

DBPs in a chlorinated indoor swimming pool: occurrences and modeling

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ABSTRACT

Swimming pool water contains higher chlorine residual and is maintained at a higher temperature than tap water. It constitutes environments with high levels of disinfection byproducts (DBPs) in water and air due to continuous disinfection and constant organic loading from the bathers. Exposure to DBPs is inevitable for any bather or trainer while such exposure can have cancer and non-cancer risks to humans. In this study, DBPs in tap water (S1) and water and air from a chlorinated indoor swimming pool before (S2) and after swimming (S3) were measured. Trihalomethanes (THMs) in S2 and S3 were 3.0–6.8 and 4.0–10.3 times the THMs in S1, respectively; and haloacetic acids (HAAs) in S2 and S3 were 2.3–4.3 and 2.5–5.5 times the HAAs in S1, respectively. THMs in air before swimming (S2-A) and after swimming (S3-A) were 60.4 and 77.5 $\mu\text{g}/\text{m}^3$, respectively. Models were developed for predicting dissolved organic carbon, THMs and HAAs in swimming pools. The models showed good to excellent performance ($R^2 = 0.70\text{--}0.87$). The model validation studies showed moderate to good performance ($r = 0.73\text{--}0.83$). The models might be useful in predicting DBP exposure in swimming pools.

Key words | disinfection byproducts, predictive model, source water quality, swimming pool

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INTRODUCTION

Swimming pool attendance is frequently advised by medical doctors as a means of sports, body fitness, improved physical activities, enhanced lung functions and recreational activities (Font-Ribera *et al.* 2011). It is often advised as an important sport for asthmatic children. Elite athletes and swimming competitors need to attend the pools on a regular basis (Fitch *et al.* 2008). Studies have also indicated that swimming pool activities can positively affect children with autism (Yilmaz *et al.* 2004). Disinfection of swimming pool water is essential to prevent outbreaks of infectious illnesses (Geldreich 1989; US CDC 1997, 2007; MOE 2002; MWH 2005). While disinfectants inactivate pathogens in swimming pools, unintended reactions between disinfectants (e.g. chlorine, chloramines, ozone, or chlorine dioxide) and natural organic matter (NOM), bromide/iodide in source water and human inputs (e.g. constituents of sweat and urine, skin particles, hair, microorganisms,

cosmetics, and other personal care products) form disinfection byproducts (DBPs) in pool water (Weisel *et al.* 2009). Swimming pools constitute environments with high levels of DBPs in water and air due to continuous disinfection and constant organic loadings from bathers (Kim *et al.* 2002; LaKind *et al.* 2010; Chowdhury *et al.* 2014). More than 100 DBPs have been identified in swimming pools. These include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), 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; Xiao *et al.* 2012; Pan & Zhang 2013).

Beech *et al.* (1980) reported THMs in fresh and saline water pools in Miami as 118–156 and 657 ± 354 $\mu\text{g/L}$, respectively, where chloroform (CHCl_3) and bromoform (CHBr_3) were the major components, respectively. In northern Italy, CHCl_3 in water was reported to be in the range of 19.5–99.3 $\mu\text{g/L}$ in 12 freshwater indoor pools (Aggazzotti *et al.* 1995). Concentrations of CHCl_3 in the air of these pools were in the range of 16–853 $\mu\text{g/m}^3$ (Aggazzotti *et al.* 1995). Parinet *et al.* (2012) reported averages of THMs in eight swimming pools in France fed with Mediterranean Sea water in the range of 234–996 $\mu\text{g/L}$. Simard *et al.* (2013) reported average THMs in indoor and outdoor swimming pools in Quebec (Canada) of 64 and 98 $\mu\text{g/L}$, respectively. Lee *et al.* (2010) noted dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) for 30 chlorinated pools, 30 ozone/chlorinated pools and 26 EGMO (electrochemically generated mixed oxidants) treated pools. Averages of DCAA were 68.3 ± 69.2 , 12 ± 8.3 and 33.7 ± 26.4 $\mu\text{g/L}$ in chlorinated, ozone/chlorinated and EGMO treated pools, respectively. Averages of TCAA were 156.4 ± 180.9 , 17.4 ± 24.6 and 97.2 ± 96.9 $\mu\text{g/L}$ in these pools, respectively. In these three types of pools, HAAs consisted of the highest fractions of DBPs in the pool water (72.6, 64.3 and 60.8%, respectively). However, in drinking water, fractions of HAAs were reported to be lower (Chowdhury 2013). Through a study in Spain, Cardador & Gallego (2011) reported DCAA and TCAA in indoor pools as 83 ± 14 and 117 ± 21 $\mu\text{g/L}$, respectively, while in the outdoor pools, DCAA and TCAA were 148 ± 15 and 118 ± 11 $\mu\text{g/L}$, respectively. In six swimming pools in France fed with Mediterranean Sea water and treated with chlorine, averages of HAAs were 323–2,233 $\mu\text{g/L}$, in which brominated HAAs constituted major fractions (Parinet *et al.* 2012). Simard *et al.* (2013) reported average HAAs from freshwater fed indoor and outdoor pools in Quebec, Canada of 412.9 and 807.6 $\mu\text{g/L}$, respectively, where DCAA and TCAA comprised about 93% of total HAAs. Concentrations of THMs and HAAs in swimming pools are likely to be much higher than when tap water feeds the pools, due possibly to the accelerated formation of THMs and HAAs in the pool water (Kanan & Karanfil 2011). Further, concentrations of HAAs in pool water were reported to be much higher than the THMs in the pool water (Simard *et al.* 2013). In addition, saline water sourced swimming pools or the

pools treated with bromide-based disinfectants were reported to contain higher levels of THMs and HAAs than the freshwater pools (Tang 2011; Parinet *et al.* 2012; Chowdhury *et al.* 2014; Tang & Xie 2016). Further, chloramines are also formed significantly in swimming pools, 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. In addition, elevated levels of ammonia in urine react with chlorine and lead to the formation of chloramines, which are also found at high concentrations in swimming pools (Zwiener *et al.* 2007; Walse & Mitch 2008; Richardson *et al.* 2010).

