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## An exploration of disinfection by-products formation and governing factors in chlorinated swimming pool water

Huma Ilyas, Ilyas Masih and Jan Peter van der Hoek

### ABSTRACT

This paper investigates disinfection by-products (DBPs) formation and their relationship with governing factors in chlorinated swimming pools. This study compares concentrations of DBPs with WHO guidelines for drinking water quality recommended to screen swimming pool water quality. The statistical analysis is based on a global database of 188 swimming pools accumulated from 42 peer reviewed journal publications from 16 countries. The mean and standard deviation of dichloroacetic acid and trichloroacetic acid were estimated as  $282 \pm 437$  and  $326 \pm 517 \mu\text{g L}^{-1}$ , respectively, which most often surpassed the WHO guidelines. Similarly, more than half of the examined pools had higher values of chloral hydrate ( $102 \pm 128 \mu\text{g L}^{-1}$ ). The concentration of total chloramines ( $650 \pm 490 \mu\text{g L}^{-1}$ ) was well above the WHO guidelines in all reported cases. Nevertheless, the reported values remained below the guidelines for most of the studied pools in the case of total trihalomethanes ( $134 \pm 160 \mu\text{g L}^{-1}$ ), dichloroacetonitrile ( $12 \pm 12 \mu\text{g L}^{-1}$ ) and dibromoacetonitrile ( $8 \pm 11 \mu\text{g L}^{-1}$ ). Total organic carbon, free residual chlorine, temperature, pH, total nitrogen and bromide ions play pivotal role in DBPs formation processes. Therefore, proper management of these governing factors could significantly reduce DBPs formation, thereby, contributing towards a healthy swimming pool environment.

**Key words** | best practices, chlorination, disinfection by-products, global database, swimming pool water, WHO guidelines

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### INTRODUCTION

Swimming is popular among people of all ages and income groups, as it can provide health benefits such as enhanced lung functions, and less respiratory symptoms especially among asthmatic children (Font-Ribera *et al.* 2011). Swimming pool activities are also beneficial for the development of physical fitness and water orientation for autistic children (Yilmaz *et al.* 2004). Considering the positive aspects of swimming, regulators, service providers and researchers have turned their attention to maintaining hygiene and bio-chemical water quality. Progress in the treatment of swimming pool water has made it an admired activity for leisure as well as exercise (Zwiener *et al.* 2007).

However, swimming pool water receives a wide variety of pathogenic micro-organisms (viruses, bacteria, protozoa

and fungi). There are a number of different routes by which these micro-organisms may be delivered: direct excretion by bathers, transport on the body or growth within the filter bed (Bonnick 2005). Therefore, the disinfection of swimming pool water is extremely essential to keep the encouraging aspect of aquatic activities, hygienic safety and protection of swimmers against infectious diseases caused by pathogenic micro-organisms (Lee *et al.* 2010; Schmalz *et al.* 2011).

In practice, chlorination is the most commonly used method of disinfection in recreational water settings, aimed at the prevention of waterborne diseases and inactivation of pathogenic micro-organisms in swimming pools (Chowdhury *et al.* 2014). The chemicals used for

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chlorination of swimming pool water are: chlorine gas, calcium/sodium/lithium hypochlorite, dichloro isocyanorates (DCCA) and trichloro isocyanorates (TCCA) (Chowdhury *et al.* 2014; Teo *et al.* 2015; Manasfi *et al.* 2017a). In the comparative studies on the use of different chemicals for chlorination of swimming pool water, TCCA showed higher concentrations of FRC and the lower DBPs formation compared with sodium hypochlorite. This indicates the feasibility of TCCA as stabilized chlorine (Yang *et al.* 2016). The stabilization effect of TCCA sustains a slower release of free chlorine, thus, less chlorine is available for DBP formation, and consequently higher FRC (Yang *et al.* 2016). Despite significantly contributing in ensuring good quality water to a certain extent, the use of chlorination in pools has some drawbacks as well, for instance, the presence of resistant micro-organism such as *Cryptosporidium parvum* and *Giardia lamblia* even after chlorination, since these micro-organisms are resistant to chemical disinfectants (Korich *et al.* 1990) and formation of potentially toxic disinfection by-products (DBPs) (Glauner *et al.* 2005a; Zwiener *et al.* 2007; Manasfi *et al.* 2017a; Vlaanderen *et al.* 2017). Past research identified more than 100 DBPs in pool water samples (Richardson *et al.* 2010; Daiber *et al.* 2016). Among the known carbonaceous DBPs (C-DBPs), the most common are trihalomethanes (THMs), haloacetic acids (HAAs) and trihaloacetaldehydes (THAs), and among the nitrogenous DBPs (N-DBPs), the most common are haloacetonitriles (HANs) and chloramines (CAMs) (Zwiener *et al.* 2007; Weaver *et al.* 2009; Lee *et al.* 2010; Manasfi *et al.* 2016). N-DBPs are formed when organic and inorganic nitrogen compounds react with chlorine (Zwiener *et al.* 2007; Richardson *et al.* 2010; Teo *et al.* 2015). Toxicological studies showed that some N-DBPs (HANs) are more genotoxic and cytotoxic than C-DBPs (THMs and HAAs) (Muellner *et al.* 2007; Richardson *et al.* 2007; Plewa *et al.* 2008; Hansen *et al.* 2012). Besides these commonly detected C-DBPs and N-DBPs, some studies have reported the formation of carbonaceous aromatic DBPs (C-ADBPs) such as halophenols (HPs) (Richardson *et al.* 2010; Xiao *et al.* 2012; Daiber *et al.* 2016), and nitrogenous aromatic DBPs (N-ADBPs) such as halonitrophenols (HNPs) (Xiao *et al.* 2012). These N-ADBPs exhibit substantially higher developmental toxicity than C-ADBPs (Yang & Zhang 2013).

Additionally, some studies also reported the use of bromine based disinfectants, using Bromochlorodimethylhydantoin (BCDMH) (Richardson *et al.* 2010; Lourencetti *et al.* 2012; Yang *et al.* 2016; Daiber *et al.* 2016) and hypobromous acid (HOBr) (Judd & Jeffrey 1995). Nevertheless, the studies with bromination are limited because BCDMH is not recommended due to its highly reactive disinfecting ingredient, HOBr, as it cannot sustain the continuous disinfection requirement (Yang *et al.* 2016). Moreover, with bromination the bromide ions ( $\text{Br}^-$ ) increase in the pool water, which favors the formation of brominated species of DBPs (Uyak & Toroz 2007; Richardson *et al.* 2010; Lourencetti *et al.* 2012; Yang *et al.* 2016). Furthermore, the brominated DBPs (Br-DBPs) are generally more toxic than their equivalent chlorinated DBPs (Cl-DBPs) (Plewa *et al.* 2002, 2008; Muellner *et al.* 2007; Daiber *et al.* 2016; Manasfi *et al.* 2017b). In spite of toxicity concerns, one recent study suggested that Br-THMs in exhaled breath could be used as a non-invasive DBP exposure biomarker in swimming pools (Font-Ribera *et al.* 2016).

The formation of toxic DBPs with chlorination and bromination has motivated further research on the use of alternative and emerging methods of disinfection such as ultraviolet (UV) irradiation (Cimetiere & De Laat 2014; Afifi & Blatchley 2016; Cheema *et al.* 2017a), ozone ( $\text{O}_3$ ) (Hang *et al.* 2016; Hansen *et al.* 2016), UV based advanced oxidation processes (AOPs) such as UV/hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Spiliotopoulou *et al.* 2015), and ozone based AOPs such as  $\text{O}_3/\text{UV}$  and  $\text{O}_3/\text{H}_2\text{O}_2$  (Glauner *et al.* 2005b; Kristensen *et al.* 2009; Cheema *et al.* 2017b) to improve the quality of swimming pool water. However, these methods are not widely used in practice, and are still in the research and development phase (Ilyas *et al.* 2018).

The DBPs classification based on their toxicity, according to US EPA (IRIS) and guidelines on limits of their concentrations in drinking water according to WHO (2017), are presented in Table 1. The guidelines for DBPs for swimming pool water are not specified by WHO. However, it is recommended to use drinking water guidelines for the screening of swimming pool waters, though keeping in view some allowance as the human consumption of water is much lower in swimming activities compared with drinking (WHO 2006). It is also recognized that the conditions for the treatment of drinking water are completely different

**Table 1** | Carcinogenic group classification and WHO guidelines for DBPs

Compound	Carcinogenic group (US EPA, IRIS)	WHO Guidelines-upper limits ( $\mu\text{g L}^{-1}$ ) (WHO 2006, 2017) <sup>a</sup>
Chloroform	B2	300
Bromodichloromethane	B2	60
Dibromochloromethane	C	100
Bromoform	B2	100
Total trihalomethanes	–	100
Monochloroacetic acid	–	20
Dichloroacetic acid	C	50
Trichloroacetic acid	B2	200
Dichloroacetonitrile	D	20
Dibromoacetonitrile	D	70
Chloral hydrate	C	10
Total chloramines	–	<200

Note: Group B2: Probable human carcinogen (sufficient data from animal studies); Group C: Possible human carcinogen; Group D: Not classifiable as to human carcinogenicity.

<sup>a</sup>The guideline value of tCAM is for swimming pool water, other parameters have only drinking water reference.

from the treatment of swimming pool water. Compared with drinking water, swimming pool water DBPs have their own distinct characteristics due to the different nature of organic precursors (Kim *et al.* 2002; WHO 2006; Keuten *et al.* 2014), and continuous loading of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON), which are released by swimmers. All these factors add an additional complication to the disinfection and toxicological safety of swimming pool water (Zwiener *et al.* 2007). Furthermore, in reasonably well managed pools, concentrations of DBPs even less than the drinking water guideline values can be achieved (WHO 2006). Following on from the WHO recommendations, some studies (e.g. Simard *et al.* 2013; Yeh *et al.* 2014) have applied drinking water guidelines for evaluating swimming pool water quality. There is very limited published information on country specific guidelines for swimming pool water (Supplementary material S1). The suggested limits by six European countries for total THMs (tTHMs) for swimming pool water were in the range of 20–100  $\mu\text{g L}^{-1}$ . These values are equal to or even stricter than the WHO guidelines for drinking water. On the other hand, total CAMs (tCAMs) limits were reported in the range of 100–1,000  $\mu\text{g L}^{-1}$  by a few countries, which are

less strict than the swimming pool water guidelines for tCAMs in some cases (WHO 2006) (Table 1). In contrast, a TCM limit of 100  $\mu\text{g L}^{-1}$  was reported for only one country (Belgium), being a more stringent limit compared with WHO guidelines for drinking water. We could not find any published guidelines on other DBPs. Therefore, from the above mentioned studies and arguments, we safely decided to use the WHO drinking water guidelines to screen swimming pool water quality for the purpose of this evaluation study.

The formation and distribution of DBPs depends on several factors such as source water, Br<sup>-</sup> concentration, chlorine dose and free residual chlorine (FRC), total organic carbon (TOC), total nitrogen (TN), temperature and pH (e.g. Kanan 2010; Simard *et al.* 2013; Teo *et al.* 2015; Hang *et al.* 2016; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a). While several individual studies have noted the impact of these factors on DBPs formation, the research synthesizing these impacts is needed. For instance, several studies showed an increase in DBPs when pool temperature increases. However, a comprehensive overview and statistical analysis on the available evidence is still missing, which limits the generalization of the nature and significance of this relationship. Another unanswered question is whether this relationship is strong enough to establish mathematical relationships (e.g. through regression analysis) that can help in predicting concentrations of DBPs. Similarly, a critical analysis of studies reporting increase, decrease or no change in certain species of DBPs with changes in pH is lacking before sound conclusions can be drawn about its impact. Moreover, the available studies, including a limited number of critical reviews (e.g. Zwiener *et al.* 2007; Chowdhury *et al.* 2014; Teo *et al.* 2015; Manasfi *et al.* 2017a), appear to assume a kind of linear relationship among water quality parameters and DBPs, which needs to be tested. Thus, in general, there is a need to conduct a comprehensive and critical review on DBPs formation, and establish the nature and significance of the relationship among DBPs and governing factors. For instance, in the previous review by Chowdhury *et al.* (2014), Teo *et al.* (2015) and Manasfi *et al.* (2017a), the occurrence of different DBPs in swimming pool water and some of the governing factors are discussed, but the statistical analysis to verify the correlation of different factors with DBPs formation has not been conducted. In fact, a recommendation was made by

Chowdhury *et al.* (2014) to compile a database from available studies (e.g. on DBPs and water quality parameters) which can significantly contribute in validating the nature and strength of such relationships, and where possible develop predictive models (e.g. regression equations and process based models). Furthermore, despite many studies having been conducted, research is lacking on distilling the best practices out of the available evidence. Thus, there is a need to conduct a synthesis to suggest best practices that can assist in ensuring good quality water for swimming pools. Similarly, a large number of studies on the subject provide an opportunity to compare swimming pool water quality with the recommended guidelines (e.g. recommended by WHO (2006, 2017)) available for some DBPs.

Therefore, the objective of this review paper is to fill the above mentioned research and knowledge gaps by conducting a comprehensive and critical review of the different factors influencing the formation of DBPs, and to compile a database for further analysis on their reported values from the available literature. The chlorinated and brominated swimming pools are the subject of this exploration. The specific research questions investigated in this study are:

- What are the values reported for DBPs and water quality parameters (temperature, pH, FRC, TOC, TN and Br<sup>-</sup>) in the peer reviewed literature?
- What is the nature of relationship (e.g. positive or negative) and statistical significance of it among most commonly reported DBPs and governing factors such as temperature, pH, FRC, TOC, TN and Br<sup>-</sup>?
  - Could the established correlation be used to develop mathematical relationships (e.g. regression equations) to reliably determine the formation of DBPs from governing factors?
- To what extent do the reported values of DBPs fall within the WHO drinking water guidelines that are recommended for screening of swimming pool water?
- What kind of best practices to limit DBPs formation could be synthesized from the available research?

While answering these questions, this review has conducted an original and novel synthesis of available studies, compiled a comprehensive database, and generated new insights, which could be instructive for improving scientific

understanding, guiding further research and practice on enhancing water quality and healthy environment around swimming pool waters.

## METHODOLOGY

The snowball sampling method yielded over 100 journal articles. The publications were searched from several sources, such as Google Scholar, Scopus and individual journal websites, related to the disinfection of swimming pool water. However, many studies only reported descriptive statistics, mostly means, standard deviations and ranges. While these statistics are very useful, they were not found fitting to conduct correlation analysis, for example, mean values carry the accumulated effect of many pools and may not be a representative pool sample. Therefore, a purposive selection of individual pools was made from all the available studies where such records were given. Thus, the global database was compiled containing information of several individual swimming pools, which was used for the purpose of this study. Consequently, this study was based on the data compiled for 188 individual swimming pools that were reported in 42 peer reviewed journal publications with case studies from 16 countries. This novel database is given as Supplementary material S2 (Tables S1–S5). This database contained concentrations of several species of different types of DBPs (THMs, HAAs, HANs, THAs and CAMs), as well as several other parameters such as water quality parameters (temperature, pH, FRC, TOC, TN and Br<sup>-</sup>), source water (e.g. fresh and sea), pool location (indoor and outdoor) and disinfection and detection methods.

Then, first a detailed analysis of the reported DBPs was conducted from the studied literature including the designed database, which focused on types, species and concentrations of DBPs and identification of the governing factors reported in the literature. Second, statistical analysis was conducted to answer the questions related to DBPs concentrations, their relationship with water quality parameters (through correlation and regression analysis) and compliance with WHO guidelines. The estimated descriptive statistics (e.g. mean, standard deviation, ranges, median and quartiles) helped in examining the central tendency and dispersion of the studied data. The well-known Pearson product-moment correlation

(r) was applied to estimate the linear correlation. The simple linear regression provided further information on the relationship between water quality parameters and DBPs. Finally, the best practices were synthesized from the reviewed studies and statistical analysis conducted in this research.

## RESULTS AND DISCUSSION

### Types and species of DBPs

The types and species of DBPs considered in this review are given in Table 2 and their detailed description is presented in this section.

Among the studied DBPs, THMs and HAAs are the most regularly measured and best studied. The other DBPs, such as HANs and THAs, have not been measured as comprehensively and hence, little information is available about these DBPs in swimming pools (Lee *et al.* 2010; Chowdhury *et al.* 2014; Teo *et al.* 2015; Manasfi *et al.* 2017a).

### THMs

As stated earlier, THMs are well studied and commonly detected DBPs compared with the other DBPs (Lee *et al.* 2010; Chowdhury *et al.* 2014; Teo *et al.* 2015). The occurrence of four THMs (Table 2) in swimming pool water has been reported in several studies. Among the four THMs, TCM (chloroform) is the most documented and most dominant in freshwater pools and TBM (bromoform) is the most dominant in seawater pools compared with the other THMs (Table S1). TCM and TBM are categorized as probable human carcinogens (US EPA, IRIS) (Table 1). The estimates from the reviewed studies indicated the concentrations of TCM, TBM and tTHMs as  $108 \pm 140$ ,  $58 \pm 152$  and  $134 \pm 160 \mu\text{g L}^{-1}$ , respectively.

