4.51)	5.1–26.5

S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session

BI_{THMs} bromide incorporation for THMs, BI_{HAA_s} bromide incorporation for HAAs

temperature difference. Little is known about the wind circulation pattern in an indoor swimming pool, although it can affect the measured concentrations of THMs (Chowdhury et al. 2014). Air circulation might have affected the volatility of THMs, which would have implications for the levels of THMs in the pool water and air. The number of swimmers had poor to moderate correlations with DBAA ($r=0.28$), CDBAA ($r=0.57$), and TBAA ($r=0.52$) in S3 (not shown in Table).

$$N_{HAA_s} = \frac{\sum (MBAA + 2 \times DBAA + 3 \times TBAA + BCAA + BDCAA + 2 \times DBCAA)}{HAA_s} \quad (7)$$

In Eq. 7, N_{HAA_s} denotes the BIF for HAAs. The concentrations of HAAs are molar. Despite BIF shows the relative distributions of brominated DBPs, it does not quantify the percentages of BI into DBPs. The percentages of BI into THMs and HAAs can be determined by following the procedure of Sohn et al. (2006) as:

$$BI_{THMs} \text{ OR } BI_{HAA_s}(\%) = \frac{Br_{THMs} \text{ OR } Br_{HAA_s}}{Br_{water}} \times 100 \quad (8)$$

$$Br_{HAA_s} = \left\{ 79.9 \left(\frac{MBAA}{138.9} + \frac{2 \times DBAA}{217.8} + \frac{3 \times TBAA}{296.7} + \frac{BCAA}{173.4} + \frac{BDCAA}{207.8} + \frac{2 \times CDBAA}{252.3} \right) \right\} \quad (10)$$

Concentrations of Br_{THMs} , Br_{HAA_s} and other DBPs in Eqs. (9–10) are in micrograms per liter. In S1, S2, S3, S2-A, and S3-A, BIF for THMs (N_{THMs}) were 1.73 (range 1.33–2.11), 2.43 (range 2.17–2.65), 2.51 (range 2.14–2.75), 2.32 (range 1.95–2.6), and 2.41 (range 1.97–2.65), respectively, which indicates higher fractions of

Bromide incorporation

The bromide incorporation factor (BIF) provides an indication of the relative distributions of brominated DBPs (Rathbun 1996). Several studies have reported the BIF and percentages of bromide incorporation (BI) for drinking water (Rathbun 1996; Sohn et al. 2006). However, little is known for swimming pools. Sohn et al. (2006) reported the BI to be 24.5 % (range 6.3–40.9 %) for THMs and 9.5 % (range 4.3–13.2 %) for HAAs in drinking water. The BI into brominated DBPs depends on several factors, which include pH, bromide, FRC, and DOC (Rathbun 1996; Sohn et al. 2006). By following the procedure of Rathbun (1996), the BIF were calculated for THMs in swimming pool (Eq. 6):

$$N_{THMs} = \frac{\sum_{n=0}^3 n(CHCl_{3-n}Br_n)}{\sum_{n=0}^3 (CHCl_{3-n}Br_n)} \quad (6)$$

In Eq. 6, N_{THMs} denotes the BIF for THMs (for $CHCl_3$, $N=0$; for $CHBr_3$, $N=3$). For a mixture of all THMs, $3 > N > 0$, and the THM concentrations are molar. Using the similar approach, BIF for HAAs can also be calculated as:

Where, BI represents the percentage of bromide incorporated into THMs or HAAs; Br_{THMs} = bromide concentration in THMs ($\mu\text{g/L}$); Br_{HAA_s} = bromide concentration in HAAs ($\mu\text{g/L}$); Br_{water} = concentration of bromide in water ($\mu\text{g/L}$); Br_{THMs} and Br_{HAA_s} can be calculated following Sohn et al. (2006) as:

$$Br_{THMs} = \left\{ 79.9 \left(\frac{BDCM}{163.8} + \frac{2 \times DBCM}{208.3} + \frac{3 \times CHBr_3}{252.7} \right) \right\} \quad (9)$$

brominated THMs in all samples. In S1, S2, and S3, N_{HAA_s} were 1.80 (range 1.62–1.97), 1.9 (range 1.57–2.21), and 1.92 (range 1.74–2.13), respectively. The values of N_{THMs} and N_{HAA_s} in S2 and S3 were higher than for S1, indicating higher fractions of brominated THMs and HAAs in S2 and S3.