While swimming, swimmers are exposed to these DBPs through inhalation, dermal absorption and accidental ingestion of pool water. Several studies have demonstrated the association of some health issues with swimming pools. There is evidence that irritant chemicals (i.e. trichloramine; TCA) from swimming pool air may contribute to the incidence of asthma in children and adults (Sherriff *et al.* 2005; Zock *et al.* 2007; Richardson *et al.* 2010). Swimming pool attendance has been associated with asthma and other respiratory effects in Olympic swimmers and pool workers, and less clearly with recreational adult swimmers and children (Bernard *et al.* 2006, 2011; Jacobs *et al.* 2007; Goodman & Hays 2008; Weisel *et al.* 2009). In addition, many DBPs are known as possible or probable human carcinogens, which can pose an elevated risk to humans (Richardson *et al.* 2010; USEPA 2014). Epidemiological studies have associated an increased risk of bladder cancer, the sixth most prevalent cancer in the USA (USNIH 2014) 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 (Weisel *et al.* 2009; Richardson *et al.* 2010) are often considered biomarkers of bladder cancer in humans and are highly carcinogenic to bladder tissue (Moore *et al.* 1985; Davis *et al.* 1991).

Although many studies have investigated DBPs in swimming pools, the availability of predictive models for DBPs in swimming pool water and air is limited (Chowdhury *et al.* 2014; Tang *et al.* 2015), due possibly to the higher levels of complexity in a pool environment. Part of the complexity may be due to the variability in source water quality,

number of swimmers and hygiene, air exchange rate, air circulation pattern, temperature difference, water retention time, swimming pool volume to water ratio and type and amount of disinfectant (Chowdhury *et al.* 2014). Weaver *et al.* (2009) reported the correlations of MCA (monochloramine) with DCA (dichloramine), CHCl_3 , CH_3NCl_2 (dichloromethylamine) and CNBr (cyanogen bromide) with correlation coefficients (r) of 0.8, 0.47, 0.69 and 0.68, respectively. However, CNCl (cyanogen chloride) and FRC (free residual chlorine) in the pools were found to be negatively correlated ($r = -0.36$) (Weaver *et al.* 2009). Walse & Mitch (2008) observed moderate to strong correlations between nitrite and NDMA ($r^2 = 0.61$) and nitrite and DMNA ($r^2 = 0.91$). Hsu *et al.* (2009) developed a model to predict the concentrations of CHCl_3 in indoor swimming pool air through incorporating environmental conditions and occupant activities. This model is complex and needs precise characterization of environmental parameters and occupant activities while such parameters are likely to have uncertainty. In this study, linear, non-linear and neural network models were investigated to predict dissolved organic carbon (DOC), THMs and HAAs in swimming pool water and THMs in swimming pool air. The model parameters were estimated using the JMP™ and Minitab™ statistical software. The best models were selected through numerical and graphical techniques. The models were validated using an additional set of data, which was not used in developing these models. The limitations and scopes of improving the models were discussed.

METHODOLOGY

Data generation

Occurrences of THMs and HAAs in tap water feeding the pool (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 sodium hypochlorite and the source water is a mixture of treated groundwater and desalinated seawater. The proportion of desalinated water to total water varies in the range of 40–60%. 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 persons. Swimming frequency was in the range of 26–48 times/year with durations of 40–85 minutes/event. Water samples were collected in duplicate through 1-L glass bottles on a bi-weekly basis for a period of 1 year (February 2014–January 2015). The bottles were filled headspace free with water from four corners at a distance of 1 m from the sidewalls and 0.15 cm below the water surface. To eliminate FRC, 100 mg of sodium thiosulfate was used. The samples were stored in a temperature adjustable refrigerator at 2 ± 0.1 °C and analyzed within 1 week. Before analyzing, the samples were taken out of the refrigerator and allowed to reach room temperature (18–20 °C). Temperature and pH were measured *in situ*, and FRC and total chlorine (TC) were measured by HACH spectrophotometer (HACH DR 3900 model) following HACH 8021 and 8167 methods, respectively (HACH 2014). DOC was measured with a Shimadzu TOC analyzer (Model: TOC-L-CSN) following filtration of water using 0.45 µm filter paper. The UV_{254} of the filtered water were measured using the Genesys 10 UV-VIS spectrophotometer. THMs (chloroform (CHCl_3), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (CHBr_3)) in the water were measured by gas chromatography–mass spectrometry (GC–MS) by following USEPA method 551.1 (USEPA 1995a). Approximately 3.0 mL of methyl-tert butyl ether (MTBE) were added as the extraction solvent to 50 mL of the sample. The extracts were placed directly into the gas chromatography vials and run by GC–MS. An auto sampler was used to ensure precise injections to the GC–MS. The GC–MS was calibrated using the calibration standards of THMs before analysis. Calibration standards (Supelco: supplied by Sigma-Aldrich, St Louis, Missouri, USA) and quality control standards of known concentrations were used for each run and compared with the analysis results to obtain the best results. Each of the samples was replicated. The MTBE and blanks were run before and after each set of runs. In addition to the replicated experiments, laboratory duplicates were analyzed, for 10% of the total samples, to confirm the efficiency of the GC–MS. HAAs were measured following USEPA method 552.2 (USEPA 1995b). A 40 mL volume of water sample was adjusted to $\text{pH} < 0.5$ and extracted with 4 mL of MTBE. The extract was converted to methyl esters by adding acidic methanol followed by warming. It was then neutralized and measured by capillary column gas chromatography using GC–MS. Further details on

the sample collection, preservation and analyses can be found in USEPA (1995a, 1995b). To measure THMs in the pool air before swimming (S2-A) and after swimming (S3-A), 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 (Supelco, Sigma-Aldrich, USA). THMs were determined through an automatic thermal desorption unit coupled to a GC-MS. Further details can be found in Richardson *et al.* (2010).