### HAAs

The occurrence of nine HAAs (Table 2) in swimming pool water has been reported in several studies (e.g. Sarrion

**Table 2** | Types and species of DBPs

DBPs type	DBPs species	Abbreviation	Chemical formula
Trihalomethanes (THMs)	Trichloromethane (chloroform)	TCM	$\text{CHCl}_3$
	Bromodichloromethane	BDCM	$\text{CHBrCl}_2$
	Dibromochloromethane	DBCM	$\text{CHBr}_2\text{Cl}$
	Tribromomethane (bromoform)	TBM	$\text{CHBr}_3$
Haloacetic acids (HAAs)	Monochloroacetic acid	MCAA	$\text{CH}_2\text{ClCOOH}$
	Dichloroacetic acid	DCAA	$\text{CHCl}_2\text{COOH}$
	Trichloroacetic acid	TCAA	$\text{CCl}_3\text{COOH}$
	Monobromoacetic acid	MBAA	$\text{CH}_2\text{BrCOOH}$
	Dibromoacetic acid	DBAA	$\text{CHBr}_2\text{COOH}$
	Bromochloroacetic acid	BCAA	$\text{CHBrClCOOH}$
	Bromodichloroacetic acid	BDCAA	$\text{CBrCl}_2\text{COOH}$
	Dibromochloroacetic acid	DBCAA	$\text{CBr}_2\text{ClCOOH}$
	Tribromoacetic acid	TBAA	$\text{CBr}_3\text{COOH}$
Haloacetoneitriles (HANs)	Dichloroacetoneitrile	DCAN	$\text{CHCl}_2\text{CN}$
	Trichloroacetoneitrile	TCAN	$\text{CCl}_3\text{CN}$
	Bromochloroacetoneitrile	BCAN	$\text{CHBrClCN}$
	Dibromoacetoneitrile	DBAN	$\text{CHBr}_2\text{CN}$
	Chloroacetoneitrile	CAN	$\text{CH}_2\text{ClCN}$
	Bromoacetoneitrile	BAN	$\text{CH}_2\text{BrCN}$
Trihaloacetaldehydes (THAs)	Chloral hydrate	CH	$\text{CCl}_3\text{CH}(\text{OH})_2$ or $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$
	Bromal hydrate	BH	$\text{CBr}_3\text{CH}(\text{OH})_2$ or $\text{C}_2\text{H}_3\text{Br}_3\text{O}_2$
Chloramines (CAMs)	Monochloramine	MCAM	$\text{NH}_2\text{Cl}$
	Dichloramine	DCAM	$\text{NHCl}_2$
	Trichloramine	TCAM	$\text{NCl}_3$

*et al.* 2000; Loos & Barceló 2001; Kanan 2010; Cardador & Gallego 2010; Parinet *et al.* 2012; Hang *et al.* 2016; Manasfi *et al.* 2016; Yang *et al.* 2016). Among the nine HAAs, DCAA and TCAA are the most common in freshwater pools (Table S2), and are categorized as possible and probable human carcinogens, respectively (US EPA, IRIS) (Table 1). DCAA and TCAA are also the most detected and dominant HAAs in indoor and outdoor swimming pools reported in some studies (Kanan 2010; Simard *et al.* 2013; Wang *et al.* 2014; Yeh *et al.* 2014; Tardif *et al.* 2016; Yang *et al.* 2016). HAAs received attention very recently and the concentrations of HAAs are much higher than THMs in chlorinated freshwater pools (Lee *et al.* 2010; Simard *et al.* 2013; Yeh *et al.* 2014; Manasfi *et al.* 2016) (Tables S1 and S2). For instance, the mean and standard deviation of two widely reported HAAs, DCAA and TCAA, were estimated as  $282 \pm 437$  and  $326 \pm 517 \mu\text{g L}^{-1}$ , respectively. However, in chlorinated seawater pools DBAA and TBAA are the most dominant among the other HAAs. The mean and standard deviation of DBAA and TBAA were estimated as  $43 \pm 145$  and  $51 \pm 86 \mu\text{g L}^{-1}$ , respectively (Table S2). The highest level of HAAs could be due to their less volatile nature compared with other DBPs (e.g. THMs) (Lee *et al.* 2010). Therefore, HAAs are more likely to remain in pool water after their formation (Chowdhury *et al.* 2014; Teo *et al.* 2015). On the other hand, turbulence caused by the movement of swimmers could influence the release of volatile DBPs (e.g. THMs) into the air (Aggazzotti *et al.* 1995, 1998). In addition to that, the very high concentrations of HAAs are likely due to bather organic loads in the swimming pool water, which tend to preferentially form HAAs than THMs. Furthermore, HAAs are highly soluble in water and do not degrade in the presence of high FRC (Kanan & Karanfil 2011).

### HANs

HANs have been investigated as nitrogenous DBPs (N-DBPs) in swimming pool water (Teo *et al.* 2015). HANs were investigated by fewer studies compared with THMs and HAAs (Chowdhury *et al.* 2014). Among HANs (Table 2), DCAN are predominant in freshwater pools and DBAN in seawater pools (Table S3). DCAN and DBAN

are not classifiable to human carcinogenicity because of conflicting information regarding their carcinogenic effects (US EPA, IRIS) (Table 1). The reported concentrations of these species were  $12 \pm 12$  and  $8 \pm 11 \mu\text{g L}^{-1}$ , respectively. Although the estimated values are much lower (Table S3) than THMs and HAAs (Tables S1 and S2), HANs are considered more toxic than THMs and HAAs (Muellner *et al.* 2007; Richardson *et al.* 2007; Plewa *et al.* 2008; Hansen *et al.* 2012).

### THAs

Among THAs, CH and BH are the most common in swimming pool water. These are the hydrated forms of trichloroacetaldehyde (TCA) and tribromoacetaldehyde (TBA), respectively, which belong to the chemical class of haloacetaldehydes. According to the haloform formation mechanism, THA is generated by the oxidation and chlorination reaction between ethanol and chlorine, which under basic (high pH) conditions and high temperature decomposes by hydrolysis to their corresponding THM (Takahashi *et al.* 2003; Koudjonou & LeBel 2006). Source tap water contains natural organic matter (NOM) (Kanan & Karanfil 2011) and NOM from humic origin (humic and fulvic acids, and humic substances) favors the formation of CH (WHO 2017). CH is classified as possible human carcinogen (US EPA, IRIS) (Table 1). BH exhibits mutagenic and genotoxic potential (Manasfi *et al.* 2017b). The information about CH and BH is very limited (Table S4) as these DBPs have not been measured extensively (Lee *et al.* 2010; Manasfi *et al.* 2017c). CH has been reported among the most abundant DBP by weight (Cimetiere & De Laet 2014; Manasfi *et al.* 2016). CH is dominant in freshwater pools and BH in seawater pools. The reported data suggest that the concentration of CH and BH was in the range of 0.2–378 and 0.1–12  $\mu\text{g L}^{-1}$ , with means and standard deviations of  $102 \pm 128$  and  $5.0 \pm 5.0 \mu\text{g L}^{-1}$ , respectively (Table S4).

### CAMs

CAMs have been investigated as N-DBPs in swimming pool water (Weaver *et al.* 2009; Hansen *et al.* 2013; Simard *et al.* 2013; Chowdhury *et al.* 2014). Ammonia (inorganic nitrogen

compound) is found in pools as a consequence of the presence of urine. Chlorine reacts with ammonia to produce CAMs such as MCAM, DCAM and TCAM (Bonnick 2005; Li & Blatchley III 2007) (Table 2). In the first step, FRC in pool water and ammonia from urine form MCAM. However, further reactions with excess FRC forms DCAM and TCAM. The production and distribution of MCAM, DCAM and TCAM are highly dependent upon pH, the ratio of chlorine to organic-nitrogen, temperature and contact time (Florentin *et al.* 2011). In addition, TCAM can be formed from nucleophilic substitution reactions of nitrogen atoms in organic molecules (Chowdhury *et al.* 2014). MCAM, DCAM and TCAM are volatile, and TCAM is the most volatile compound of the three. The volatility of TCAM is about 300 times higher than MCAM (Florentin *et al.* 2011). Therefore, the concentration of MCAM is higher compared with DCAM and TCAM in chlorinated pools (Table S5). TCAM is slightly soluble in water ( $0.025 \text{ mol L}^{-1}$ ,  $25^\circ\text{C}$ , pH 1.0–10), therefore, its concentrations above this limit volatilize into the air and it is four times more volatile than TCM. TCAM is an irritant and in higher concentrations an explosive compound of penetrating odor (Schmalz *et al.* 2011). Exposure of children to TCAM may adversely affect the lung epithelium permeability (Bernard *et al.* 2003) and increase the risk of developing asthma in children and adults (Bernard *et al.* 2003; Richardson *et al.* 2010; Parrat *et al.* 2012). A guideline value of  $500 \mu\text{g m}^{-3}$  for TCAM for indoor air quality at swimming pools has been proposed by INRS (French institute for Occupational Health and Safety), based on findings that no irritating effects were reported below this level (Gagnaire *et al.* 1994; Hery *et al.* 1995). However, Parrat *et al.* (2012) demonstrated an increasing risk of irritative symptoms due to TCAM up to a level of 200–300  $\mu\text{g m}^{-3}$  for indoor pools in Switzerland. Therefore, they strongly suggest fixing the TCAM occupational exposure limit at  $300 \mu\text{g m}^{-3}$ . The reported concentration of TCAM and tCAMs in pool water was  $149 \pm 136$  and  $650 \pm 490 \mu\text{g L}^{-1}$ , respectively and TCAM in air was  $216 \pm 76 \mu\text{g m}^{-3}$ .

### Effect of different factors on DBPs formation

The available studies have given much attention to describing the effect of different factors on DBPs formation

(Table 3). From the reported factors in literature, the impacts of pool location, source water, and disinfection and detection method are discussed in detail. A comprehensive descriptive and statistical analyses was conducted on water quality parameters (temperature, pH, FRC TOC, TN and  $\text{Br}^-$ ), for which a reasonably good amount of data was available from the reviewed studies. An overview of typical and possible values of these parameters can be seen in Table 4 where some descriptive statistics estimated for the studied pools are presented.

### Effect of pool location

Most of the studies presented in Table S1 were conducted on chlorinated indoor swimming pools. Zwiener *et al.* (2007) indicated that the relative concentration of THMs was higher in indoor pools compared with outdoor pools, due to wind-enhanced volatilization of THMs from outdoor pools. On the contrary, Beech *et al.* (1980) reported a higher level of tTHMs ( $118\text{--}657 \mu\text{g L}^{-1}$ ) in outdoor pools (Table S1). Similarly, Simard *et al.* (2013) observed a higher level of tTHMs (up to  $311 \mu\text{g L}^{-1}$ ) in outdoor pools compared with indoor pools (up to  $114 \mu\text{g L}^{-1}$ ). This was attributed to the fact that outdoor pools are exposed to the external environment, and some additional factors such as wind, grass, soil, leaves, insects, rain and temperature may be able to increase the level of contamination of water leading to poor quality of water. Furthermore, photo-degradation of TOC is increased by UV irradiation in outdoor pools and subsequently the formation of tTHMs.

In the comparative studies of indoor and outdoor pools, the reported concentration of HAAs in indoor pools is high compared with the concentration in outdoor pools (Wang *et al.* 2014; Yeh *et al.* 2014) (Table S2). For instance, Wang *et al.* (2014) reported a concentration of total HAAs (tHAAs) up to 3,980 and  $2,430 \mu\text{g L}^{-1}$  in indoor and outdoor pools, respectively. Contrarily, some studies observed a high level of HAAs in outdoor pools compared with the level in indoor pools (Cardador & Gallego 2011; Simard *et al.* 2013) (Table S2). For instance, Simard *et al.* (2013) reported a concentration of tHAAs up to 1,195 and  $2,224 \mu\text{g L}^{-1}$  in indoor and outdoor pools, respectively.

The concentration of tCAMs was less in outdoor pools ( $8.0\text{--}854 \mu\text{g L}^{-1}$ ) compared with the concentration in



**Table 3** | Summary of the effects of different factors on DBPs formation in chlorinated swimming pool water

Factors increase	DBPs formation	Effect	Author
Temperature	THMs	Increase	Chu & Nieuwenhuijsen (2002); Kanan (2010); Hansen <i>et al.</i> (2012); Simard <i>et al.</i> (2013)
	HAAs	Increase	Kanan (2010); Hansen <i>et al.</i> (2012); Simard <i>et al.</i> (2013)
	HANs	Increase	Kanan (2010); Hansen <i>et al.</i> (2012)
	CAMs	Decrease	Simard <i>et al.</i> (2013)
pH	THMs	Increase	Kanan (2010); Hansen <i>et al.</i> (2012)
	HAAs	Increase/No change	Kanan (2010); Hansen <i>et al.</i> (2012)
	HANs	Decrease	Kanan (2010); Lee <i>et al.</i> (2010); Hansen <i>et al.</i> (2012)
	CAMs	Decrease	Schmalz <i>et al.</i> (2011); (Hansen <i>et al.</i> (2012)
Total organic carbon	THMs	Increase	Chu & Nieuwenhuijsen (2002); Kanan (2010); Lee <i>et al.</i> (2010); Parinet <i>et al.</i> (2012); Simard <i>et al.</i> (2013); Hang <i>et al.</i> (2016)
	HAAs	Increase	Lee <i>et al.</i> (2010); Parinet <i>et al.</i> (2012); Simard <i>et al.</i> (2013); Hang <i>et al.</i> (2016)
	HAN	Increase	Kanan (2010); Lee <i>et al.</i> (2010); Hang <i>et al.</i> (2016)
	CH	Increase	Lee <i>et al.</i> (2010)
Free residual chlorine	THMs	Increase	Hansen <i>et al.</i> (2012); Simard <i>et al.</i> (2013); Hang <i>et al.</i> (2016)
	HAAs	Increase	Hansen <i>et al.</i> (2012); Wang <i>et al.</i> (2014); Hang <i>et al.</i> (2016)
	HANs	Increase/decrease	Hang <i>et al.</i> (2016)/Weng <i>et al.</i> 2012; Hansen <i>et al.</i> (2013)
	CAMs	Decrease	Li & Blatchley III (2009)
Total nitrogen			
Urea and ammonia	THMs	Decrease	Judd & Jeffrey (1995); Kim <i>et al.</i> (2002); Yang <i>et al.</i> (2016)
Amino acids	HAAs	Increase	Kanan (2010); Kanan & Karanfil (2011); Parinet <i>et al.</i> (2012)
Amino acids	HANs	Increase	Kim <i>et al.</i> (2002); Li & Blatchley (2007); Weaver <i>et al.</i> (2009); Weng <i>et al.</i> (2012)
Urea and ammonia	CAMs	Increase	Li & Blatchley III (2007); Schmalz <i>et al.</i> (2011)
Bromide ion	Brominated species of DBPs	Increase	Lourencetti <i>et al.</i> (2012); Parinet <i>et al.</i> (2012); Yang <i>et al.</i> (2016); Daiber <i>et al.</i> (2016); Manasfi <i>et al.</i> (2016, 2017c); Cheema <i>et al.</i> (2017a)

**Table 4** | A statistical summary of the water quality parameters in the studied pools

Statistics	Temperature	pH	FRC	TOC	TN	Br <sup>-</sup>
No. of observations	110	146	150	110	28	30
Mean	32	7.5	1.9	15	3.7	47
STDEV	5.4	0.4	1.8	23	2.9	41
Min	18	6.7	0.2	0.9	0.7	0.1
Quartile 1	28	7.4	0.8	3.4	1.8	0.4
Median	30	7.5	1.5	6.2	2.8	71
Quartile 3	40	7.6	2.1	15	4.6	78
Max	40	8.5	11	155	12	107

Note: FRC, free residual chlorine; TOC, total organic carbon; TN, total nitrogen; Br<sup>-</sup>, bromide ion.

indoor pools (311–1,723 µg L<sup>-1</sup>) (Simard *et al.* 2013) due to a less confined atmosphere in outdoor pools which leads to the higher volatility of CAMs. In outdoor pools there is

also the possibility of photo-degradation of CAMs by UV irradiation (WHO 2006; Li & Blatchley III 2009). Therefore, it may be possible that the concentration of tCAMs that may form during the chlorination of water in outdoor pools was underestimated (Simard *et al.* 2013). Analogous to tCAMs, a lower concentration of TCAM in outdoor pool water was observed (Li & Blatchley III 2007) (Table S5). Some other studies also reported a higher concentration of tCAMs in indoor pool water (Judd & Black 2000; Weaver *et al.* 2009; Catto *et al.* 2012; Mah & Heacock 2014) (Table S5). Similarly, higher levels of TCAM were observed in indoor pool air (Jacobs *et al.* 2007; Bessonneau *et al.* 2011; Tardif *et al.* 2016). For instance, Bessonneau *et al.* (2011) observed levels of TCAM up to 1,260 µg m<sup>-3</sup>, which indicates that indoor pools need better ventilation system (Chowdhury *et al.* 2014).

The above evidence indicates both advantages and disadvantages of pool location, thus, it seems difficult to indicate which location is the best to control a wide range of DBPs.

### Effect of source water

The source water used to fill the swimming pool was freshwater from all sources (tap, ground and surface) and seawater. Past research reveals that the nature of source water affects the level and speciation of DBPs. For instance, chlorination of the materials of human origin mixed with ground water or surface water indicated a significant correlation between TOC and DBPs formation, but the types, species and level of DBPs were different due to different water sources (Kim *et al.* 2002). They assumed that the ground water did not contain nitrogen-containing compounds, including ammonia. The level of THMs (TCM) decreased when urine was added to the ground water matrix. This was attributed to the depletion of active FRC due to the formation of less reactive CAMs. Surface water already contains nitrogen-containing compounds of natural origin, therefore, the introduction of urine into surface water may not sharply change the FRC to combined chlorine ratio which leads to the formation of TCM. Some studies indicated that chlorinated tap water used as source water also contained DBPs (Lee *et al.* 2010; Simard *et al.* 2013; Daiber *et al.* 2016). In contrast, in the recent study of Peng *et al.* (2016), it was reported that non-chlorinated tap water did not contain, or contained very little, THMs, which was below the detection limit ( $<0.4 \mu\text{g L}^{-1}$ ). However, source tap water contains NOM (Kanan & Karanfil 2011), and the NOM from humic origin (humic and fulvic acids, and humic substances) favors the formation of DBPs such as THMs (Lahl *et al.* 1981; Thacker & Nitnaware 2003; WHO 2006, 2017; Kanan & Karanfil 2011; Yang *et al.* 2016) and CH (WHO 2017). The presence of  $\text{NH}_4^+\text{-N}$  in source tap water may be a nitrogen source for the formation of HANs (Hang *et al.* 2016). Seawater contains  $\text{Br}^-$ , when it is used as source water the formation of brominated species of DBPs is promoted (Parinet *et al.* 2012; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a).