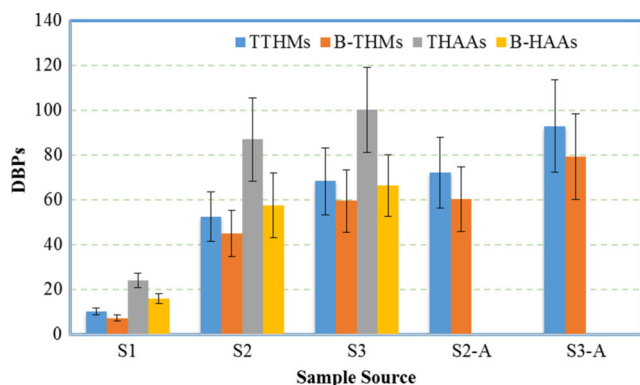


Fig. 3 DBPs and contribution of bromide in THMs and HAAs. S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session; S2-A: Air samples from the pool area before the swim session begins; S3-A: Air samples from the pool area at the end of swim session. *TTHMs* total THMs ($\mu\text{g/L}$), *B-THMs* bromide concentration in THMs ($\mu\text{g/L}$), *THAAs* total HAAs ($\mu\text{g/L}$), *B-HAAs* bromide concentration in HAAs ($\mu\text{g/L}$); concentrations in water and air are in micrograms per gram and micrograms per cubic meter, respectively. The error bars represent the standard deviations

The percentages of BI into brominated THMs and HAAs are shown in Table 4. In S1, the average percentage of BI_{THMs} was 2.96, which was increased to 9.34 and 10.64 in S2 and S3, respectively. The average percentages of BI_{HAAs} were 6.55, 12.01, and 12.2 in S1, S2, and S3, respectively. The BI_{THMs} and BI_{HAAs} increased significantly in the swimming pool environment relative to tap water. This percentage was found to further increase during swimming related activities in the pool (e.g., increase from S2 to S3). The higher levels of bromide in swimming pool water might be partially responsible for higher percentages of BI_{THMs} and BI_{HAAs} in swimming pool. Past studies have reported higher levels of BIF in water with higher levels of bromide (Rathbun 1996). The increased values of BI

in the pool water can increase the levels of brominated DBPs, which can pose higher risks to human, and thus it can be a concern from a human health perspective. Better understanding on the BI into brominated DBPs might assist in minimizing human health risks.

Further investigation was performed on the contribution of bromide in THMs and HAAs. The contribution of bromide in THMs and HAAs are shown in Fig. 3. Average concentrations of THMs in S1, S2, and S3 were 10.1, 52.5, and 68.3 $\mu\text{g/L}$, respectively, in which 7.1, 45.0, and 59.5 $\mu\text{g/L}$, respectively, were bromide. In S2-A and S3-A, THMs were 72.2 and 93.0 $\mu\text{g/m}^3$, in which bromide were 60.3 and 79.3 $\mu\text{g/m}^3$, respectively. In S1, S2, S3, S2-A, and S3-A, bromide concentrations were in the ranges of 59.7–79.2, 80.3–89.2, 79.8–90.9, 75.6–88.4, and 76.1–89.2 % of total THMs, respectively. Average concentrations of HAAs in S1, S2, and S3 were 24.1, 86.9, and 100.2 $\mu\text{g/L}$, respectively, in which bromide concentrations were 15.9, 57.6, and 66.4 $\mu\text{g/L}$, respectively. The percentages of bromide in HAAs in S1, S2, and S3 were in the ranges of 62.3–68.7, 60.1–73.9, and 63.2–78.5, respectively. The higher fractions of bromide in THMs and HAAs for the samples from S2 and S3 can be partially explained by the effects of the higher concentrations of bromide in S2 and S3.

Predicting bromide conversion

To better understand the role of physical and chemical parameters on the percentage of BI, a pairwise correlation analysis was performed. However, no single parameter was found to explain the higher values of BI in S2 and S3 comprehensively (Table 5). The BI for THMs (BI_{THMs}) had positive correlations with bromide ($r=0.61$), N_2 ($r=0.36$), turbidity ($r=0.20$), TOC ($r=0.19$), and conductivity ($r=0.16$), and negative

Table 5 Correlation analysis for bromide conversion and other parameters in swimming pool