Data analysis and model estimation

Descriptive analysis of the data was performed using Minitab statistical software (Minitab Inc. 2014; Version 16), whereas the models were investigated using the JMP statistical software (SAS Inc. 2014; Version 10). Analysis by means of boxplots was performed to explain DBPs variability. Three types of models (linear, nonlinear and neural network) were investigated to predict DOC, THMs and HAAs in the pool water and THMs in pool air. 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 (LMF) are the simplest form of multiple linear models (Montgomery & 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 (LMFI), the significant main factors, effect of two factors that vary together (e.g. DOC and free residual chlorine), 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 characterized 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 & Runger 2007).

The linear models have been well explained in statistical textbooks (e.g. Montgomery & Runger 2007).

The nonlinear (NL) 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 one predictor variable. To construct nonlinear models, initial models are defined by observing data plots (e.g. matrix plot), and 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). Formulation of a four parameter Logistic model is presented in Equation (3), where y represents the output, θ_1 – θ_4 represent model parameters and x represents predictor variables. The general form for a four-hidden-node neural network (NN) model is presented in Equations (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 node, H_γ is estimated as the hyperbolic tangent function of the linear combinations of the predictor variables. In Equation (5), factors α_0 and α_i denote the intercept and coefficients of the predictor variables associated with each hidden node.

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

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

$$y = \theta_1 + \frac{\theta_2 - \theta_1}{[1 + \text{Exp}(x - \theta_3/\theta_4)]} \quad (3)$$

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

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

Further details on these models, their advantages, limitations and applications can be found elsewhere (Montgomery & Runger 2007; Minitab Inc. 2014; SAS Inc.

2014). For the models in this study, statistically significant main factors, interaction terms and higher-order terms were identified through the screening test module of JMP™ and MINITAB™, normal probability plots of residuals, effects analysis and parameter estimates (Minitab Inc. 2014; 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. The models were validated using additional data, which were not used in model training. In this study, 90 data points were generated for swimming pool water, from which 60 data points were randomly selected for model development and the remaining 30 data points were used for model validation.

RESULTS AND DISCUSSION

DBP concentrations and related parameters

The water quality parameters in tap water feeding the pool (S1), pool water before swimming (S2) and after swimming (S3) were significantly variable (Table 1). The DOC in S2 and S3 were higher than in S1 ($S2/S1 = 1.27$; $S3/S1 = 1.41$). Higher levels of DOC in S2 and S3 than S1 indicate additional organic matter in pool water (Table 1). Higher UV_{254} absorbance of pool water also indicates additional

organic matter. In addition, ammonia nitrogen (NH_3-N_2 : N_2 in the paper) was detected in S2 (0.05–0.18 mg/L) and S3 (0.13–0.37 mg/L), but not in S1. Average concentrations of bromide in S1, S2 and S3 were 0.65, 0.85 and 1.01 mg/L with the corresponding ranges of 0.27–1.25, 0.48–1.37 and 0.51–1.48 mg/L, respectively. In S2 and S3, average levels of turbidity were 1.3 and 1.6 times the turbidity in S1, respectively. The relatively high concentrations of bromide and turbidity in the pool water may be associated with desalinated seawater and human inputs, such as, dust, particles, cosmetics and personal care products. Evaporation from the swimming pool might also be partially responsible for the increased concentrations of salts in the pool water after swimming (S3). The swimming pool activities between before (S2) and after (S3) swimming could have affected the rate of evaporation. Further, conductivity was highest in S3 ($714.5 \pm 234.2 \mu S/cm$) followed by S2 ($415.3 \pm 72.4 \mu S/cm$) and S1 ($230.4 \pm 43.9 \mu S/cm$). Overall, DOC, N_2 , turbidity, conductivity, bromide and UV_{254} absorbance were in the order of $S3 > S2 > S1$, which indicate additional contamination of the pool water.

Figure 1 shows the summary of THMs in S1, S2 and S3. In S1, S2 and S3, average concentrations of $CHBr_3$ were 4.6, 33.7 and 45.6 $\mu g/L$, respectively (Figure 1). Average concentration of $CHBr_3$ in S2 were relatively higher than S1. The pool water had higher levels of bromide (Table 1) and had

Table 1 | Physical and operational parameters for the swimming pool

	S1		S2		S3	
	Average	Range	Average	Range	Average	Range
DOC (mg/L)	1.79 (0.43)	0.99–2.27	2.27 (0.40)	1.40–3.14	2.52 (0.44)	1.51–3.60
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)	0.55 (0.09)	0.33–0.72	1.1 (0.23)	0.69–1.54	0.69 (0.13)	0.41–0.98
FRC (mg/L)	0.44 (0.16)	0.24–0.72	0.82 (0.23)	0.07–1.29	0.59 (0.17)	0.21–0.87
Bromide (mg/L)	0.65 (0.42)	0.27–1.25	0.85 (0.41)	0.48–1.37	1.01 (0.54)	0.51–1.48
Water temperature (°C)	29.3 (3.8)	22–33	30.9 (1.4)	28–33	30.9 (1.4)	28–33
Air temperature (°C)			32.2 (1.3)	29.5–34.9	32.2 (1.3)	29.5–34.9
pH	7.14 (0.49)	7.1–8.0	7.33 (0.12)	7.21–7.68	7.5 (0.24)	7.21–7.79
Turbidity (NTU)	0.26 (0.09)	0.13–0.38	0.33 (0.15)	0.14–0.46	0.42 (0.2)	0.2–0.69
UV_{254} (/cm)	0.025 (0.01)	0.01–0.05	0.04 (0.01)	0.02–0.055	0.05 (0.01)	0.02–0.07
Conductivity ($\mu S/cm$)	230.4 (43.9)	149–348.7	415.3 (72.4)	266.4–552.5	714.5 (234.2)	166.2–343.3

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 swimming session. Values within brackets are standard deviations.