In freshwater and seawater pools, the dominant THMs and HANs were analogous compounds though with a

molecular difference due to the nature of halogen incorporated in the compound (chlorine versus bromine). For instance, chlorinated THMs (e.g. TCM) were the predominant species in freshwater pools (Manasfi *et al.* 2016), while in the chlorinated pools fed by seawater, brominated THMs (e.g. TBM) were the predominant species (Parinet *et al.* 2012; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a) (Table S1). A similar trend was observed in the case of HANs. Brominated HANs (DBAN) were the predominant species in seawater pools and chlorinated HANs (DCAN) were the predominant species in freshwater pools (Table S3). Hansen *et al.* (2012) also reported that the level of HANs increases in the presence of  $\text{Br}^-$  due to the formation of brominated HANs such as DBAN and BCAN. However, in the case of brominated HAAs, DBAA were the predominant species followed by TBAA in seawater pools (Parinet *et al.* 2012; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a), while chlorinated HAAs (TCAA) were the predominant species in the freshwater pool (Manasfi *et al.* 2016) (Table S2). The predominance of DBAA over TBAA indicated the lower stability of TBAA compared with DBAA, while TCAA is a stable HAA (Zhang & Minear 2002; Lifongo *et al.* 2010; Cardador & Gallego 2015). It has been reported that TBAA may decompose to form the corresponding THM, TBM, in aqueous solutions (Zhang & Minear 2002). This finding also indicated that bromine substitution into THMs and HANs is more efficient than into HAAs (Hua *et al.* 2006).

Some studies reported a lower level of CH (up to  $35 \mu\text{g L}^{-1}$ ) in chlorinated freshwater pools (Lee *et al.* 2010; Yeh *et al.* 2014). However, in some other studies CH was considered among the most abundant DBPs in chlorinated freshwater pools with levels reaching up to  $380 \mu\text{g L}^{-1}$  (Cimetiere & De Laat 2014; Manasfi *et al.* 2016) (Table S4). The occurrence of BH is scarcely reported in literature. Baudisch *et al.* (1997) reported a very high level of BH ( $230 \mu\text{g L}^{-1}$ ) in seawater swimming pools compared with the level of BH ( $0.4\text{--}12 \mu\text{g L}^{-1}$ ) reported by Manasfi *et al.* (2016, 2017c) (Table S4). The lower level of BH in the seawater pool compared with the high level of CH ( $190 \mu\text{g L}^{-1}$ ) in the freshwater pool may be due to the particular stability of these compounds. THAs (BH) decompose to their corresponding THMs (TBM) at high pH and temperature. The seawater pools had relatively

high pH and temperature, which may lead to the low levels of BH in these pools contrary to the more stable chlorinated analog CH in the freshwater pool (Manasfi *et al.* 2016) (Table S4). In a study of the molecular structures of CH and BH, Jain & Soundararajan (1964) found that BH is less stable than CH based on their dipole moment. The dipole moment of CH is 2.07 and 2.65 D at 35 °C in benzene and dioxane solutions, respectively and BH is 2.56 D in benzene solution. The high level of TBM in seawater pools compared with TCM in fresh water pools explains the decomposition of BH to TBM (Manasfi *et al.* 2016). Nevertheless, the lower level of TCM in chlorinated freshwater pools compared with TBM in seawater pools indicates that TCM is more volatile than TBM, even when comparing the volatility of TCM in freshwater with the volatility of TBM in seawater (Moore *et al.* 1995).

#### Effect of disinfection method

The method of disinfection plays an important role in the speciation of THMs. For instance, in chlorinated pools, TCM accounted for about 97% of the tTHMs (TCM, BDCM, DBCM and TCM) found in 54 swimming pools, which were investigated over a one year period (Simard *et al.* 2013). Similarly, TCM had the highest concentration among THMs in ten out of the eleven swimming pools that were sampled over a six month period (Weaver *et al.* 2009) (Table S1). Other studies also observed the predominance of TCM in chlorinated swimming pool water (Judd & Jeffrey 1995; Aggazzotti *et al.* 1995, 1998; Thacker & Nitnaware 2003; Kanan 2010; Lee *et al.* 2010; Bessonneau *et al.* 2011; Maia *et al.* 2014; Tardif *et al.* 2016; Daiber *et al.* 2016). On the other hand, TBM was dominant in the pools, which were disinfected with bromine based disinfectants. The levels of TBM in pools increased due to the formation of HOBr from bromine disinfection (Chambon *et al.* 1983; Benoit & Jackson 1987; Judd & Jeffrey 1995; Richardson *et al.* 2010; Lourencetti *et al.* 2012; Daiber *et al.* 2016) (Table S1). In the comparative studies of the use of hypochlorous acid (HOCl) and HOBr disinfectants it was reported that HOBr disinfectant yielded 74% (by weight) more THMs than HOCl disinfectant under the same conditions. The principal product was TBM in the case of HOBr and TCM in the case of HOCl (Judd & Jeffrey 1995).

Among the nine HAAs, DCAA and TCAA are the most common (Lee *et al.* 2010) and are also the most detected and dominant HAAs in chlorinated indoor and outdoor swimming pools, as reported by some studies (Kanan 2010; Simard *et al.* 2013; Wang *et al.* 2014; Yeh *et al.* 2014; Daiber *et al.* 2016; Tardif *et al.* 2016; Yang *et al.* 2016). For instance, Simard *et al.* (2013) found that DCAA and TCAA accounted for almost 93% of the tHAAs detected in 54 swimming pools. However, some studies reported the predominance of TCAA among the tHAAs. For instance, Lee *et al.* (2010) observed the concentration of TCAA (20–636  $\mu\text{g L}^{-1}$ ), corresponding alone to 70% of tHAAs (35–747  $\mu\text{g L}^{-1}$ ) and Manasfi *et al.* (2016) found the concentration of TCAA (461  $\mu\text{g L}^{-1}$ ), corresponding alone to 92% of tHAAs (498  $\mu\text{g L}^{-1}$ ) (Table S2). Similarly, in the case of bromination, Yang *et al.* (2016) observed the predominance of TBAA (17–22  $\mu\text{g L}^{-1}$ ) over DBAA (8.9–10  $\mu\text{g L}^{-1}$ ). However, Daiber *et al.* (2016) reported the predominance of DBAA (115–131  $\mu\text{g L}^{-1}$ ) over TBAA (50–93  $\mu\text{g L}^{-1}$ ) analogous to chlorinated seawater pools (Parinet *et al.* 2012; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a).

DCAN was the most frequently detected among HANs (Table S3). The concentration of DCAN is higher than the concentration of BCAN and TCAN in chlorinated pool water, which are known to hydrolyze quickly (Kramer *et al.* 2009; Kanan 2010; Lee *et al.* 2010; Yeh *et al.* 2014; Daiber *et al.* 2016; Hang *et al.* 2016; Manasfi *et al.* 2016; Cheema *et al.* 2017b). In brominated pools, DBAN was the dominant among all types of HANs (Daiber *et al.* 2016). Contrarily, in the comparative studies of chlorination and bromination, the predominance of TCAN (2.9–7.2  $\mu\text{g L}^{-1}$ ) over DCAN (0.1–1.1  $\mu\text{g L}^{-1}$ ) in chlorinated pools and the occurrence of DBAN and BCAN in brominated pools was reported by Hansen *et al.* (2012).

#### Effect of detection method

Beech *et al.* (1980) reported the presence of THMs for the first time in swimming pool water disinfected by chlorination. Later on, several studies reported the presence of THMs in swimming pool water in different countries all over the world, disinfected by chlorination and bromination (Table S1). Early studies reported high concentrations of THMs in swimming pool water (Beech *et al.* 1980; Lahl

*et al.* 1981; Chambon *et al.* 1983; Benoit & Jackson 1987; Judd & Jeffrey 1995; Chu & Nieuwenhuijsen 2002). Considering that some early studies may have methodological limitations, the occurrence of THMs and the methods used to detect them in swimming pools are summarized in Table S1. The method of detection could have played an important role in the level of THMs data. Regarding the method of detection, several studies using headspace gas chromatographic analysis have shown the overestimation of THM levels due to the decarboxylation of HAAs into THMs at elevated headspace temperature (60 °C) (Cammann & Hübner 1993; Takahashi *et al.* 2003). Studies using headspace gas chromatographic analysis to detect THM levels, and where the headspace temperature was above 60 °C or temperature was not reported, may not reflect accurate levels of THMs in swimming pools. For instance, Chu & Nieuwenhuijsen (2002) reported headspace temperature above 60 °C and the studies that did not report headspace temperature were Chambon *et al.* (1983), Aggazzotti & Predieri (1986), Aggazzotti *et al.* (1995), Fantuzzi *et al.* (2001), Villanueva *et al.* (2007), Mallika *et al.* (2008) and Parinet *et al.* (2012). In the studies of Erdinger *et al.* (2004) and Maia *et al.* (2014), the headspace temperature was 45 °C. However, some recent studies have also reported high levels of THMs (Simard *et al.* 2013; Maia *et al.* 2014; Hang *et al.* 2016) (Table S1), suggesting that the method of detection may not be the only cause of high levels of THMs in the early studies.

Some studies reported very high levels of TCAM in the indoor air (Jacobs *et al.* 2007; Bessonneau *et al.* 2011; Tardif *et al.* 2016). For instance, the reported level of TCAM was 630 µg m<sup>-3</sup> (Jacobs *et al.* 2007) and 20–1,260 µg m<sup>-3</sup> (Bessonneau *et al.* 2011). In swimming pool water the very high concentration of tCAMs was observed (Weaver *et al.* 2009; Richardson *et al.* 2010; Catto *et al.* 2012; Simard *et al.* 2013; Mah & Heacock 2014) (Table S5). The method of detection could have played an important role in the level of TCAM data in swimming pool water. For comparative analysis Weng & Blatchley III (2011) used two methods of detection; Diethyl-p-phenylenediamine (DPD) followed by colorimetric method (KI) and membrane introduction mass spectrometry (MIMS). They found that with the DPD/KI method, the concentrations of MCAM, DCAM and TCAM did not change substantially over the study

period but the reported concentrations of them were very high. Some other studies also reported high concentrations of tCAMs with this method (Richardson *et al.* 2010; Catto *et al.* 2012; Simard *et al.* 2013; Mah & Heacock 2014). The high concentration with DPD/KI method may be due to its susceptibility of interference (Harp (2002) cited in Weng & Blatchley III (2011)), and organic CAMs are responsible for this interference (Weaver *et al.* (2009)). However, with MIMS method, the concentration of TCAM increased rapidly and DCAM showed a small increase, the overall concentrations of MCAM, DCAM and TCAM were lower than the DPD/KI method. Thus, MIMS provided an accurate measurement of inorganic CAMs (Weng & Blatchley III 2011). Some other studies reported similar results with the MIMS method of detection (Li & Blatchley III 2007; Weaver *et al.* 2009; Affi & Blatchley III 2016).

Moreover, the effect of HOBr on DPD/KI analysis is missing in the available studies. Some brominated pools used DPD/KI for the analysis of CAMs (Richardson *et al.* 2010), but it is not stated that results are measured and calibrated as HOBr and not as HOCl. The reported concentration of all types of CAMs (MCAM, DCAM and TCAM) were higher in the case of chlorination (100–640, <10–650 and <100 µg L<sup>-1</sup>, respectively) compared with bromination (240–300, <10 and <100 µg L<sup>-1</sup>, respectively) (Richardson *et al.* 2010) (Table S5). The brominated pools are expected to have bromamines (BAMs) instead of CAMs (WHO 2006). Richardson *et al.* (2010) did report CAMs in a brominated pool, but there is no chlorine in a brominated pool to form CAMs. The analysis was carried out with DPD/KI, which also reacts with BAMs. The results need to be recalibrated because the calibration curve for CAMs with DPD/KI is different than for BAMs. However, Daiber *et al.* (2016) also detected the CAMs in brominated pools with the MIMS method, though in a lower concentration compared with the chlorinated pools indicating that the method of detection is not the only reason to have CAMs in brominated pools (Table S5). However, conclusions cannot be drawn based on the limited number of studies.

### Effect of temperature

Research revealed that the higher temperature in swimming pools leads to the generation of higher levels of THMs

(Chu & Nieuwenhuijsen 2002; Kanan 2010; Hansen *et al.* 2012; Simard *et al.* 2013) (Table 3). Hang *et al.* (2016) recommended a temperature in the range of 23–30 °C. Kanan (2010) showed that at 40 °C, the level of THMs was twice the level at 26 °C. Benoit & Jackson (1987) observed a high concentration (up to 674  $\mu\text{g L}^{-1}$ ) of THMs in a whirlpool spa at 39.5 °C (Table S1). Similarly, in the comparative studies of heated and unheated outdoor pools, the higher level of THMs (up to 200  $\mu\text{g L}^{-1}$ ) was observed in heated outdoor pools compared with unheated pools (up to 150  $\mu\text{g L}^{-1}$ ) (Simard *et al.* 2013).

Analogous to THMs, the formation of HAAs increased with increasing temperature (Kanan 2010; Hansen *et al.* 2012; Simard *et al.* 2013) (Table 3). In comparative studies of heated and unheated outdoor pools, the higher level of DCAA (in the range of 800–1,200  $\mu\text{g L}^{-1}$ ) was observed in heated outdoor pools compared with unheated pools (in the range of 250–1,260  $\mu\text{g L}^{-1}$ ) (Simard *et al.* 2013).

The occurrence of BH is scarcely reported in literature. Baudisch *et al.* (1997) reported a very high level of BH (230  $\mu\text{g L}^{-1}$ ) compared with the level of BH (0.1–12  $\mu\text{g L}^{-1}$ ) reported by Manasfi *et al.* (2016, 2017c) in seawater swimming pools (Table S4). This low level of BH may be due to the high temperature (31–33 °C) of the seawater swimming pool which leads to the decomposition of BH to TBM, as indicated by THAs decomposition to their corresponding THMs at high temperature (Takahashi *et al.* 2003; Koudjonou & LeBel 2006). Thus, in contrast to THMs and HAAs, a decrease in THAs has been observed when the temperature is increased.

Similar to THAs, the formation of CAMs in swimming pool water is reported to decrease with an increase in temperature, as with high temperature the rate of volatility of CAMs increases in warmer water (Simard *et al.* 2013).

### Effect of pH

The research shows diverging findings on the effect of pH on most of the studied DBPs. For instance, Kanan (2010) and Hansen *et al.* (2012) indicated that increased pH values can have a positive effect on the formation of THMs. Few studies reported high level of THMs with the pH >7.8 (Chu & Nieuwenhuijsen 2002; Thacker & Nitware 2003; Parinet *et al.* 2012; Simard *et al.* 2013). However, in some

studies a high pH of >7.8 did not reflect the high level of THMs (Lee *et al.* 2009, 2010; Bessonneau *et al.* 2011), and some studies reported elevated levels of THMs at pH <7.8 (Weaver *et al.* 2009; Kanan 2010; Hang *et al.* 2016) (Table S1).

The levels of HAAs are known to increase at low pH in drinking water (Singer 1994; American Water Works Association (AWWA) 1999; Liang & Singer 2003). Some studies reported the value of pH <7.0 (Table S2), which is below the recommended pH value (7.2–7.8) (WHO 2006), and the level of HAAs was very high (Parinet *et al.* 2012; Simard *et al.* 2013; Wang *et al.* 2014). In contrast, Hansen *et al.* (2012) found that HAAs are not affected with the increase in pH from 6.0 to 8.0 and the concentration of DCAA and TCAA remained stable.

Several studies indicated that an increase in pH value leads to a decrease in HANs formation (Kanan 2010; Lee *et al.* 2010; Hansen *et al.* 2012) (Table 3). This decrease in concentration of HANs may be due to their possibility of decomposing into HAAs at pH >7.0 (Hansen *et al.* 2012). Therefore, in the studies with the pH value above 7.0, the reported concentration of HANs is low, whereas some studies reported comparatively high levels of HANs at a pH value of 7.0 (e.g. Manasfi *et al.* 2016) (Table S3).

Baudisch *et al.* (1997) reported a very high level of BH (230  $\mu\text{g L}^{-1}$ ) in seawater swimming pools compared with the low level of BH (0.1–12  $\mu\text{g L}^{-1}$ ) reported by Manasfi *et al.* (2016, 2017c) in seawater swimming pools (Table S4). This low level of BH may be due to the high pH (8.3–8.5) of seawater swimming pools, which leads to the decomposition of BH to TBM, as indicated by THAs decomposition to their corresponding THMs at high pH (Takahashi *et al.* 2003; Koudjonou & LeBel 2006). Since in seawater pools bromination is the predominant method of disinfection due to the presence of free bromine, the pH should be maintained between 7.2 and 8.0 for bromine-based disinfectants (WHO 2006).