Row	TOC	N_2	TC	FRC	T_w	pH	TURB	UV ₂₅₄	COND	BI_{THMs}	BI_{HAAs}	Br^-
TOC	1.00	0.17	-0.36	-0.35	0.01	-0.11	0.27	0.78	0.17	0.19	0.23	0.13
N_2	0.17	1.00	-0.63	-0.58	-0.05	0.19	0.27	0.19	0.43	0.36	0.18	0.22
TC	-0.36	-0.63	1.00	0.90	0.09	-0.01	-0.30	-0.36	-0.45	-0.12	-0.21	-0.13
FRC	-0.35	-0.58	0.90	1.00	0.07	0.05	-0.31	-0.34	-0.52	-0.15	-0.24	-0.13
T_w	0.01	-0.05	0.09	0.07	1.00	0.08	0.08	-0.02	0.01	0.04	0.09	-0.08
pH	-0.11	0.19	-0.01	0.05	0.08	1.00	-0.09	-0.21	-0.07	-0.13	-0.10	0.17
TURB	0.27	0.27	-0.30	-0.31	0.08	-0.09	1.00	0.28	0.35	0.20	-0.02	0.07
UV ₂₅₄	0.78	0.19	-0.36	-0.34	-0.02	-0.21	0.28	1.00	0.18	0.14	0.17	0.13
COND	0.17	0.43	-0.45	-0.52	0.01	-0.07	0.35	0.18	1.00	0.16	0.14	0.07
BI_{THMs}	0.19	0.36	-0.12	-0.15	0.04	-0.13	0.20	0.14	0.16	1.00	0.59	0.61
BI_{HAAs}	0.23	0.18	-0.21	-0.24	0.09	-0.10	-0.02	0.17	0.14	0.59	1.00	0.74
Br^-	0.13	0.22	-0.13	-0.13	-0.08	0.17	0.07	0.13	0.07	0.61	0.74	1.00

TOC total organic carbon, N_2 ammonia nitrogen, TC total chlorine, FRC free residual chlorine, Br^- bromide, T_w water temperature, TURB turbidity, UV₂₅₄ UV absorbance at 254 nm, COND conductivity, BI_{THMs} bromide incorporation in THMs (%), BI_{HAAs} bromide incorporation in HAAs (%)

Table 6 Input parameters for modeling bromide incorporation

Output	Model type	Input variables	R ²
BI _{THMs} (%)	LMF	Br ⁻ , N ₂ , TURB, pH, TOC, TC	0.19
	LMFI	Br ⁻ , N ₂ , TOC, TURB and Br ⁻ × TURB	0.26
	NL	Br ⁻ and N ₂ separately	0.21
	NN	Br ⁻ , N ₂ , TURB, pH, T _w , FRC, TOC, TC	0.31
BI _{HAA5} (%)	LMF	Br ⁻ , N ₂ , TURB, pH, TOC, TC	0.16
	LMFI	Br ⁻ , N ₂ , TOC, TC, pH, Temp, and pH × Temp	0.21
	NL	Br ⁻ , N ₂ , and TOC separately	0.22
	NN	Br ⁻ , N ₂ , TURB, pH, T _w , FRC, TOC	0.16

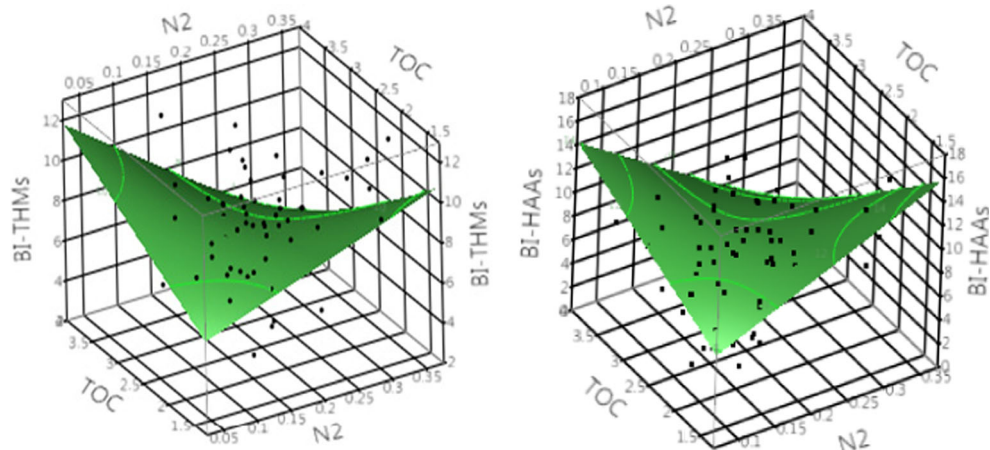
LMF linear main factor model, LMFI linear main factor and interaction effects model, NL nonlinear model, NN neural network model, TOC total organic carbon, N₂ ammonia nitrogen, TC total chlorine, FRC free residual chlorine, Br⁻ bromide, T_w water temperature, TURB turbidity, BI_{THMs} bromide incorporation in THMs (%); BI_{HAA5} bromide incorporation in HAA5 (%)

correlations with TC ($r=-0.12$), pH ($r=-0.13$), and FRC ($r=-0.15$). The BI for HAA5 (BI_{HAA5}) was positively correlated with bromide ($r=0.74$), TOC ($r=0.23$), N₂ ($r=0.18$), and conductivity ($r=0.14$), and negatively correlated with TC ($r=-0.21$) and FRC ($r=-0.24$). Further details on the correlation structure can be obtained from Table 5.