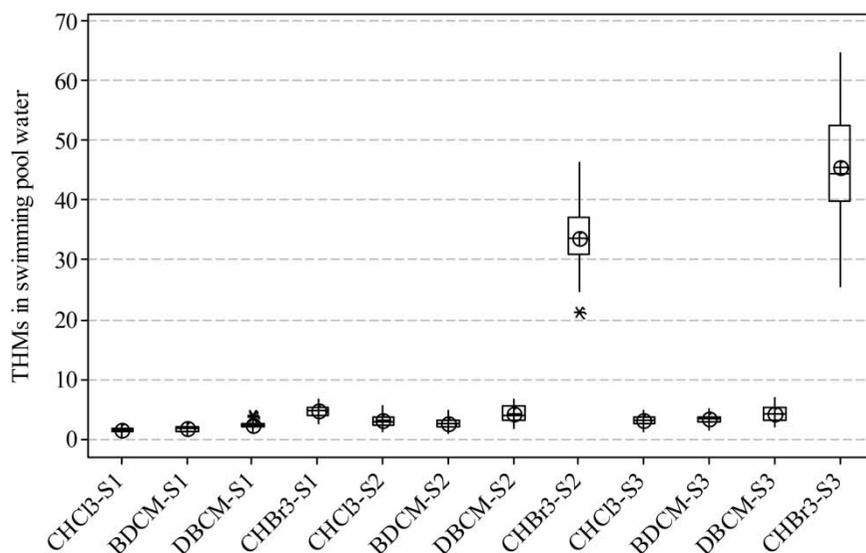


Figure 1 | Summary of CHCl_3 , BDCM, DBCM and CHBr_3 in the swimming pool water. S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session; concentrations are in $\mu\text{g/L}$. 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 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.

a long reaction period prior to the collection of S2 samples, which might have led to the increased formation of CHBr_3 in S2. Average concentrations of CHCl_3 , BDCM, and DBCM were $<5 \mu\text{g/L}$ in all three samples (Figure 1). Brominated THMs comprised the majority of total THMs in S1, S2 and S3, with average percentages of 86.0, 93.1, and 94.4%, respectively. In S1, CHBr_3 was 45.7% of total THMs, whereas in S2 and S3, these percentages were 77.5 and 81.0%, respectively. For swimming pool air, CHBr_3 in S2-A and S3-A were 43.9 and $59.4 \mu\text{g/m}^3$, respectively, which were approximately 72.6 and 76.7% of total THMs in air, respectively (Table 2). In S2-A and S3-A, brominated

THMs were 91.9 and 93.5% of the total THMs, respectively (Table 2). Higher fractions of brominated THMs can be explained by the higher concentrations of bromide in the pool water, which is a mixture of groundwater and desalinated seawater. In this study, concentrations of bromide in pool water were in the ranges of 0.48 – 1.37 and 0.51 – 1.48 mg/L in S2 and S3, respectively (Table 1), which were relatively higher than the typical freshwater pools (Richardson *et al.* 2010; Parinet *et al.* 2012; Chowdhury *et al.* 2014).

The concentrations of THMs and HAAs in S1, S2 and S3 are summarized in Figure 2. Average concentrations of THMs in S1, S2, and S3 were 10.2 , 43.4 and $56.3 \mu\text{g/L}$, respectively and their corresponding ranges were 6.3 – 14.2 , 31.1 – 55.3 and 38.5 – $76.6 \mu\text{g/L}$, respectively (Figure 2). THMs in S2 and S3 were 4.4 (3.0 – 6.8) and 5.7 (4.0 – 10.3) times to the THMs in S1, respectively (Figure 2). In swimming pool air, average THMs in S2-A and S3-A were 60.4 (40.4 – 79.8) and 77.5 (46.1 – 106.1) $\mu\text{g/m}^3$, respectively (Table 2). Average concentrations of HAAs in S1, S2, and S3 were 25.3 , 77.9 and $96.3 \mu\text{g/L}$, respectively and their corresponding ranges were 17.2 – 31.8 , 57.9 – 101.1 and 67.7 – $129.2 \mu\text{g/L}$, respectively. In S2 and S3, HAAs were 3.1 (2.3 – 4.3) and 3.8 (2.5 – 5.5) times to the HAAs in S1,

Table 2 | THMs in swimming pool air ($\mu\text{g/m}^3$)

	S2-A		S3-A	
	Average	Range	Average	Range
CHCl_3	4.9 (1.6)	1.5–8.9	5.1 (1.6)	1.7–9.2
BDCM	5.1 (2.2)	1.3–9.7	6.3 (2.1)	2.2–12.8
DBCM	6.5 (2.3)	2.8–11.2	6.7 (2.0)	3.2–11.8
CHBr_3	43.9 (8.0)	26.2–65.2	59.4 (14)	32.8–88.4
THMs	60.4 (8.3)	46.8–79.8	77.5 (14.4)	46.1–106.2

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.

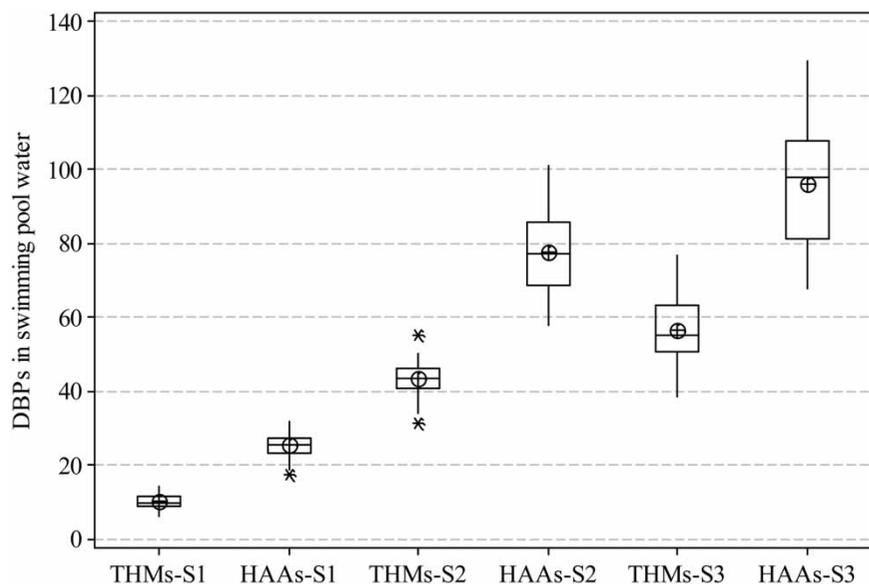


Figure 2 | Summary of THMs and HAAs in the swimming pool water. S1: Water samples from the tap that feeds the swimming pool; S2: Water samples from the swimming pool just before swimmers are allowed to enter the water; S3: Water samples from the swimming pool at the end of the swim session; concentrations of DBPs are in $\mu\text{g/L}$. 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 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.