The formation of TCAM decreases with increasing pH of swimming pool water (Table 3). The highest concentration of TCAM (3,615  $\mu\text{g L}^{-1}$ ) was detected at a pH value of 6.0 and it decreased continuously with increasing pH value. It was measured at 241  $\mu\text{g L}^{-1}$  at a pH value of 8.0 (Hansen *et al.* 2012). This pH dependency of TCAM formation was also confirmed by Schmalz *et al.* (2011) (Table 3).

They investigated the formation of TCAM from different nitrogenous compounds. Each compound was investigated at different pH values (2.5, 4.0, 5.9, 6.3, 6.7, 7.1 and 7.7) to identify the individual effect on TCAM formation. For instance, from urea at a pH value of 5.9, the yield of TCAM was 95% and it was significantly reduced to 24% at a pH value of 7.7.

### Effect of FRC

The FRC is the sum of the concentrations of HOCl and hypochlorite ion ( $\text{OCl}^-$ ) (White 1992; WHO 2006). High doses of chlorine enhance the level of DBPs in swimming pool water (Hansen *et al.* 2012; Simard *et al.* 2013; Hang *et al.* 2016). For instance, the higher chlorine doses favor the formation of HAAs (Hansen *et al.* 2012), and the formation of HAAs over THMs (Singer 1994). Some studies reported a high level of FRC ( $>2.0 \text{ mg L}^{-1}$ ) compared with the level recommended by WHO (2006) in swimming pool water ( $1.2 \text{ mg L}^{-1}$ ) and accordingly the reported level of TCM is very high (Judd & Jeffrey 1995; Kanan 2010; Hang *et al.* 2016) (Table S1). Similarly, the level of HAAs also increased with high doses of FRC (Kanan 2010; Wang *et al.* 2014; Yeh *et al.* 2014; Hang *et al.* 2016) (Table S2). Furthermore, the high level of FRC favors the formation of higher levels of HANs. For instance, with FRC in the range of  $1.5\text{--}5.8 \text{ mg L}^{-1}$  the level of HANs was in the range of  $<0.56\text{--}42 \mu\text{g L}^{-1}$  (Hang *et al.* 2016).

Considering the positive effect of FRC on the reduction of CAMs, which can decrease at high FRC levels due to 'breakpoint' chlorination, pool operators generally try to add enough chlorine to get beyond the breakpoint, such that these CAMs can be destroyed, leaving FRC (Ford 2007; Li & Blatchley III 2009). The breakpoint corresponds to the chlorine to nitrogen ratio at which ammonia-nitrogen is (almost) completely oxidized by FRC to nitrogen gas, nitrite, nitrate and other products (Li & Blatchley III 2009). However, the amount of chlorine needed to reach breakpoint is also dependent on other amines in the water and the goal is not always achieved because of continuous human inputs and rapid reactions forming CAMs (Richardson *et al.* 2010). Therefore, when ammonia-nitrogen concentration in source water is high, types of chlorine is in the form of CAMs. During chloramination some other

DBPs are formed such as N-nitrosamines. The occurrence of six N-nitrosamines in swimming pool water has been reported in some studies such as: N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosomorpholine (NMOR), N-nitrosopyrrolidine (NPyr), N-nitrosopiperidine (NPiP), N-nitrosodibutylamine (NDBA) (Walse & Mitch 2008; Jurado-Sánchez *et al.* 2010; Kanan 2010; Kim & Han 2011; Pozzi *et al.* 2011; Teo *et al.* 2015). Among them, NDMA has been identified as the most dominant (Walse & Mitch 2008; Jurado-Sánchez *et al.* 2010; Kanan 2010; Kim & Han 2011), which is formed by the reaction of MCAM with dimethylamine (DMAM) (WHO 2017). Since NDMA has been classified as probable human carcinogen (US EPA, IRIS), WHO (2017) recommended a guideline value of  $0.1 \mu\text{g L}^{-1}$  for NDMA in drinking water.

### Effect of TOC

The high levels of TOC trigger higher chlorine demand, which consequently favor the formation of higher levels of DBPs (Simard *et al.* 2013; Hang *et al.* 2016). Simard *et al.* (2013) argued that the higher level of THMs in outdoor pools compared with indoor pools was due to a higher level of TOC ( $17 \text{ mg L}^{-1}$ ) in outdoor pools, which was almost twice the TOC level in the indoor pool ( $8.7 \text{ mg L}^{-1}$ ). Contrarily, Lee *et al.* (2009) reported the higher level of TOC in indoor pools compared with the level reported by Simard *et al.* (2013) for outdoor pools and the concentration of THMs in those pools was less than reported for outdoor pools. This may be due to a higher level of TN (not reported) in the indoor pools studied by Lee *et al.* (2009). The level of TN increases due to the presence of nitrogen-containing compounds, which come from sweat and urine in swimming pool water (Kim & Han 2011). Some studies reported that the level of THMs decreased when urine was added to model solutions. This was attributed to the depletion of active FRC due to the formation of less reactive CAMs (Judd & Jeffrey 1995; Kim *et al.* 2002). However, some other studies also indicated the formation of high concentration of THMs with high levels of TOC/DOC in indoor pools (Chu & Nieuwenhuijsen 2002; Lee *et al.* 2010; Parinet *et al.* 2012; Hang *et al.* 2016) (Table S1). For instance, Hang *et al.* (2016) reported a high level of DOC ( $30 \text{ mg L}^{-1}$ ) and consequently, the level of TCM and BDCM was 220 and  $202 \mu\text{g L}^{-1}$ . Chu &

Nieuwenhuijsen (2002) observed that DOC significantly increased with the number of swimmers, ranging from 3.3 to 13 mg L<sup>-1</sup>. In a study of two outdoor swimming pools, it was estimated that on average 1.09 g of DOC per person is brought into swimming pool water (Glauner (2007) cited in Peng *et al.* (2016)). Manasfi *et al.* (2016) attributed that the higher level of DBPs in freshwater pools was due to more bathers compared with seawater pools. However, Peng *et al.* (2016) concluded from their results that the introduction of anthropogenic pollutants and consequent DBPs formation in swimming pool water cannot be predicted simply from the number of visitors. The actual DBPs formation can be estimated with the content of organic matter in the pool water. Thus, DOC is proved to be a suitable parameter for precursor to predict THMs production in the pool water.

Similar to THMs, the high level of HAAs in outdoor pools compared with the level in indoor pools was related to the high level of TOC in outdoor pools compared with indoor pools (Cardador & Gallego 2011; Simard *et al.* 2013). However, Wang *et al.* (2014) observed a high level of TOC (up to 27 mg L<sup>-1</sup>) in indoor pools compared with the level in outdoor pools (up to 13 mg L<sup>-1</sup>) and the level of HAAs was higher in outdoor pools compared with the level in indoor pools (Table S2). In further contrast, some other studies also indicated the formation of high concentrations of HAAs with high levels of TOC/DOC in indoor pools (Lee *et al.* 2010; Parinet *et al.* 2012; Hang *et al.* 2016) (Table S2).

The formation of HANs increased with increasing concentrations of TOC (Kanan 2010; Lee *et al.* 2010; Hang *et al.* 2016) (Table 3). The studies which reported the high level of TOC also reported a high level of HANs (Kanan 2010; Manasfi *et al.* 2016; Tardif *et al.* 2016) (Table S3).

CH was considered among the most abundant DBPs by weight in chlorinated freshwater pools (Baudisch *et al.* 1997; Kim 1997; Cimetiere & De Laet 2014; Manasfi *et al.* 2016) and the levels reached up to 380 µg L<sup>-1</sup> (e.g. Cimetiere & De Laet 2014) (Table S4). The high concentration of CH may be due to the high level of TOC because an increase in the level of TOC enhances the formation of CH (Lee *et al.* 2010) (Table 3). The TOC concentration reported by Cimetiere & De Laet (2014) and Manasfi *et al.* (2016) was 5.5 and 12 mg L<sup>-1</sup>, respectively (Table S4).

## Effect of TN

Human body fluid discharges in swimming pools are believed to be a major source of nitrogen in swimming pools, which leads to the formation of N-DBPs such as CAMs and HANs (Chowdhury *et al.* 2014). DON (i.e. creatinine and amino-acids) and inorganic nitrogen compounds (ammonia) have been found to be the main precursors of N-DBPs (Florentin *et al.* 2011; Shah & Mitch 2011). These nitrogen-containing compounds come from sweat and urine in swimming pool water (Kim & Han 2011). Weng & Blatchley III (2011) calculated the releases of sweat and urine into the pool water as 823–1,760 and 55–117 mL per person, respectively. The concentrations of nitrogen-containing compounds introduced by swimmers in the swimming pool water are given in Table 5.

Keuten *et al.* (2012) studied the release of anthropogenic pollutants in swimming pools and estimated that TN released per person is 46 mg within the first 60 seconds of showering. During 30 minutes exercise, it was estimated that TN release reached up to 77.3 mg per bather (Keuten *et al.* 2014).

Studies have shown that urea and ammonia (the major nitrogen-containing compounds of sweat and urine) are the main precursors of TCAM formation (Li & Blatchley III 2007; Schmalz *et al.* 2011). Urea reacts with chlorine to form carbon dioxide, DCAM and TCAM. The reaction is slow and takes place over several tens of hours. Ammonia reacts rapidly with chlorine to form gaseous nitrogen, MCAM, DCAM, water and hydrochloric acid (HCl) (De

**Table 5** | Nitrogen-containing compounds in sweat and urine (WHO 2006; Florentin *et al.* 2011)

Nitrogen-containing compounds	Sweat		Urine		By swimmers Estimated range of input (mg)
	Mean content (mg L <sup>-1</sup> )	Portion of TN (%)	Mean content (mg L <sup>-1</sup> )	Portion of TN (%)	
Urea	680	68	10,240	84	320–840
Ammonia	180	18	560	5.0	30–60
Amino acids	45	5.0	280	2.0	15–50
Creatinine	7.0	1.0	640	5.0	10–25
Other compounds	80	8.0	500	4.0	20–45
Total nitrogen (TN)	990	100	12,200	100	400–1,000

Laat *et al.* (2009) cited in Florentin *et al.* (2011)). The presence of urea and proteins of human origin promoted the formation of HANs in chlorinated pool water (Kim *et al.* 2002). Furthermore, amino acids in sweat and urine (e.g. histidine and arginine) have been recognized as effective precursors for the formation of DCAN (Li & Blatchley III 2007; Weaver *et al.* 2009; Weng *et al.* 2012). Several studies reported the formation of HAAs with some amino acids (i.e. histidine) during chlorination (Hong *et al.* 2009; Kanan 2010; Kanan & Karanfil 2011), which is expected since it is observed that urea contributes to about 6.3% of TOC in a swimming pool (De Laat *et al.* 2011). Analogous to that, Parinet *et al.* (2012) also attributed the formation of higher levels of tHAAs ( $626 \mu\text{g L}^{-1}$ ) with a high level of TN ( $7.7 \text{ mg L}^{-1}$ ) in the seawater pool (Table S2).

Although an increase of FRC enhanced the formation of THMs, the presence of urea and ammonia through human inputs may decrease its formation due to competitive reactions among different DBPs precursors (Yang *et al.* 2016). These findings are consistent with previous studies, which reported that the level of THMs decreased when urine was added to model solutions. This was attributed to the depletion of active FRC due to the formation of less reactive CAMs (Judd & Jeffrey 1995; Kim *et al.* 2002). Parinet *et al.* (2012) reported that TN shifts the speciation of DBPs from Cl-DBPs to Br-DBPs (Table S2). If ammonia and  $\text{Br}^-$  are both present in chlorinated pool water, then FRC reacts simultaneously with ammonia to form CAMs and with  $\text{Br}^-$  to form HOBr, which favors the formation of Br-DBPs.

Therefore, TN is a crucial parameter that increases for the formation of HAAs, HANs and CAMs in swimming pool water while reducing the production of THMs. The reviewed studies estimated the level of TN in ground water, tap water and seawater as 1.2, 1.2–12 and 0.7–7.7  $\text{mg L}^{-1}$ , respectively, but not in surface water (Table S1). Among the studies that investigated the formation of CAMs, only Judd & Black (2000) reported the level of TN in swimming pool water (Table S5). Among the studies which considered the formation of HANs, only Kanan (2010), Yeh *et al.* (2014) and Manasfi *et al.* (2017c) reported the level of TN. Thus, most of the studies did not measure or relate the formation and/or reduction of C-DBPs and

N-DBPs with TN, which is an essential parameter to be considered in future research.

### Effect of $\text{Br}^-$

The bromination of freshwater pool with BCDMH has shown that after dissolution, bromine in BCDMH is released as HOBr. BCDMH dissolves in water to release HOBr and HOCl (WHO 2006; Lourencetti *et al.* 2012; Daiber *et al.* 2016; Yang *et al.* 2016). Both HOBr and HOCl can oxidize and inactivate pathogens (Daiber *et al.* 2016). Most of the HOBr rapidly reduced to  $\text{Br}^-$  and part reacted with organic matter and was transformed to Br-DBPs. Further, the hydrolyzed product HOCl reacts with  $\text{Br}^-$  (formed by the reduction of HOBr) to form more HOBr (WHO 2006; Daiber *et al.* 2016). If BCDMH is used as a bromine source for swimming pool water disinfection, the level of dimethylhydantoin (DMH) must not exceed  $200 \text{ mg L}^{-1}$  (WHO 2006).

In the case of chlorination of a seawater pool, a similar phenomenon has been observed (Parinet *et al.* 2012; Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a). When chlorine gas or hypochlorite is added to water, HOCl is formed, which can rapidly oxidize  $\text{Br}^-$  present in the seawater to form HOBr and hypobromite ion ( $\text{BrO}^-$ ) (Heeb *et al.* 2014; Manasfi *et al.* 2016, 2017c). Most of the HOBr is rapidly reduced to  $\text{Br}^-$ , which promotes the formation of Br-DBPs by bromine substitution of Cl-DBPs or further halogenations of organic matter (Hua *et al.* 2006). As a halogenating agent, bromine is 10 times more reactive than chlorine (Westerhoff *et al.* 2004), especially with body fluid compounds added by swimmers (Manasfi *et al.* 2017c). HOBr is more reactive towards organic compounds compared with HOCl (Kampioti & Stephanou 2002; Fabbicino & Korshin 2009; Tian *et al.* 2013). While HOCl is known to be a stronger oxidant than HOBr, it is a less efficient substitution agent. Therefore, when  $\text{Br}^-$  is oxidized by HOCl to form HOBr, bromine substitution into organic compounds is favored (Uyak & Toroz 2007). Consequently, if  $\text{Br}^-$  is present in the source water or bromination is the method of disinfection, Br-DBPs are likely to be formed.

Moreover, tap water and ground water also contain  $\text{Br}^-$  (Mallika *et al.* 2008; Kanan 2010; Kanan & Karanfil 2011; Yeh *et al.* 2014; Hang *et al.* 2016), though the level of  $\text{Br}^-$  was



relatively low in tap water ( $0.1\text{--}7.3\text{ mg L}^{-1}$ ) and subsequently the level of Br-DBPs was also low in the tap water pools (Table S1). The detection of Br-DBPs in mixed tap and ground water pool samples indicated the presence of  $\text{Br}^-$  ( $2.2\text{ mg L}^{-1}$ ) in the ground water (Mallika *et al.* 2008; Kanan 2010) (Table S1). However, the level of  $\text{Br}^-$  ( $68\text{--}107\text{ mg L}^{-1}$ ) was very high in seawater pools which promoted the formation of Br-DBPs.

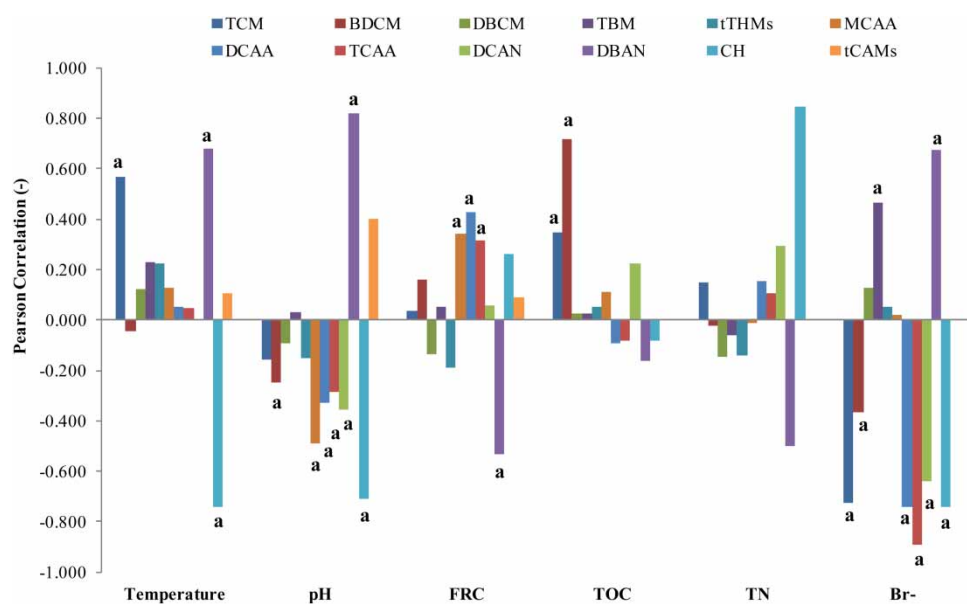
Nevertheless, it is not confirmed that the substitution reactions were the only pathway of increased formation of Br-DBPs in the seawater ( $\text{Br}^-$  rich) swimming pools and the increase in different types of DBPs such as tTHMs, tHAAs and total HANs (tHANs) by weight was due to the substitution of chloride ion ( $\text{Cl}^-$ ) by  $\text{Br}^-$ . Further studies are therefore necessary to explain this distribution (Parinet *et al.* 2012; Chowdhury *et al.* 2014). In recent studies on chlorinated seawater pools by Manasfi *et al.* (2016, 2017c) and Cheema *et al.* (2017a), the reaction pathways for the formation of Br-DBPs are not described.