The models discussed in the methodology section were trained to predict BI_{THMs} and BI_{HAA5} in swimming pool water. The model outputs were BI_{THMs} and BI_{HAA5} while the input variables were one or more from TOC, N₂, TC, FRC, T_w, pH, TURB, UV₂₅₄, COND, and Br⁻ and the interaction terms. The significant main factors and interaction effects were identified using the screening tool, matrix plots, and graphical tests from the JMP software (SAS Inc 2014). The model specific input parameters are shown in Table 6. In Table 6, model expressions were not included because none of these models showed good predictive ability. The R² values of these models varied from 0.16 to 0.31. The lowest and highest values of R² were obtained for the NN models to predict BI_{HAA5} and BI_{THMs}, respectively. The low predictive abilities of the models might be explained by the complex interactions in swimming pool (e.g., air circulation pattern, composition and distribution of

organic and inorganic loads, hydraulic retention time, and air renewal rate), and the effects of these factors are not yet well understood. In this study, efforts were made to obtain an idea on the complexity in this swimming pool. The main factors (e.g., TOC, N₂, TC, FRC, T_w, pH, TURB, UV₂₅₄, COND, and Br⁻) had effects on BI_{THMs} and BI_{HAA5}. The interaction of Br⁻ and TURB was also found to be positive on BI_{THMs}. Increase in N₂, TOC, turbidity, conductivity, and Br⁻ showed increasing trends of BI_{THMs}, whereas increases in TC, FRC, and pH showed decreasing trends of BI_{THMs} and BI_{HAA5}. To explain the complexity of interaction effects, the interaction effect of N₂ and TOC on BI_{THMs} and BI_{HAA5} are shown in Fig. 4. Figure 4 showed that the particular ranges of TOC and N₂ could decrease BI_{THMs} and BI_{HAA5}. Beyond these ranges, BI_{THMs} and BI_{HAA5} were likely to increase. The findings are inconclusive on such ranges, which needs better understanding and further investigation. To develop a predictive model for BI_{THMs} and BI_{HAA5}, future study may explain the effects of the related main factors and their interactions in more details and/or adopt an innovative approach for modeling. In addition, the role of air circulation, temperature variability, and air exchange rate on bromide incorporation needs better understanding.

Fig. 4 Interaction effects of N₂ and TOC on the percentage bromide incorporation into THMs and HAA5; BI-THMs bromide incorporation into THMs (%), BI-HAA5 bromide incorporation into HAA5 (%)



Conclusions

For the first time, the BIF and BI were determined for THMs and HAAs in an indoor swimming pool. Three types of models (linear, nonlinear, and neural network [NN] models) were trained to predict the BI into THMs and HAAs in pool water. Swimming pool water contained higher levels of NOM than tap water, which led to increased formation of THMs, HAAs, and CAs. Brominated species constituted the majority of DBPs in the tap water, pool water before the start of a swim session, pool water after a swim session, pool air before the start of a swim session, and pool air after a swim session, which indicated the effects of bromide on DBPs in the source and pool water. The higher levels of bromide in the source water might be due to the mixture of desalinated seawater and treated groundwater. The bromide incorporation factors for THMs and HAAs were in the range of 1.33–2.75 and 1.57–2.21 in all sources, which indicated a higher percentage of bromide incorporation into brominated DBPs. The bromide incorporation into THMs in the pool water and air was significantly higher than in tap water. Furthermore, bromide incorporation were higher in the pool water after a swim session (10.6 %) than that of the before (9.3 %). Accumulation of bromide in the pool water and the human inputs might be responsible for the increased levels of bromide in the pool water, which might have increased the bromide incorporation in the pool water. Future study may better explain such effects.

The empirical models were not found to be suitable to explain the bromide incorporation into THMs and HAAs, which indicated the need for additional factors, interaction effects (e.g., air circulation pattern, temperature profile, water retention time, and air exchange rate) and/or the innovative approach of modeling. The interaction effects showed variable behavior, which need to be better understood. The reduction of bromide incorporation might assist in reducing brominated DBPs, which can assist in reducing health risks. Future study should incorporate multiple swimming pools (indoor and outdoor) and develop a data bank, which might be useful for developing models and/or control exposure to potentially harmful DBPs in swimming pools. Despite these limitations, this study provides a basis for understanding bromide incorporation into brominated DBPs, which is useful in developing a related strategy.

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