respectively. In S1, S2, and S3, total HAAs were higher than the corresponding THMs. The ratios of HAAs to THMs in S1, S2 and S3 were 2.0–3.6, 1.4–2.4 and 1.0–2.7, respectively. The concentrations of brominated HAAs were much higher than the chlorinated HAAs. In S1, average concentrations of DBAA, CDBAA, and TBAA were 8.3, 4.9 and 6.5 $\mu\text{g/L}$ with ranges of 2.2–14.0, 1.4–7.8 and 3.4–10.6 $\mu\text{g/L}$, respectively. These three compounds shared 77.9% of total HAAs in S1. In S2, DBAA, CDBAA, and TBAA were 15.4 (19.8%), 17.7 (22.8%), and 29.1 $\mu\text{g/L}$ (37.3%), respectively. However, in S3, these DBPs were 15.7 (16.3%), 25.4 (26.3%) and 38.0 $\mu\text{g/L}$ (39.5%), respectively.

Overall, brominated DBPs comprised the majority of THMs and HAAs. The swimming pool is fed with tap water, which is a mixture of desalinated and ground water. The fraction of desalinated water varied in the range of 40–60% of total water. The source of the desalinated water is saline water from the Arabian Gulf. In addition, groundwater in the Gulf coast might have been contaminated by saline water intrusion from the Gulf. Past studies have indicated higher levels of bromide in groundwater in this region. The World Health Organization reported that seawater could contain bromide in the range 65 to >80 mg/L (WHO 2007, 2010). Abdel-Wahab *et al.* (2010) reported

bromide concentrations in the Arabian Gulf water of 64.0 mg/L. In these studies, concentrations of bromide in S1, S2 and S3 were found to be higher than the typical concentrations in drinking water (Table 1). Some studies have also 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 samples after swimming (S3 and S3-A) were higher than those before swimming (S2 and S2-A). The increase can be explained by the higher concentrations of organic matter in pool water (e.g. higher organics, N_2 , UV_{254}) owing to swimmers, higher water temperatures and higher concentrations of FRC.

Predictive models

DOC in water

DOC in swimming pool water depends on many factors including DOC in the tap water feeding the pool and human inputs. Precise measurement on the type and quantity of human inputs is difficult due to variability in personal hygiene, swimming duration, sweat and urinal

discharges and accumulation of contaminants in the pool water over time. The correlation analysis through Scatter-plot matrix showed that DOC in S2 and S3 are strongly correlated with DOC in S1 ($r = 0.85$ and 0.68 , respectively). The DOC in S3 were also correlated with the number of swimmers (N) with correlation coefficients (r) of 0.71 while DOC in S2 did not show significant correlation with N , indicating the possible contamination for S3 samples by the swimmers. The correlation coefficient between DOC and temperature and pH were not significant ($r = 0.06$ – 0.13 and $r = -0.08$ to -0.132 , respectively). The models in Equations (1)–(4) were trained and parameters were estimated using JMP™ and Minitab™ statistical software. The model performances were tested using the graphical (predicted vs. residual plot; normal probability plot) and numerical (F ratio; R^2 , RMSE, significance probability and lack of fit test) techniques. Among these models, the LMF and NN models showed good performance ($R^2 = 0.71$ and 0.60 , respectively). However, the LMF model was selected for better performance (Equation (6)).

$$\begin{aligned} \ln(DOC_{SPW}) = & -(0.2308 \pm 0.124) + (0.2718 \pm 0.0436) \\ & \times \ln(N) + (0.2882 \pm 0.064) \\ & \times \ln(DOC_{TW}) \end{aligned} \quad (6)$$

where DOC_{SPW} represents the DOC in the pool water after swimming, N = no. of swimmers and DOC_{TW} = DOC in the tap water feeding the pool. The F ratio and RMSE of the model are 108 and 0.103, indicating that the model has a good fit. The lack of fit was found to be insignificant with Prob > F of 0.2564 (Minitab Inc. 2014; SAS Inc. 2014). The residual vs. predicted plot were scattered and did not show any trend. The model was validated using an additional set of data, which was not used in model development. The original and modeled data plot is shown in Figure 3. The plot shows very good agreement between the original and modeled data ($r = 0.78$). Despite the variability related to personal hygiene, gap between showering, sweat and urinal discharges, swimming duration and water retention time, the LMF model was found to provide moderately acceptable results. The uncertainty in the parameters was incorporated using standard error (SE) terms in model parameters (Equation (6)). Through better understanding of the effects of these factors, a better model could be developed in the future. It is to be noted that the other factors, such as external pollution (e.g. air blown dust), evaporation and water retention time, can also affect the concentrations of DOC in water. Future study may also understand the effects from these factors to develop a better model.

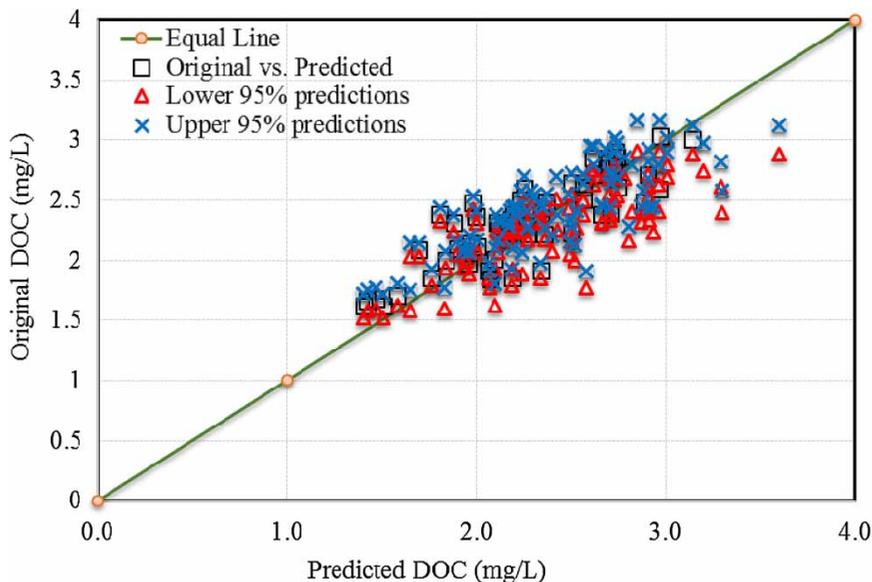


Figure 3 | Model validation using an additional set of measured and predicted DOC in pool water; DOC: dissolved organic carbon (mg/L).