### Relationship of temperature, pH, FRC, TOC, TN and $\text{Br}^-$ with DBPs formation

The Pearson correlation analysis of temperature, pH, FRC, TOC, TN and  $\text{Br}^-$  was made with the DBPs, such as TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN, CH and tCAMs, for which the WHO guidelines (WHO 2006, 2017), as well as sufficient data, was available for the analysis.

### Correlation analysis based on all pools

The Pearson correlation of all the indoor/outdoor pools using all types of fresh water (tap, fresh and ground) and seawater as source water is presented in Figure 1. The correlation of TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN, CH and tCAMs with temperature, pH, FRC, TOC, TN and  $\text{Br}^-$  is discussed in this section. It is evident from Figure 1 that temperature,



**Figure 1** | Correlation statistics among the studied factors and DBPs, established using data of all types of studied pools with all types of fresh and seawater as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature were 99, 51, 62, 49, 48, 27, 42, 44, 43, 18, 11 and 14 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN, CH and tCAMs, respectively. In the case of pH the number of observations were 111, 59, 71, 55, 58, 27, 70, 71, 48, 18, 11 and 14 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN, CH and tCAMs, respectively. In the case of FRC the number of observations were 114, 61, 73, 59, 59, 27, 70, 70, 48, 18, 11 and 14 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN, CH and tCAMs, respectively. In the case of TOC the number of observations were 78, 43, 46, 31, 35, 25, 63, 65, 31, 18 and 11 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN and CH, respectively. In the case of TN the number of observations were 28, 28, 28, 13, 26, 11, 11, 11, 3, 3 and 3 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN and CH, respectively. In the case of  $\text{Br}^-$  the number of observations were 30, 27, 30, 30, 24, 15, 15, 15, 9, 12 and 7 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA, TCAA, DCAN, DBAN and CH, respectively. 'a' indicates a significant correlation between the parameters at 90% confidence level.

pH, FRC, TOC, TN and  $\text{Br}^-$  play an important role in the formation of DBPs in swimming pool water, albeit with different levels of influence. For instance, temperature is the most significant parameter, as indicated by its positive correlation with TCM, BDCM, TBM, tTHMS, MCAA, DCAA, TCAA, DCAN, DBAN and tCAMs, though significant correlation was only exhibited with TCM and DBAN (Figures 1 and 2(a)), signifying that the high temperature enhanced the formation of DBPs. The significant negative correlation with CH (Figures 1 and 2(b)) shows that at high temperature, CH is converted into its corresponding THM (TCM).

pH shows a negative correlation with TCM, BDCM, BDCM, tTHMs, MCAA, DCAA, TCAA, DCAN and CH, although significant correlation is with BDCM, MCAA, DCAA, TCAA, DCAN and CH. However, pH shows a positive correlation with DBAN and tCAMs, though significant correlation is only with DBAN (Figures 1 and 2(c)). The significant negative correlation with CH (Figures 1 and 2(d)) shows that at high pH, CH is converted into its corresponding THM (TCM).

The increase in FRC shows the increase in TCM, BDCM, TBM, MCAA, DCAA, TCAA, DCAN, CH and tCAMs, though a significant positive correlation is found with MCAA, DCAA and TCAA. Nevertheless, formation of tCAMs is positively correlated with FRC, indicating that a high chlorine dose facilitates the formation of tCAMs (Table S5). A significant negative correlation of FRC with DBAN indicates that when FRC decreases due to the presence of  $\text{Br}^-$ , the formation of DBAN is promoted.

TOC shows a positive correlation with TCM, BDCM, BDCM, TBM, tTHMs, MCAA and DCAN (Figure 1), though significant correlation is with TCM and BDCM. This indicates that the high level of TOC enhanced the formation of DBPs. In contrast, there is a negative correlation with DCAA, TCAA, DBAN and CH. The negative correlation of TOC with CH indicated the predominance of temperature and pH for the formation of CH as it has negative correlation with temperature and pH which is required for its formation and/or reduction. The correlation of TOC with tCAMs is not made because of the lesser number of data points (Table S5).

TN shows a positive correlation with TCM, DCAA, TCAA, DCAN and CH. A positive correlation of TN with DCAA,

TCAA and DCAN, though not significant, indicates that their formation is promoted in the presence of nitrogen-containing compounds. The correlation of TN with tCAMs is not made because of the lesser number of data points (Table S5).

$\text{Br}^-$  shows a significant negative correlation with TCM, BDCM, DCAA, TCAA, DCAN and CH. The formation of brominated species of different types of DBPs in the presence of high levels of  $\text{Br}^-$  is evident due to a positive correlation with BDCM, TBM, tTHMs and DBAN, though significant correlation is with TBM and DBAN (Figures 1, 2(e) and 2(f)).

### Correlation analysis of indoor pools with tap water

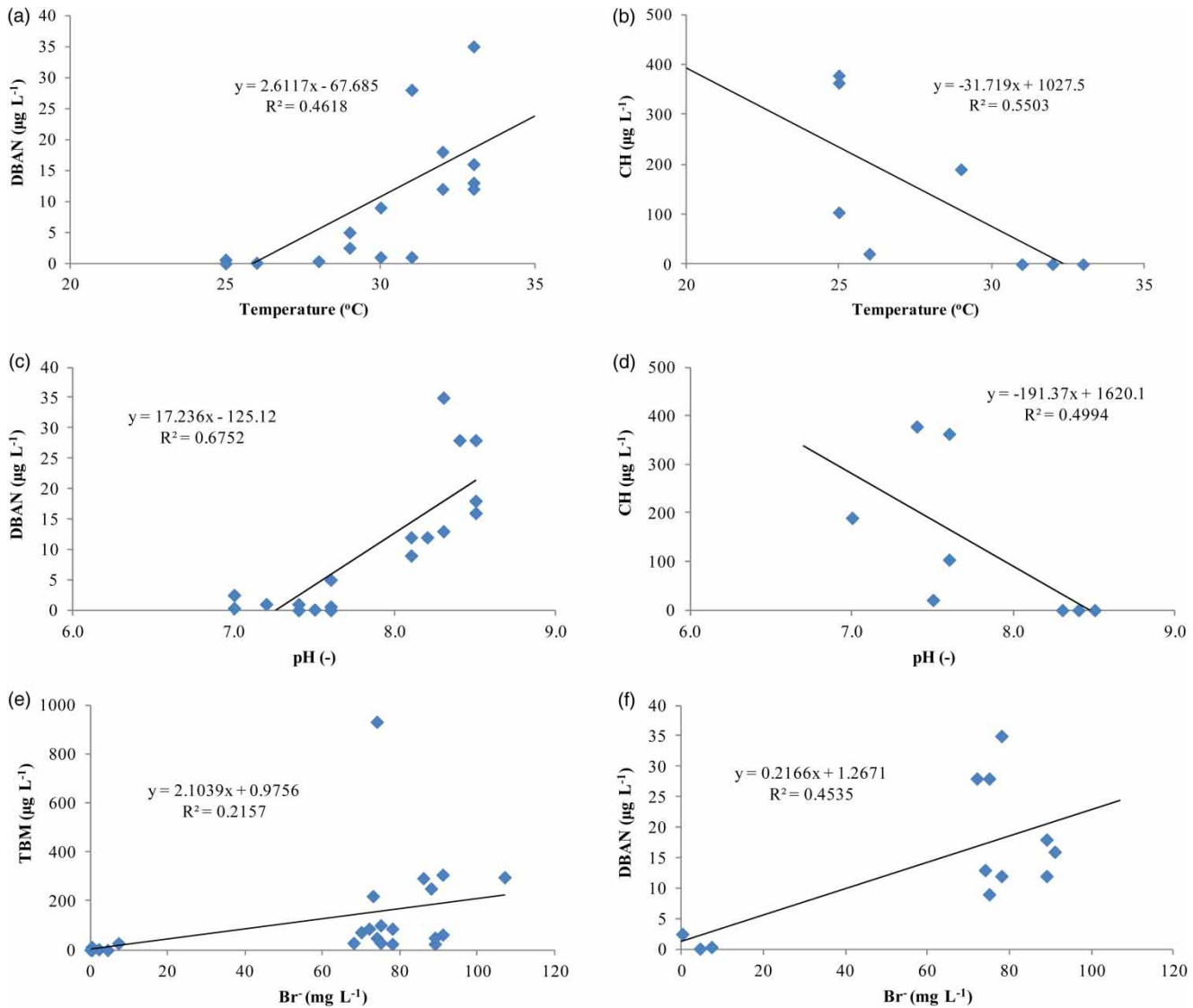
The correlation of TCM, BDCM, BDCM, tTHMs, DCAA, TCAA and DCAN with temperature, pH, FRC, TOC and TN is discussed in this section, except for TBM, MCAA, DBAN, CH and tCAMs due to the lesser number of data points; for similar reasons, the correlation of DBPs with  $\text{Br}^-$  is not made (Figure 3).

The correlation of TCM, BDCM, tTHMs, DCAA, TCAA and DCAN with temperature is similar as with all types of pools and all sources of water, though significant correlation is with DCAA, TCAA and DCAN (Figures 3 and 4(a)). Additionally, BDCM also shows positive correlation in indoor pools using tap water (Figure 3).

Similarly, pH showed a similar nature of correlation with TCM, BDCM, BDCM, tTHMs, DCAA and TCAA in the case of indoor pools with tap water when compared with all types of pools and all sources of water, although significant correlation is only with BDCM (Figure 3). However, in indoor pools with tap water, DCAN showed a positive correlation with pH.

The correlation of TCM, BDCM, BDCM, DCAA and TCAA with FRC is analogous to all types of pools and all sources of water, although significant correlation is with TCM and DCAA (Figures 3 and 4(b)). Moreover, tTHMs show a positive correlation with FRC (Figure 3) and DCAN shows a negative correlation with FRC.

TOC plays a major role for the formation of DBPs, which is clear with the positive correlation of TOC with TCM, BDCM, BDCM, tTHMs and DCAN, which was significant with TCM, BDCM, BDCM and tTHMs (Figures 3, 4(c) and 4(d)). The correlation of tTHMs and DCAN with



**Figure 2** | The emerging relationship between the selected water quality parameters and DBPs, established using data of all types of studied pools with all types of fresh and seawater as source water: (a) DBAN and temperature; (b) CH and temperature; (c) DBAN and pH; (d) CH and pH; (e) TBM and  $\text{Br}^-$ ; (f) DBAN and  $\text{Br}^-$ .

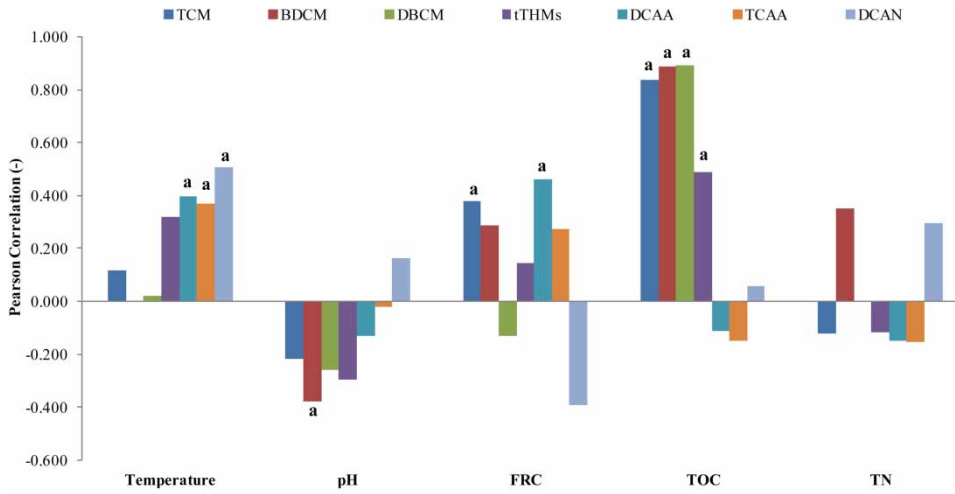
TN is similar to all types of pools and all sources of water (Figure 3).

### The correlation analysis of indoor pools with seawater

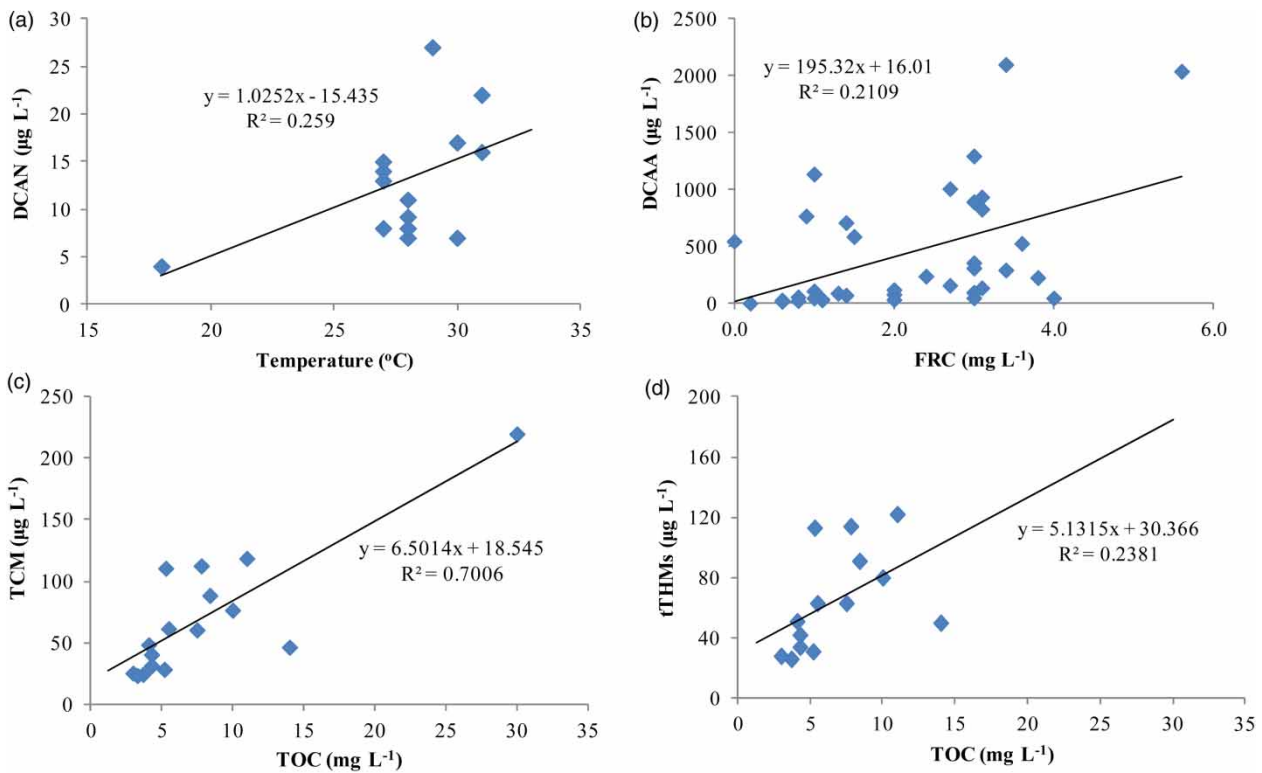
The correlation of TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA and TCAA with temperature, pH, FRC, TOC, TN and  $\text{Br}^-$  is discussed in this section. Due to the lesser number of data points in the case of DCAN, DBAN, CH and tCAMs, the analysis was not carried out (Figure 5).

The correlation of TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA and TCAA with temperature is perpetual with all types of pools and all sources of water but is not significant. However, BDCM shows a negative correlation with temperature in indoor pools using seawater (Figure 5), which is contrary with the use of tap water. This finding indicates the dominance of more brominated species (DBCM and TBM) with the use of seawater compared with tap water.

The correlation of BDCM, DBCM, tTHMs, MCAA, DCAA and TCAA with pH is analogous to all types of



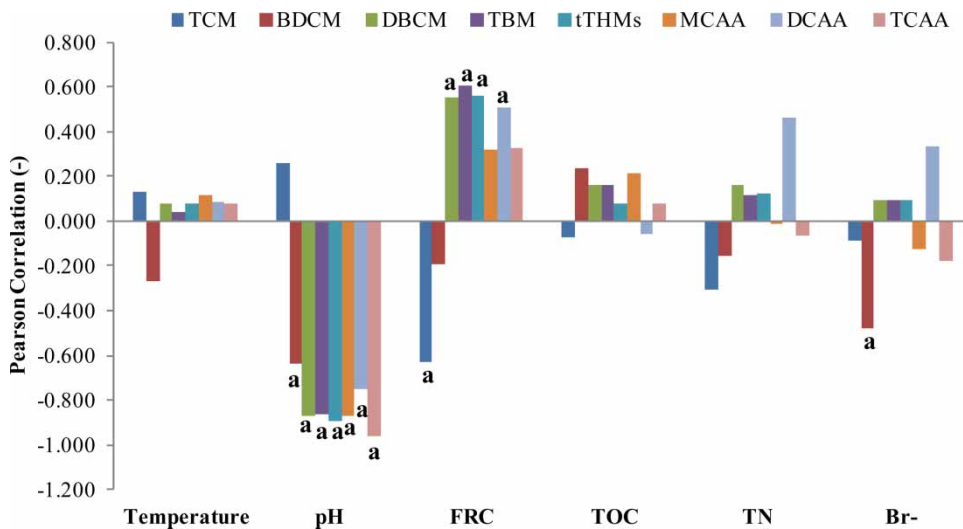
**Figure 3** | Correlation statistics among the studied factors and DBPs, established using data of studied indoor pools with tap water as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature were 26, 22, 22, 17, 22, 22 and 16 for TCM, BDCM, DBCM, tTHMs, DCAA, TCAA and DCAN, respectively. In the case of pH the number of observations were 25, 22, 21, 17, 37, 37 and 16 for TCM, BDCM, DBCM, tTHMs, DCAA, TCAA and DCAN, respectively. In the case of FRC the number of observations were 25, 22, 22, 17, 37, 37 and 16 for TCM, BDCM, DBCM, tTHMs, DCAA, TCAA and DCAN respectively. In the case of TOC the number of observations were 16, 16, 16, 14, 30, 30 and 15 for TCM, BDCM, DBCM, tTHMs, DCAA, TCAA and DCAN, respectively. In the case of TN the number of observations were 14 for TCM, BDCM, DBCM, tTHMs, DCAA, TCAA and DCAN. 'a' shows a significant correlation between the parameters at 90% confidence level.