THMs in pool water and air

To develop models for THMs in swimming pool water and air, the models in Equations (1)–(4) were trained using the JMP™ and Minitab™ statistical packages and the model parameters were estimated. The significant model parameters were identified through the screening module of JMP™ software (SAS Inc. 2014). The best models were selected through the graphical and numerical techniques as discussed earlier (SAS Inc. 2014). The LMFI model was found to be better than the other models (e.g. LMF, NL and NN models) for predicting THMs in the pool water. The model is presented in Equation (7):

$$\begin{aligned} THMs_{SPW} = & (5.61 \pm 3.29) + (12.74 \pm 1.29) \times DOC_{SPW} \\ & + (30.57 \pm 10.0) \times N_{2-SPW} + (0.014 \pm 0.003) \\ & \times COND_{SPW} + (117.24 \pm 20.5) \\ & \times (DOC_{SPW} - 2.37) \times (N_{2-SPW} - 0.16) \end{aligned} \quad (7)$$

where $THMs_{SPW}$ = THMs in swimming pool water ($\mu\text{g/L}$); DOC_{SPW} = DOC in pool water after swimming (mg/L), N_{2-SPW} = ammonia-nitrogen in pool water (mg/L); and $COND_{SPW}$ = conductivity in pool water ($\mu\text{S/cm}$). The actual vs. the predicted plot is presented in Figure 4. The R^2 value of the model was 0.70, the F ratio = 53.4 and the RMSE was 5.5 (Figure 4). The model validation study

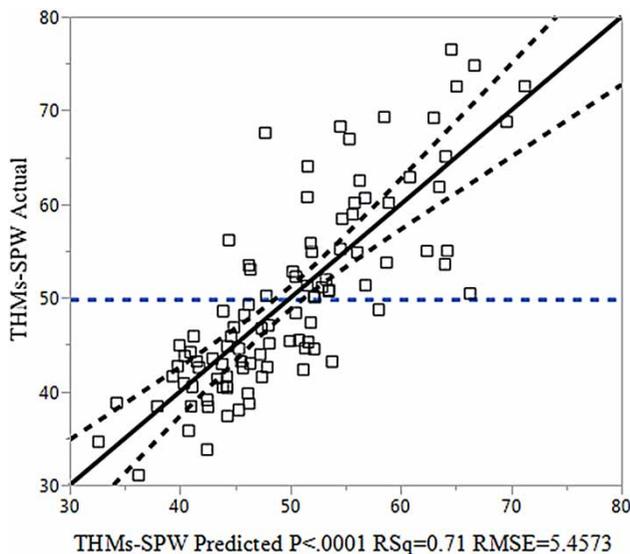


Figure 4 | Actual versus predicted plot for THMs in swimming pool water; THMs in $\mu\text{g/L}$.

showed (r) between the measured THMs and model predictions as 0.73, representing good agreement between the measured and predicted data. However, THM formation is relatively straightforward and thus higher values of R^2 and r were anticipated (Chowdhury *et al.* 2009). It is to be noted that swimming pool environment is complex (Hsu *et al.* 2009). The relatively low performance of the model may be partially explained by the variability in types and concentrations of organics, organics age in the pool water, air circulation pattern, air–water temperature difference, air exchange rate, which in combination, might affect the partition of THMs into the pool air (Chowdhury *et al.* 2014).

The effects of DOC_{SPW} , N_{2-SPW} , $COND_{SPW}$ and their interactions on THM formation were found to be significant (Equation (7)). The predictor profiler in Figure 5 shows that DOC_{SPW} , N_{2-SPW} and $COND_{SPW}$ had effects with positive slope. Higher conductivity might have increased the rate of reaction due to salting effects because of salt accumulation over time and evaporation of pool water. Further, the interaction effect of DOC_{SPW} and N_{2-SPW} was found to be significant (Figure 6). The contour profiler shows that the same level of THMs can be formed at lower N_{2-SPW} and higher DOC_{SPW} or at higher N_{2-SPW} and lower DOC_{SPW} beyond the corresponding thresholds (Figure 6). This is a major difference in context to drinking water, where such interaction was not found, possibly due to lower concentrations of N_2 in drinking water and/or DOC than the thresholds in most cases. The chemistry behind this interaction effect and the effects of conductivity is not clear. One possibility may be due to increased reactivity of organics at higher N_2 . Future study may further investigate such effects.

Predicting THMs in swimming pool air is complex. THMs in the pool air is likely to be affected by the activities of the attendants, water–air partition coefficients, open space to water ratio, difference in air–water temperature, air replacement rate, etc. (Hsu *et al.* 2009). Further, analytical measurement of THMs in the pool air is also a complicated job, which needs an air sample collection from the representative air space and a thermal desorption unit coupled to a gas chromatography. A reliable model can overcome such complex work. Using the experimental data, the models (Equations (1)–(4)) were trained. THMs

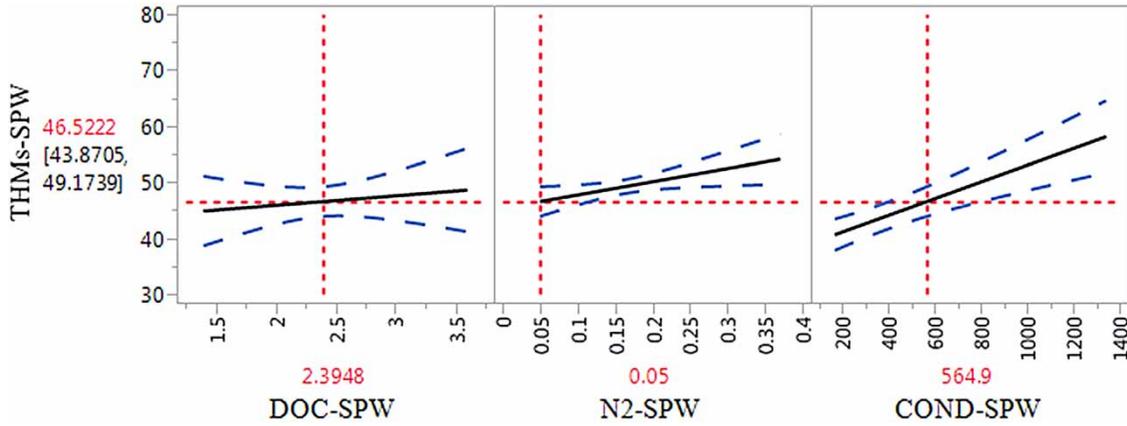


Figure 5 | Predictor profiler for DOC_{SPW} , N_{2-SPW} and $COND_{SPW}$ on THM formation (DOC_{SPW} : dissolved organic carbon in pool water (mg/L); N_{2-SPW} : ammonia nitrogen in pool water (mg/L); and $COND_{SPW}$: conductivity in pool water ($\mu S/cm$); THMs in $\mu g/L$).

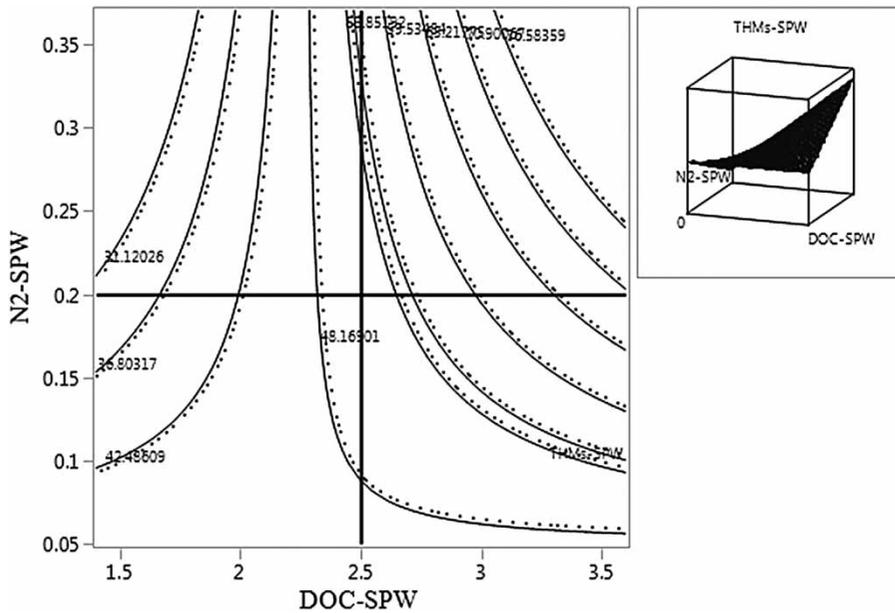


Figure 6 | Interaction effects of DOC_{SPW} and N_{2-SPW} on formation of THMs (DOC_{SPW} : dissolved organic carbon in pool water (mg/L); N_{2-SPW} : ammonia nitrogen in pool water (mg/L); THMs in $\mu g/L$).

in pool air were best represented by the four-parameter Logistic model (Equation (8)):

$$THM_{SPA} = 172.6 + \frac{(-46.0 - 172.6)}{[1 + \text{Exp}((THM_{SPW} - 45.7)/38.9)]} \quad (8)$$

The model has the R^2 and RMSE values of 0.87 and 3.9, respectively. The model plot for the 95-percentile confidence interval (CI) and the 95 percentile predicted interval (PI) are shown in Figure 7. Only two data points

were outside of the band of 95 percentile PI (Figure 7), indicating that the model predictive ability is good. The validation study resulted in high correlation coefficient for the measured and modeled data ($r=0.76$). As THM_{SPW} was the only predictor variable for the nonlinear model, the implications from the other factors and interactions were not represented in this model. To date, not much is known on such interactions. Future study is warranted to better understand these effects.

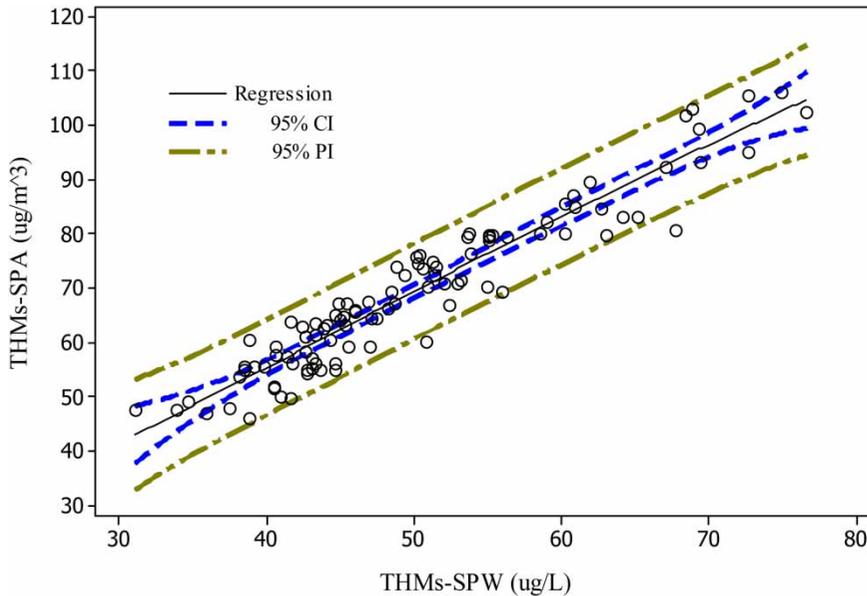


Figure 7 | The 95 percentile CI for the model training and the predicted values; THMs-SPA: THMs in swimming pool air ($\mu\text{g}/\text{m}^3$); THMs-SPW: THMs in pool water ($\mu\text{g}/\text{L}$).