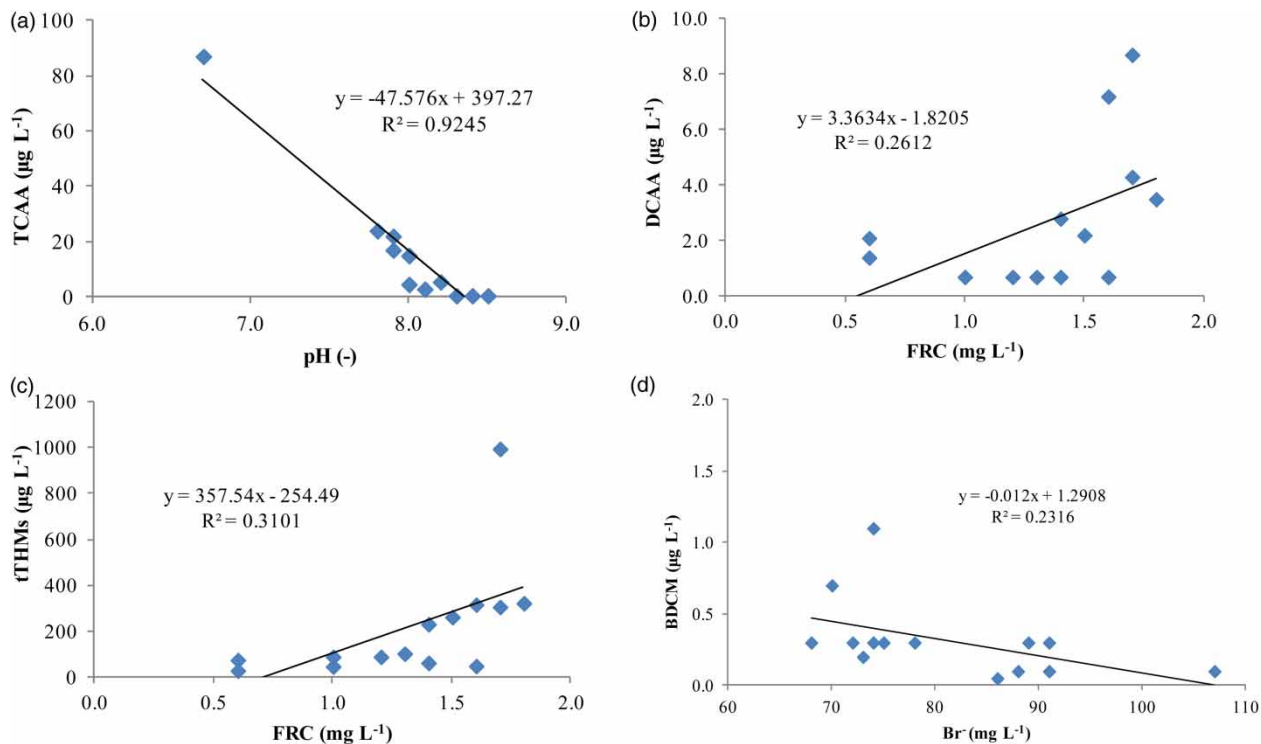
**Figure 4** | The emerging relationship between the selected water quality parameters and DBPs, established using data of studied indoor pools with tap water as source water: (a) DCAN and temperature; (b) DCAA and FRC; (c) TCM and TOC; (d) tTHMs and TOC.

pools and all sources of water, as well as indoor pools with tap water, but is significant in the case of seawater pools with BDCM, DBCM, TBM, tTHMS, MCAA, DCAA and

TCAA (Figures 5 and 6(a)). However, a positive correlation of pH with TCM in the case of seawater pools, though not statistically significant, is contrary to all types of pools and



**Figure 5** | Correlation statistics among the studied factors and DBPs, established using data of studied indoor pools with seawater as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature, pH, FRC, TOC and Br<sup>-</sup> were 17, 14, 17, 17, 14, 14, 14 and 14 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA and TCAA, respectively. In the case of TN the number of observations were 11 for TCM, BDCM, DBCM, TBM, tTHMs, MCAA, DCAA and TCAA. 'a' shows a significant correlation between the parameters at 90% confidence level.



**Figure 6** | The emerging relationship between the selected water quality parameters and DBPs, established using data of studied indoor pools with seawater as source water: (a) TCAA and pH; (b) DCAA and FRC; (c) tTHMs and FRC; (d) BDCM and Br<sup>-</sup>.

all sources of water, as well as indoor pools with tap water (Figure 5).

The correlation of TBM, MCAA, DCAA and TCAA with FRC is comparable to all types of pools and all sources of water, but is significant only with TBM and DCAA (Figures 5 and 6(b)). Moreover, DBCM, TBM and tTHMs also show a significant positive correlation with FRC (Figures 5 and 6 (c)). However, a negative correlation of FRC with TCM and BDCM (Figure 5) indicates that in seawater pools, even with the increase in FRC, the level of brominated species remain significantly high.

The correlation of BDCM, DBCM, TBM, tTHMs, MCAA and DCAA with TOC is consistent with all types of pools using all sources of water, although it is not significant. The correlation of TOC with BDCM, DBCM, tTHMs and DCAA is analogous to indoor pools using tap water, though in the case of seawater pools it is not significant.

The correlation of BDCM, MCAA and DCAA with TN is similar with all types of pools using all sources of water and the correlation of TCM and TCAA with TN is consistent with indoor pools using tap water. The correlation of TCM, BDCM, DBCM, TBM, tTHMs and TCAA with  $\text{Br}^-$  is consistent with all types of pools using all sources of water, though it is only significant with BDCM (Figures 5 and 6(d)).

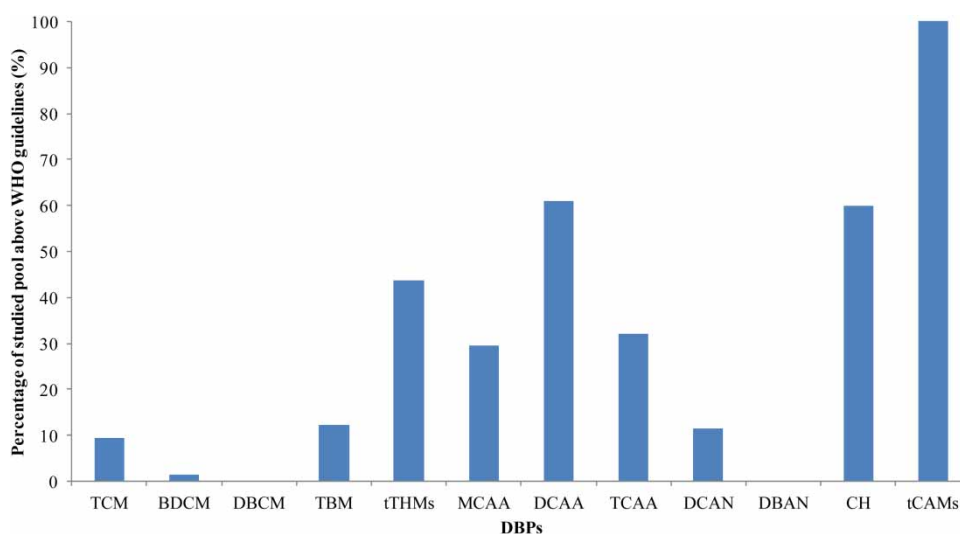
## WHO guidelines and observed levels of DBPs

The comparative analysis of the levels of different DBPs reported by several research studies in swimming pool water with the levels suggested by WHO (2017) shows that the level of most of the DBPs is very high compared with the WHO guidelines for drinking water (Figures 7–9).

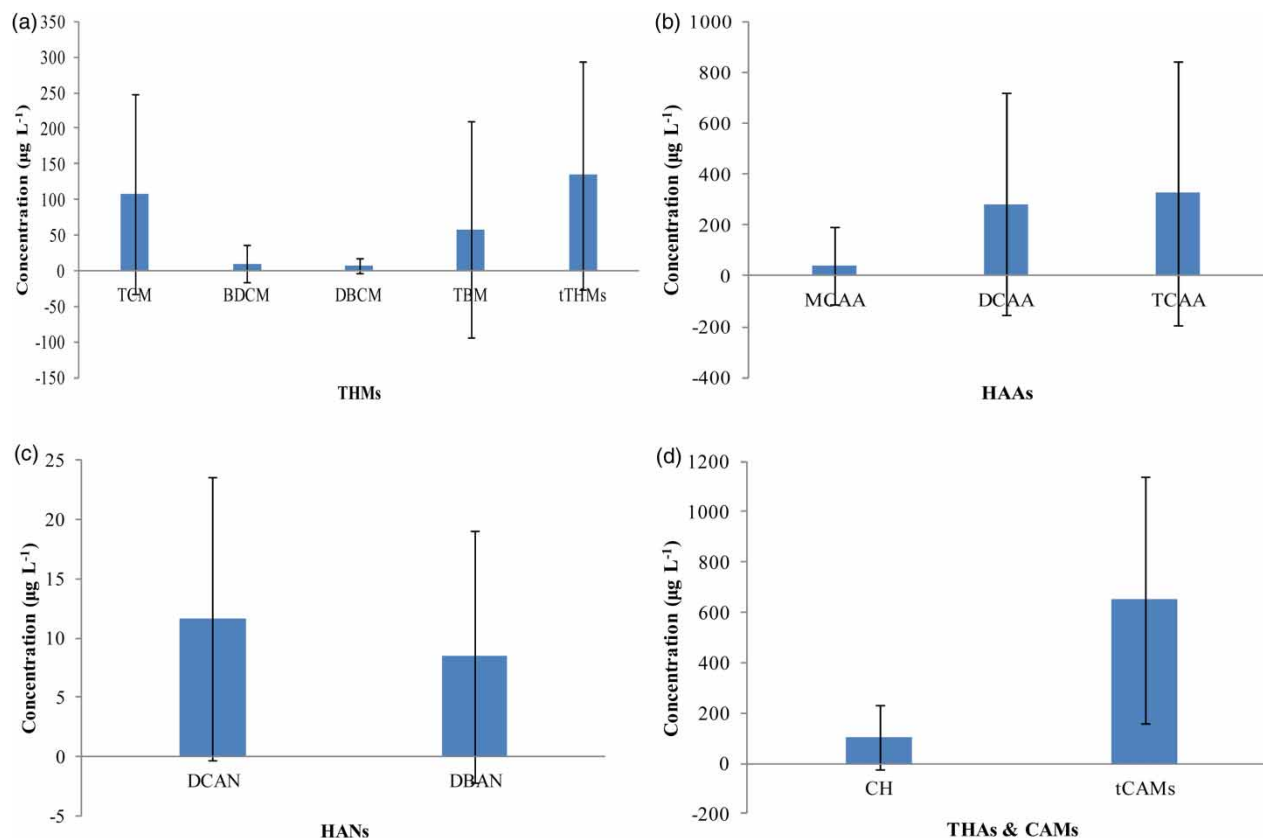
## Comparison for THMs

TCM and TBM are most dominant among tTHMs. In the case of chlorination, 13 out of 137 (9%) research studies observed TCM values ( $324\text{--}674\ \mu\text{g L}^{-1}$ ) above the WHO standard (Tables 1 and S1) and eight out of 66 (12%) reported elevated levels of TBM ( $101\text{--}931\ \mu\text{g L}^{-1}$ ). The target level of BDCM and DBCM is met by almost all the studies, except one out of 68 (1.5%) in the case of BDCM ( $202\ \mu\text{g L}^{-1}$ ). However, the level of tTHMs ( $102\text{--}996\ \mu\text{g L}^{-1}$ ) exceeded in almost half (27 out of 62) of the research studies compared with the target level set by WHO (Figures 7, 8(a) and 9 and Table S1).

The higher level of tTHMs may be due to the higher level of TOC ( $\geq 5.0\ \text{mg L}^{-1}$ ) which was reported in five out of 12 studies, since 15 out of 27 studies did not report the level of TOC. Similarly, higher temperature ( $\geq 30\ ^\circ\text{C}$ ) and pH ( $\geq 7.8$ ) also increase the level of THMs and was observed in 10 out



**Figure 7** | Percentage of studied pools above WHO guidelines for drinking water quality for different DBPs species.



**Figure 8** | Overall statistics (mean and standard deviation) of different DBPs species for which the guideline is set by WHO for drinking water quality.

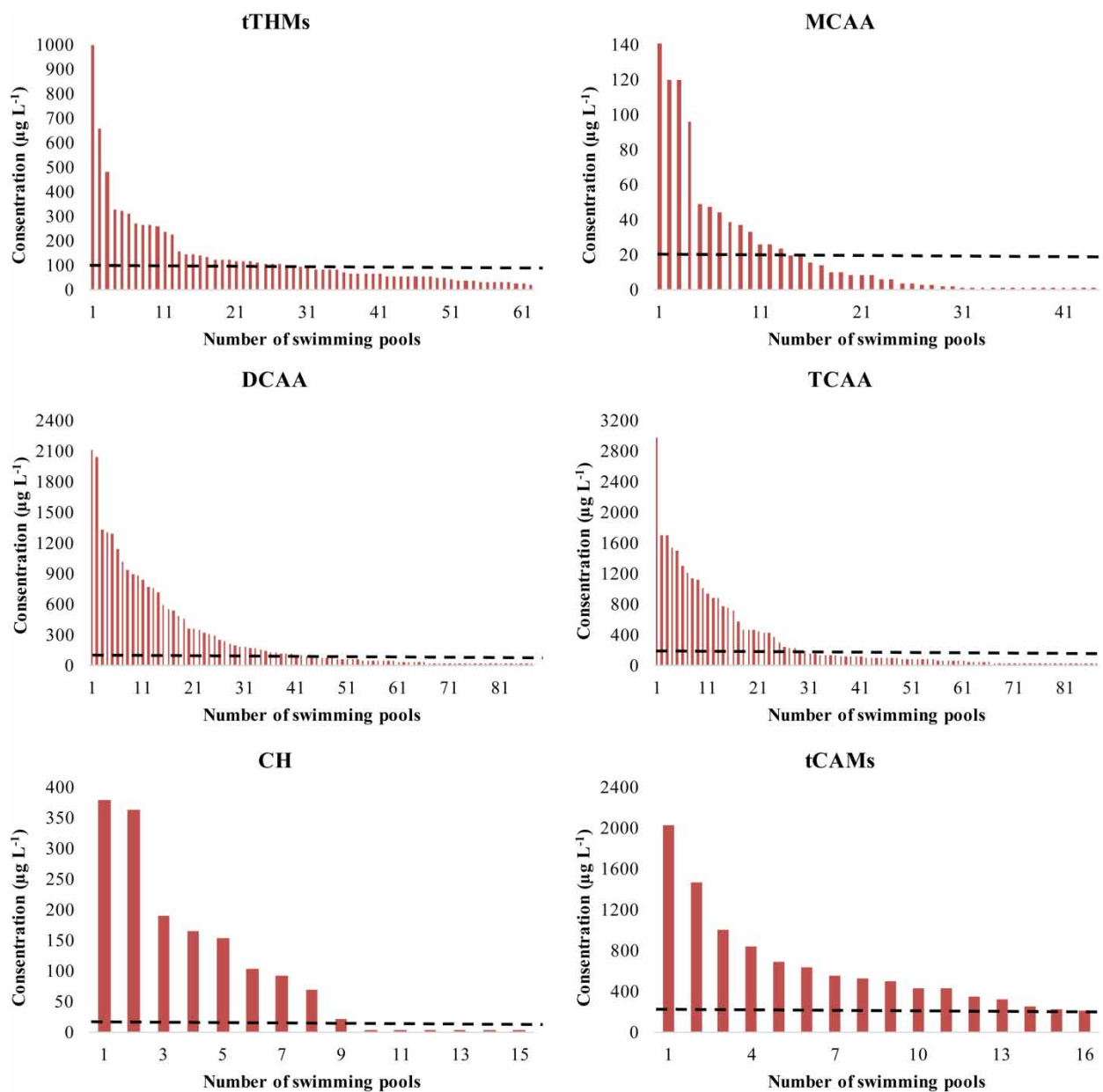
of 16 and seven out of 24 studies, while 11 and three out of 27 studies, respectively, did not report the level of temperature and pH (Table S1). The nature of source water also plays a major role for their formation. The level of tTHMs can also be increased when the level of brominated species increases due to higher levels of  $\text{Br}^-$  in seawater pools. Eight out of 27 studies used seawater as source water. The higher level of  $\text{Br}^-$  ( $>70 \text{ mg L}^{-1}$ ) was reported in seven out of eight studies. In the case of tap water, the presence of natural organic matter (NOM) from humic origin (humic and fulvic acids, and humic substances) can increase the level of tTHMs and 11 out of 27 studies used tap water as source water. The nature of source water may be another reason that 19 out of 27 studies reported higher levels of tTHMs.

### Comparison for HAAs

Most of the research studies observed very high levels of MCAA, DCAA and TCAA (Figure 9 and Table S2). In the

case of chlorination, 13 out of 44 (30%) studies reported levels of MCAA ( $23\text{--}1,000 \text{ } \mu\text{g L}^{-1}$ ) above the WHO guidelines (Tables 1 and S2). Similarly, DCAA ( $52\text{--}2,100 \text{ } \mu\text{g L}^{-1}$ ) and TCAA ( $106\text{--}2,970 \text{ } \mu\text{g L}^{-1}$ ) were above the guidelines in 61% (53 out of 87) and 32% (28 out of 87) of the research studies, respectively (Figures 7, 8(b) and 9 and Table S2).

The level of DCAA is extremely high  $\geq 500 \text{ } \mu\text{g L}^{-1}$  in 17 out of 53 (32%) of the studies (Figure 8). The higher level of DCAA in swimming pool water may be due to higher temperature ( $\geq 30^\circ \text{C}$ ), reported in 10 out of 29 studies, since 24 out of 53 studies which reported the exceeding levels of DCAA did not report the level of temperature (Table S2). Similarly, the studies which reported the increased level of DCAA also observed an increased level of TOC ( $\geq 5.0 \text{ mg L}^{-1}$ ) and low level of pH ( $\leq 7.2$ ) in 23 out of 37 and nine out of 44 studies, respectively, while 16 and nine out of 53 studies did not report the level of TOC and pH, respectively (Table S2).



**Figure 9** | A comparison of the concentrations of selected DBPs with WHO guidelines for drinking water. Note: the horizontal dash-line indicates the value of the WHO guideline for a given DBP.

### Comparison for HANs

In chlorinated pools the level of DCAN ( $22\text{--}75\ \mu\text{g L}^{-1}$ ) in six out of 52 (12%) research studies exceeded the limits set by WHO. However, the target level of DBAN was met by almost all the studies (Tables 1 and S3; Figures 7 and 8 (c)). The higher level of DCAN may be due to the higher level of TOC ( $\geq 5.0\ \text{mg L}^{-1}$ ) which was reported in three

out of four studies. Two out of six studies which reported the exceeding levels of DCAN did not report the level of TOC (Table S3).

### Comparison for THAs

Among the reviewed studies, nine out of 15 (60%) reported levels of CH ( $21\text{--}378\ \mu\text{g L}^{-1}$ ) which were above the limits



set by WHO (Figures 7, 8(d) and 9; Tables 1 and S4). The higher level of CH may be due to the higher level of TOC ( $\geq 5.0 \text{ mg L}^{-1}$ ) which was reported in three out of nine studies (Table S4). Furthermore, the tap water used as source water, reported in six out of nine studies, may also contain NOM, and the NOM of humic origin (humic and fulvic acids, and humic substances) favors the formation of CH (WHO 2017).

### Comparison for tCAMs

WHO (2006) proposed that the level of combined chlorine should not be more than half of the level of FRC ( $1.2 \text{ mg L}^{-1}$ ), but the concentration of combined chlorine should be as low as possible and preferably remain  $< 200 \text{ } \mu\text{g L}^{-1}$  in swimming pool water (Table 1). The combined chlorine is the difference between total residual chlorine and free available residual chlorine, corresponding to tCAMs in indoor swimming pool water (Simard et al. 2013; Mah & Heacock 2014). Among the reviewed studies, 16 studies reported the level of tCAMs and 100% of the studies reported levels of tCAMs ( $213\text{--}2,020 \text{ } \mu\text{g L}^{-1}$ ) above the WHO guidelines (Figures 7, 8(d) and 9 and Table S5). This may be due to higher FRC ( $\geq 2.0 \text{ mg L}^{-1}$ ), which was reported in almost half (six out of 14) of the reviewed studies, whereas two out of 16 studies which reported the exceeding levels of tCAMs did not report the level of FRC (Table S5).

### Best practices

Based on a comprehensive synthesis of the reviewed studies, following best practices can be recommended.

### Water quality parameters

**Temperature:** Pool temperature in the range of  $24\text{--}28 \text{ }^\circ\text{C}$  seems a best option as this can provide reasonably enjoyable conditions in the pool and do not excessively facilitate DBPs formation. However, the levels of temperature recommended in swimming pools may be difficult to maintain, particularly in summer and in outdoor pools. Higher temperature leads to more sweat production which is an organic precursor from anthropogenic inputs (e.g.

Teo et al. 2015). Since higher temperature accelerates the consumption of FRC, higher doses of chlorine are required to ensure FRC in the swimming pool water (Weisel et al. 2009; Richardson et al. 2010; Yang et al. 2016). The formation of DBPs is correlated with FRC, therefore higher temperature promotes the formation of DBPs (Chu & Nieuwenhuijsen 2002; Kanan 2010; Kanan & Karanfil 2011; Hansen et al. 2012; Simard et al. 2013).

**FRC:** The level of FRC is of major concern (Weisel et al. 2009; Richardson et al. 2010; Hang et al. 2016; Yang et al. 2016), and it plays a vital role in the formation of DBPs (Figure 3). It is recommended to maintain the FRC in the range of  $0.8\text{--}2.0$  and  $0.8\text{--}3.0 \text{ mg L}^{-1}$  in the case of indoor and outdoor pools, respectively (Simard et al. 2013). According to WHO (2006), levels of FRC above  $1.2 \text{ mg L}^{-1}$  should not be necessary in pools unless they are not well designed or well operated. However, it is suggested that fundamental problems be dealt with (design and/or operation), instead of increasing the disinfection levels.

**TOC/TN:** Correlation analysis showed that TOC was highly correlated with concentrations of several DBPs (Figure 3), which indicates that TOC is a dominant factor influencing the formation of DBPs (Lee et al. 2010). To minimize the formation of DBPs in swimming pool water, the organic precursor needs to be reduced, which can be NOM from the source water used to fill the pool and many other anthropogenic inputs such as sweat, urine, lotions, cosmetics, sunscreens and soap residuals (Kim et al. 2002; WHO 2006; Weaver et al. 2009; Lee et al. 2010; Teo et al. 2015; Peng et al. 2016; Yang et al. 2016) as well as skin lipids (Keuten et al. 2014). The main carbon sources in swimming pools are skin lipids, which may possibly be the important contributor in the production of C-DBPs (Keuten et al. 2014). In swimming pool water the continuous loading of DOC and DON is obtained from swimmers, which adds an additional complication to the disinfection and toxicological safety of swimming pool water (Zweiner et al. 2007; Chowdhury et al. 2014). DOC is proved to be a suitable parameter for precursor to predict THMs (C-DBP) production in swimming pool water (Peng et al. 2016). DON leads to the formation of N-DBPs (HANs and CAMs) (Richardson et al. 2010; Florentin et al. 2011; Chowdhury et al. 2014). Some amino acids (nitrogen-containing compounds), such as histidine present in sweat and

urine, favor the formation of HAAs (C-DBPs) during chlorination (Hong *et al.* 2009; Kanan 2010). This finding is consistent with the observation that urea (nitrogen-containing compound) contributes to about 6.3% of TOC in a swimming pool (De Laat *et al.* 2011). Therefore, it is essential to reduce the levels of TOC and TN in swimming pool water, which can be done by pre-swim showering, no use of cosmetics and by avoiding excretion in the pool (Zwiener *et al.* 2007; Keuten *et al.* 2012, 2014; Chowdhury *et al.* 2014). In general, a TOC value of  $<5.0 \text{ mg L}^{-1}$  could be recommended as the best option, since most of the investigated pools could meet the WHO guidelines on most of the DBPs below this limit. The level of TN cannot be recommended since a very limited number of studies estimated and related this parameter with DBPs formation and/or reduction, which should be considered in future research.

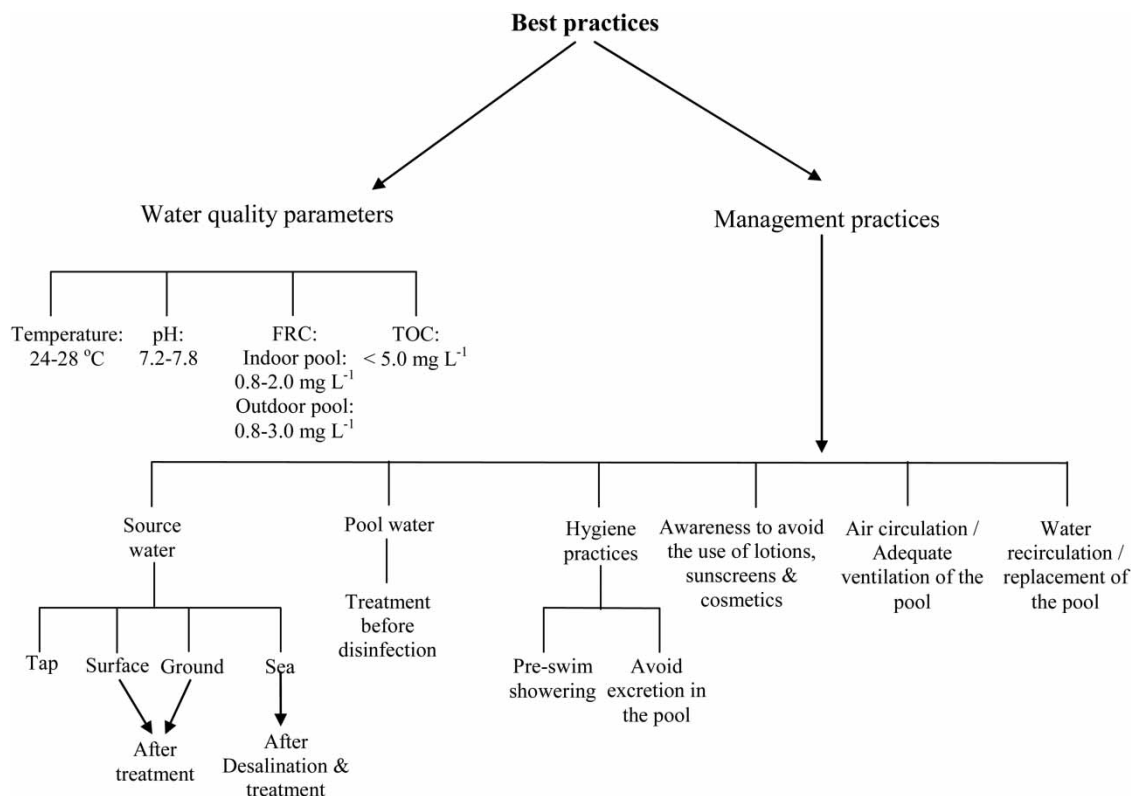
**pH:** Unlike temperature and TOC, which have positive correlations with most of the studied DBPs, pH has both positive and negative relationships with DBPs. This mixed impact makes pH management a more complicated task. However, most of the research indicated that at  $\text{pH} < 7.0$  the formation of THMs decreased, the formation of HAAs remained constant but the level of HANs increased, and the level of TCAM was drastically increased (Hansen *et al.* 2012). Therefore, the pH of swimming pool water should not be  $< 7.0$  to reduce the level of THMs because the formation of more toxic DBPs increases. Moreover, in the case of chlorine-based disinfection, the dissociation of HOCl depends on pH and at a pH of 7.5 it dissociates in water to  $\text{OCl}^-$ . HOCl is a much stronger, faster and oxidizing disinfectant compared with  $\text{OCl}^-$  (White 1992; WHO 2006). At pH levels of 6.5–8.5, HOCl is changed from undissociated to almost completely dissociated form. At a pH of 8.0 only 21% of the FRC exists in the HOCl form which is reduced to 12% at a pH of 8.5. Coagulation is also pH dependent and most of the coagulants work best in a specific pH range. Therefore, pH should be maintained between 7.2 and 7.8 for chlorine based disinfectants to ensure efficient disinfection and coagulation as well as user comfort (WHO 2006). Thus, the recommended pH range of 7.2–7.8 for chlorinated swimming pool water remains the best option. To maintain a constant level of pH in the pool at all times, it should ideally be controlled by an automated system (Bonnick 2005).

The emerging best practices from the studies reviewed in this paper are summarized in Figure 10, which could serve as a quick guide to control a swimming pool environment and formation of DBPs. Following these basic recommendations can significantly reduce health risks associated with undesirable concentrations of DBPs.

### Management practices

**Source water selection/treatment:** To reduce the level of DBPs the selection of source water is of major concern (Chowdhury *et al.* 2014). Since the source waters generally have precursors, which react with chlorine to form DBPs, the source water should be treated before it enters the pool because as soon as it enters the pool it becomes more complex to remove the DBPs and their precursors. Based on the reviewed studies the use of freshwater, especially tap water, helps to control the formation of DBPs. In addition to tap water, ground water can also be an alternative source water. Seawater contains higher levels of  $\text{Br}^-$  compared with freshwater (tap, surface or ground) and leads to the formation of Br-DBPs (Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a), which are more toxic (Daiber *et al.* 2016; Manasfi *et al.* 2017b). The level of  $\text{Br}^-$  in seawater ranges from 65 to over  $80 \text{ mg L}^{-1}$ , in freshwater from trace amounts to about  $0.5 \text{ mg L}^{-1}$ , and in desalinated waters up to  $1.0 \text{ mg L}^{-1}$ . In surface and ground water the level of  $\text{Br}^-$  can increase due to saltwater intrusion (WHO 2017). Therefore, fresh water (preferably tap water), treated surface water and ground water or desalinated and treated seawater can be used to improve the quality of swimming pool water and maintain the encouraging aspects of swimming. Mallika *et al.* (2008) reported that the lower level of tTHMs was due to the use of treated raw (ground) water.

**Pool water treatment:** Analogous to source water, pool water treatment with appropriate treatment technologies is also very important to reduce the level of DBPs and their precursors (TOC, TN and  $\text{Br}^-$ ) (WHO 2006; Parinet *et al.* 2012). Peng *et al.* (2016) acknowledged that the treatment process consisted of an inline flocculation, powdered activated carbon dosage and ultra-filtration was not sufficient for the removal of DOC from pool water. However, Richardson *et al.* (2010) reported that the level of tTHMs when compared on a molar basis were lower in brominated pools



**Figure 10** | Summary of the best practices for controlling DBPs in swimming pool water.

(242 nM) compared with chlorinated pools (306 nM) due to the carbon filtration used at the brominated pools. Similarly, due to the treatment of chlorinated pool water with sand filter/flocculation and activated carbon filtration, the level of DBPs (THMs and HANs) was very low (Spiliotopoulou *et al.* 2015; Cheema *et al.* 2017b), though the source water was groundwater which is expected to contain  $\text{Br}^-$ . The sea-water pools ( $\text{Br}^-$  rich) used sand filters to remove particulates and pollutants (Manasfi *et al.* 2016, 2017c; Cheema *et al.* 2017a). Furthermore, for the treatment of pool water, Aprea *et al.* (2010) suggested that due to the presence of  $\text{Br}^-$  impurities in the treatment reagents, it is important to use high purity reagents for treatment.

**Hygiene practices:** The formation of DBPs can be controlled by assuring the hygiene of swimmers (Weaver *et al.* 2009; Lee *et al.* 2010), since the unhygienic behavior of swimmers can lead to a significant amount of anthropogenic pollution in swimming pools (Keuten *et al.* 2012, 2014). Therefore, the implementation of preventive measures such as public awareness and improvement in hygiene of

swimmers is an important step to reduce the formation of DBPs, as well as other chemicals entering in the pool. These additional chemicals include bodily excretions, lotions, cosmetics, sunscreens, and soap residuals (Zwiener *et al.* 2007; Kanan & Karanfil 2011; Teo *et al.* 2015).

**Air circulation/ventilation of the pool:** Air circulation in indoor pool settings can be increased to reduce the level of volatile DBPs (THMs and CAMs) (Zwiener *et al.* 2007), since the level of CAMs was higher in indoor pools compared with outdoor pools (Simard *et al.* 2013). Considering the fact that the source water also contains DBPs and their precursors, adequate ventilation in indoor pools should be considered (WHO 2006). A ventilation system with 30% fresh-pulsed air assures good management practice (Parrat *et al.* 2012).

**Water recirculation/replacement of the pool:** Pools filled with the same source water (tap water) showed great variability in tTHM, tHAA and CAMs levels, suggesting that management strategies play a major role in DBP formation and removal. For instance, Kim *et al.* (2002) suggested that

lower levels of DBPs in swimming pool can be achieved by circulating pool water regularly through appropriate filtering systems, or with frequent replacement with fresh water. However, with recirculation of the pool water without the addition of fresh water, the accumulation of HAAs can be accelerated over time (Simard *et al.* 2013). Therefore, it is most important that proper consideration is given to the replacement of water as well as frequent dilution of pool water with fresh water, to prevent excessive build-up of ions (WHO 2006; Simard *et al.* 2013; Peng *et al.* 2016; Yang *et al.* 2016). To maintain a certain water volume in swimming pools, considering water loss due to back-washing of filtration facility, vaporization and bather activities, the amount of fresh filling water should be at least  $0.03 \text{ m}^3$  per swimmer according to DIN 19643-1 (2012). Peng *et al.* (2016) assumed that due to the exchange with filling water, the removal of THMs could be facilitated.