HAAs in pool water

In many swimming pools, concentrations of HAAs were reported to be much higher than THMs (Lee *et al.* 2010; Simard *et al.* 2013), while in drinking water, the opposite is normally the case (Kanan & Karanfil 2011; Chowdhury 2013). In this study, HAAs was found to be 50.3–72.7% of the total DBPs with an average of 63.5%. This finding is consistent with past studies (Lee *et al.* 2010). Analytical measurement of HAAs is much more complex and time consuming than THMs in water (USEPA 1995a, 1995b). Availability of the model can assist in predicting HAAs in water following the use of selected parameters. As such, the complex experiments of determining HAAs can be minimized. Following model training, parameter estimation and graphical and numerical diagnostics (Equations (1)–(4)), the LMF model was found to be the best to predict HAAs in the pool water while the LMF, NL and NN models showed weaker performance. The model is represented in Equation (9) as:

$$\begin{aligned} HAAs_{SPW} = & (35.22 \pm 5.86) + (22.89 \pm 2.60) \\ & \times DOC_{SPW} + (0.30 \pm 0.11) \times N - (15.19 \pm 2.93) \times TC_{SPW} \\ & + (5.11 \pm 1.16) \times (N - 31.15) \times (N_{2-SPW} - 0.16) \end{aligned} \quad (9)$$

where $HAAs_{SPW}$ = HAAs in pool water ($\mu\text{g}/\text{L}$); TC = total chlorine (mg/L); N_{2-SPW} = ammonia nitrogen in water

(mg/L); and N = no. of pool attendants. The values of F ratio, R^2 and RMSE of the model were 87.1, 0.81 and 7.3, respectively. The model validation is presented in Figure 8. The correlation coefficient (r) between the measured and predicted HAAs is 0.83. The 95-percentile lower and upper values did not show significant variability, indicating good predictive capacity of the model. It is to be noted that the interaction of N and N_{2-SPW} were significant and positive for HAAs while interaction of DOC and N_{2-SPW} were significant and positive for THMs. However, N was also an important factor for predicting DOC_{SPW} . The results showed that the presence of N_{2-SPW} could have effects on the rate of THM and HAA formation. Better understanding is warranted to explain this effect.

Overall, the models developed in this study showed moderate to good performance. It is to be noted that the models developed in this study were based on the data from one swimming pool with specific characteristics. As such, applicability of these models to the swimming pools with different characteristics is likely to be limited. These models can be improved using additional data from multiple swimming pools with different characteristics in future. Further, conductivity and nitrogen were found to affect DBP formation in the pool water. Better understanding is needed on these factors in future.

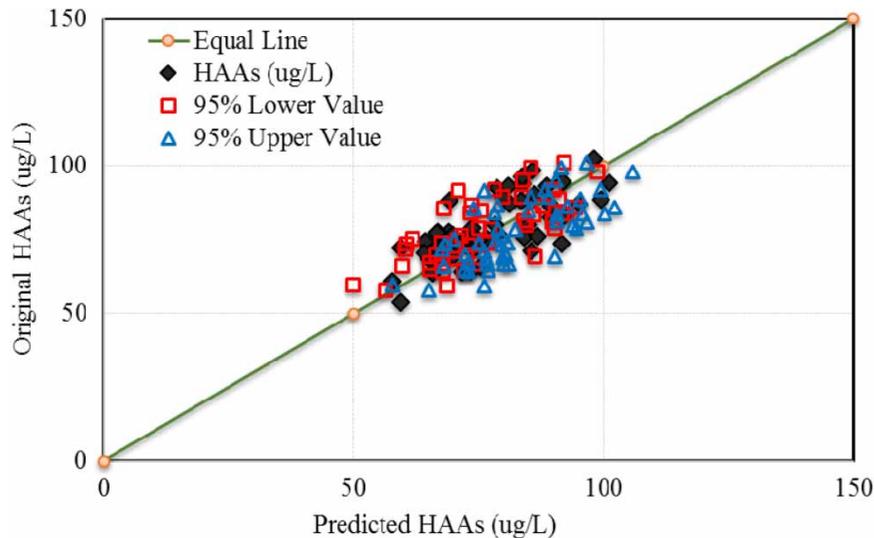


Figure 8 | Model validation using an additional set of measured and predicted HAAs in pool water.

CONCLUSIONS

Swimming pool water contains higher levels of NOM than tap water, which can lead to elevated formation of THMs and HAAs. Predictive models for THMs in pool water and air and HAAs in water are important to better manage DBPs in swimming pools. To date, limited studies have focused on model developments for THMs and HAAs in a swimming pool. In this study, four models are presented to predict DOC in pool water, THMs in pool water, THMs in pool air and HAAs in pool water. To develop each model, four types of generic models (Equations (1)–(4)) were trained and the parameters were estimated using Minitab™ and JMP™ statistical software. The best models were identified through comparing F ratio, R^2 , probability of significance (e.g. Prob > F), RMSE, lack of fit test, predicted vs. residual plots and predicted vs. actual plots. These models were validated using an additional set of data, which were not used in model training. A few interesting findings were noted in this study. The interaction of DOC and N_2 had a significant effect on THM formation, while the interaction of number of attendants (N) and N_2 had a significant effect on HAA formation. Further, conductivity was found to positively affect THM formation. This study has a few limitations in terms of data generation from a single swimming pool and future work should incorporate multiple swimming pools (indoor and outdoor) and develop

a data bank, which might be useful in developing better models and/or control exposure to potentially harmful DBPs in swimming pools. Despite these limitations, this study provides a basis for predicting DOC, THMs and HAAs in a swimming pool, which can be useful in developing the strategy for controlling potentially harmful DBPs.

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