## CONCLUSIONS

Chlorination is the most widely used method of disinfection for swimming pool water, and several studies have been conducted on DBPs formation, governing factors, health risks and possible measures to reduce or eliminate DBPs. The large number of published studies provided the basis of this review where DBPs values were analyzed for concentrations, and compared with the available WHO guidelines set for DBPs for drinking water quality. This study compiled a novel database, which was also used in statistical analysis in this study, on DBPs concentrations and governing factors from the information of 188 swimming pools given in 42 peer reviewed journal publications from 16 countries. The following specific conclusions could be inferred from this research:

1. The available evidence provides a reasonably good oversight on the concentrations of a few key species of DBPs, with large variations among individual swimming pools. For instance, the mean and standard deviation of tTHMs, tHAAs, tHANs and CH concentrations in chlorinated pool water were  $134 \pm 160$ ,  $679 \pm 874$ ,  $21 \pm 17$  and  $102 \pm 128 \mu\text{g L}^{-1}$ , respectively. Among the CAMs the mean concentration of MCAM, DCAM, TCAM and tCAMs was  $201 \pm 124$ ,  $171 \pm 370$ ,  $149 \pm 136$  and  $650 \pm 490 \mu\text{g L}^{-1}$ , respectively. The concentration of TCAM in the air was  $216 \pm 76 \mu\text{g m}^{-3}$ .
2. In general, the concentration of HAAs is much higher than THMs, because of bather organic loads in the swimming pool water, which tend to form HAAs more preferentially than THMs. Furthermore, HAAs are highly soluble in water and do not degrade in the presence of high FRC. Due to low volatility, HAAs accumulate in the swimming pool water leading to their higher concentrations over time compared with THMs, which are more volatile and escape into the air over pool water.
3. The dominant species among THMs, HAAs, HANs and THAs are TCM, DCAA and TCAA, DCAN and CH, respectively.
4. The TOC, temperature, FRC and pH play a pivotal role in the formation of DBPs, however, with distinct differences (positive or negative correlation) and level of influence (significant or non-significant correlation), which makes management of these governing factors a challenging undertaking. TOC emerged as the most influential factor affecting the formation of DBPs in the case of indoor pools using tap water as source water. The temperature and FRC could be stated as the second and third most influencing factors with significant correlation with three and two of the seven DBPs, respectively. The pH is also a significant factor, though it has the least influence on DBPs formation in freshwater pools compared with sea water pools. Additionally, the presence of TN catalyzes the formation of N-DBPs, as suggested by (limited) available evidence.
5. To reduce the level of DBPs in swimming pool water the quality and nature of source water needs to be carefully considered. Similarly, the type of disinfectant also needs to be considered to reduce the toxicity of swimming pool water. Between chlorination and bromination, chlorination appears as the best choice because bromination leads to the formation of Br-DBPs.
6. Contrary to the suggested levels of DBPs, concentrations of HAAs and CAMs were alarmingly higher than WHO guidelines for drinking water quality in the majority of the pools sampled in this study. Nevertheless, the reported concentrations were mostly below the WHO

guidelines in the case of HANs and THMs, with the exception of tTHMs. Therefore, a lack of compliance with recommended guidelines in several instances seems to be a considerable health risk that needs additional measures to ensure safe swimming pool environments.

7. Chlorination and bromination often result in harmful DBPs, which on many occasions could be much higher than the levels set by WHO, which are anticipated to reflect tolerable risks over a lifetime. Therefore, further research is needed to improve these traditional methods, but also emerging methods of disinfection such as UV, O<sub>3</sub>, and UV and ozone based AOPs could be further developed.
8. The best practices, outlined in this paper, on controlling water quality parameters and other environmental conditions could provide useful information to improve the quality of swimming pool water and consequently contribute to health risk reduction.

## REFERENCES

- Affifi, M. Z. & Blatchley III, E. R. 2016 [Effects of UV-based treatment on volatile disinfection byproducts in a chlorinated, indoor swimming pool](#). *Water Res.* **105**, 167–177.
- Aggazzotti, G. & Predieri, G. 1986 [Survey of volatile halogenated organics \(VHO\) in Italy: levels of VHO in drinking waters, surface waters and swimming pools](#). *Water Res.* **20** (8), 959–963.
- Aggazzotti, G., Fantuzzi, G., Righi, E. & Predieri, G. 1995 [Environmental and biological monitoring of chloroform in indoor swimming pools](#). *J. Chromatogr. A.* **710** (1), 181–190.
- Aggazzotti, G., Fantuzzi, G., Righi, E. & Predieri, G. 1998 [Blood and breath analyses as biological indicators of exposure to trihalomethanes in indoor swimming pools](#). *Sci. Total Environ.* **217** (1–2), 155–163.
- American Water Works Association (AWWA) 1999 *Water Quality and Treatment: A Handbook of Community Water Supplies*, Vol. 12, 5th edn. McGraw-Hill, New York, pp. 11–42.
- Aprèa, M. C., Banchi, B., Lunghini, L., Pagliantini, M., Peruzzo, A. & Sciarra, G. 2010 [Disinfection of swimming pools with chlorine and derivatives: formation of organochlorinated and organobrominated compounds and exposure of pool personnel and swimmers](#). *Nat. Sci.* **2** (2), 68–78.
- Barbot, E. & Moulin, P. 2008 [Swimming pool water treatment by ultrafiltration-adsorption process](#). *J. Membr. Sci.* **314** (1), 50–57.
- Baudisch, C., Pansch, G., Prösch, J. & Puchert, W. 1997 [Determination of Volatile Halogenated Hydrocarbons in Chlorinated Swimming Pool Water](#). Research Report, Ausnstelle Schwerin, Landeshygieneinstitut Mecklenburg-Vorpommern (in German) (cited in WHO (2000) Guidelines for Safe Recreational-Water Environments, Vol. 2, Swimming Pools, Spas and Similar Recreational-Water Environments, Geneva).
- Beech, J. A., Diaz, R., Ordaz, C. & Palomeque, B. 1980 [Nitrates, chlorates and trihalomethanes in swimming pool water](#). *Am. J. Public Health* **70** (1), 79–82.
- Benoit, F. M. & Jackson, R. 1987 [Trihalomethane formation in whirlpool spas](#). *Water Res.* **21** (3), 353–357.
- Bernard, A., Carbonnelle, S., Michel, O., Higuët, S., de Burbure, C., Buchet, J.-P., Hermans, C., Dumont, X. & Doyle, I. 2003 [Lung hyperpermeability and asthma prevalence in schoolchildren: unexpected associations with the attendance at indoor chlorinated swimming pools](#). *Occup. Environ. Med.* **60**, 385–394.
- Bessonneau, V., Derbez, M., Clément, M. & Thomas, O. 2011 [Determinants of chlorination by-products in indoor swimming pools](#). *Int. J. Hyg. Environ. Health* **215**, 76–85.
- Bonnick, D. M. 2005 [Swimming pool disinfection techniques and pitfalls](#). In: *Paper Presented at CIWEM's 'Swimming Pools & Spa Baths-Effective Control of Water Quality and Public Health' Conference at the Chancellors Hotel & Conference Centre*, 30th November 2005, Manchester.
- Cammann, K. & Hübner, K. 1993 [False results in headspace-gas chromatographic analysis of trihalomethanes in swimming pool water due to elevated headspace temperatures](#). *J. Chromatogr. A.* **648** (1), 294–298.
- Cardador, M. J. & Gallego, M. 2010 [Optimisation and comparison of several microextraction/ methylation methods for determining haloacetic acids in water using gas chromatography](#). *Anal. Bioanal. Chem.* **396** (3), 1331–1343.
- Cardador, M. J. & Gallego, M. 2011 [Haloacetic acids in swimming pools: swimmer and worker exposure](#). *Environ. Sci. Technol.* **45**, 5783–5790.
- Cardador, M. J. & Gallego, M. 2015 [Haloacetic acids content of fruit juices and soft drinks](#). *Food Chem.* **173**, 685–693.
- Caro, J. & Gallego, M. 2007 [Assessment of exposure of workers and swimmers to trihalomethanes in an indoor swimming pool](#). *Environ. Sci. Technol.* **41** (13), 4793–4798.
- Caro, J. & Gallego, M. 2008 [Alveolar air and urine analyses as biomarkers of exposure to trihalomethanes in an indoor swimming pool](#). *Environ. Sci. Technol.* **42** (13), 5002–5007.
- Catto, C., Sabrina, S., Ginette, C. T., Manuel, R. & Robert, T. 2012 [Occurrence and spatial and temporal variations of disinfection by-products in the water and air of two indoor swimming pools](#). *Int. J. Environ. Res. Public Health* **9** (8), 2562–2586.
- Chambon, P., Taveau, M., Morin, M., Chambon, R. & Vial, J. 1983 [Survey of trihalomethane levels in Rhône-Alps water supplies. Estimates on the formation of chloroform in wastewater treatment plants and swimming pools](#). *Water Res.* **17** (1), 65–69.

- Cheema, W. A., Manasfi, T., Kaarsholm, K. M. S., Andersen, H. R. & Boudenne, J.-L. 2017a *Effect of medium-pressure UV-lamp treatment on disinfection by-products in chlorinated seawater swimming pool. Sci. Total Environ.* **599–600**, 910–917.
- Cheema, W. A., Kaarsholm, K. M. S. & Andersen, H. R. 2017b *Combined UV treatment and ozonation for the removal of by-product precursors in swimming pool water. Water Res.* **110**, 141–149.
- Chen, M. J., Lin, C. H., Duh, J. M., Chou, W. S. & Hsu, H. T. 2011 *Development of a multi-pathway probabilistic health risk assessment model for swimmers exposed to chloroform in indoor swimming pools. J. Hazard. Mater.* **185**, 1037–1044.
- Chowdhury, S., Alhooshani, K. & Karanfil, T. 2014 *Disinfection by-products in swimming pool: occurrences, implications and future needs. Water Res.* **53**, 68–109.
- Chu, H. & Nieuwenhuijsen, M. 2002 *Distribution and determinants of trihalomethane concentrations in indoor swimming pools. Occup. Environ. Med.* **59** (4), 243–247.
- Cimetiere, N. & De Laat, J. 2014 *Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: a lab-scale study. Microchem. J.* **112**, 34–41.
- Daiber, E. J., DeMarini, D. M., Ravuri, S. A., Liberatore, H. K., Cuthbertson, A. A., Thompson-Klemish, A., Byer, J. D., Schmid, J. E., Affi, M. Z., Blatchley, E. R. & Richardson, S. D. 2016 *Progressive increase in disinfection byproducts and mutagenicity from source to tap to swimming pool and spa water: impact of human inputs. Environ. Sci. Technol.* **50**, 6652–6662.
- De Laat, J., Feng, W., Freyfer, D. A. & Dossier-Berne, F. 2011 *Concentration levels of urea in swimming pool water and reactivity of chlorine with urea. Water Res.* **45** (3), 1139–1146.
- DIN 2012 *DIN 19643-1-Treatment of Water of Swimming Pools and Baths-Part 1: General Requirements.* Beuth Verlag GmbH, Berlin.
- Erdinger, L., Kühn, K. P., Kirsch, F., Feldhues, R., Fröbel, T., Nohynek, B. & Gabrio, T. 2004 *Pathways of trihalomethane uptake in swimming pools. Int. J. Hyg. Environ. Health.* **207** (6), 571–575.
- Fabbricino, M. & Korshin, G. V. 2009 *Modelling disinfection by-products formation in bromide-containing waters. J. Hazard. Mater.* **168** (2–3), 782–786.
- Fantuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F. & Aggazzotti, G. 2001 *Occupational exposure to trihalomethanes in indoor swimming pools. Sci. Total Environ.* **264** (3), 257–265.
- Florentin, A., Hautemanière, A. & Hartemann, P. 2011 *Health effects of disinfection by-products in chlorinated swimming pools. Int. J. Hyg. Environ. Health* **214**, 461–469.
- Font-Ribera, L., Villanueva, C. M., Nieuwenhuijsen, M. J., Zock, J. P., Kogevinas, M. & Henderson, J. 2011 *Swimming pool attendance, asthma, allergies, and lung function in the Avon longitudinal study of parents and children cohort. Am. J. Respir. Crit. Care Med.* **183** (5), 582–588.
- Font-Ribera, L., Kogevinas, M., Schmalz, C., Zwiener, C., Marco, E., Grimalt, J. O., Liu, J., Zhang, X., Mitch, W., Critelli, R., Naccarati, A., Heederik, D., Spithoven, J., Arjona, L., Bont, J., Gracia-Lavedan, E. & Villanueva, C. M. 2016 *Environmental and personal determinants of the uptake of disinfection by-products during swimming. Environ. Res.* **149**, 206–215.
- Ford, R. L. 2007 *Certified Pool-Spa Operator Handbook.* National Swimming Pool Foundation, Colorado Springs, CO.
- Gagnaire, F., Azim, S., Bonnet, P., Hecht, G. & Hery, M. 1994 *Comparison of the sensory irritation response in mice to chlorine and nitrogen trichloride. J. Appl. Toxicol.* **14** (6), 405–409.
- Glauner, T., Waldmann, P., Frimmel, F. H. & Zwiener, C. 2005a *Swimming pool water fractionation and geno-toxicological characterization of organic constituents. Water Res.* **39** (18), 4494–4502.
- Glauner, T., Kunz, F., Zwiener, C. & Frimmel, F. H. 2005b *Elimination of swimming pool water disinfection byproducts with advanced oxidation processes (AOPs). Acta Hydrochim. Hydrobiol.* **33**, 585–594.
- Hang, C., Zhang, B., Gong, T. & Xian, Q. 2016 *Occurrence and health risk assessment of halogenated disinfection byproducts in indoor swimming pool water. Sci. Total Environ.* **543** (Part A), 425–431.
- Hansen, K. M. S., Willach, S., Antoniou, G. M., Mosbæk, H., Albrechtsen, H. J. & Andersen, H. R. 2012 *Effect of pH on the formation of disinfection byproducts in swimming pool water – is less THM better? Water Res.* **46** (19), 6399–6409.
- Hansen, K. M. S., Zorzea, R., Piketty, A., Vega, S. R. & Andersen, H. R. 2013 *Photolytic removal of DBPs by medium pressure UV in swimming pool water. Sci. Total Environ.* **443**, 850–856.
- Hansen, K. M. S., Spiliotopoulou, A., Cheema, W. A. & Andersen, H. R. 2016 *Effect of ozonation of swimming pool water on formation of volatile disinfection by-products – A laboratory study. Chem. Eng.* **289**, 277–285.
- Harp, D. L. 2002 *Current Technology of Chlorine Analysis for Water and Wastewater.* Retrieved from: [www.hach.com/fmminghach?/CODE:L70191473%7C1//true](http://www.hach.com/fmminghach?/CODE:L70191473%7C1//true).
- Heeb, M. B., Criquet, J., Zimmermann-Steffens, S. G. & von Gunten, U. 2014 *Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds—a critical review. Water Res.* **48**, 15–42.
- Hery, M., Hecht, G., Gerber, J., Gender, J., Hubert, G. & Rebuffaud, J. 1995 *Exposure to chloramines in the atmosphere of indoor swimming pools. Ann. Occup. Hyg.* **39** (4), 427–439.
- Hong, H. C., Wong, M. H. & Liang, Y. 2009 *Amino acids as precursors of trihalomethane and haloacetic acid formation during chlorination. Arch. Environ. Contam. Toxicol.* **56**, 638–645.
- Hsu, H., Chen, M., Lin, C., Chou, W. & Chen, J. 2009 *Chloroform in indoor swimming-pool air: monitoring and modeling coupled with the effects of environmental conditions and occupant activities. Water Res.* **43** (15), 3693–3704.
- Hua, G., Reckhow, D. A. & Kim, J. 2006 *Effect of bromide and iodide ions on the formation and speciation of disinfection*

- byproducts during chlorination. *Environ. Sci. Technol.* **40** (9), 3050–3056.
- Ilyas, H., Masih, I. & van der Hoek, J. P. 2018 Disinfection methods for swimming pool water: byproduct formation and control. *Water* **10** (6), 1–29.
- Jacobs, J., Spaan, S., Van Rooy, G., Meliefste, C., Zaat, V., Rooyackers, J. & Heederik, D. 2007 Exposure to trichloramine and respiratory symptoms in indoor swimming pool workers. *Eur. Respir. J.* **29** (4), 690–698.
- Jain, S. R. & Soundararajan, S. 1964 The dipole moments and molecular structure of chloral and bromal hydrates. *Tetrahedron* **20**, 1589–1592.
- Judd, S. J. & Black, S. H. 2000 Disinfection by-product formation in swimming pool waters: a simple mass balance. *Water Res.* **34** (5), 1611–1619.
- Judd, S. J. & Jeffrey, J. A. 1995 Trihalomethane formation during swimming pool water disinfection using hypobromous and hypochlorous acids. *Water Res.* **29** (4), 1203–1206.
- Jurado-Sánchez, B., Ballesteros, E. & Gallego, M. 2010 Screening of N-nitrosamines in tap and swimming pool waters using fast gas chromatography. *J. Separ. Sci.* **33** (4–5), 610–616.
- Kampioti, A. A. & Stephanou, E. G. 2002 The impact of bromide on the formation of neutral and acidic disinfection by-products (DBPs) in Mediterranean chlorinated drinking water. *Water Res.* **36** (10), 2596–2606.
- Kanan, A. 2010 Occurrence and Formation of Disinfection By-Products in Indoor Swimming Pools Water. PhD thesis, Clemson University, SC, USA.
- Kanan, A. & Karanfil, T. 2011 Formation of disinfection by-products in indoor swimming pool water: the contribution from filling water natural organic matter and swimmer body fluids. *Water Res.* **45** (2), 926–932.
- Keuten, M., Schets, F., Schijven, J., Verberk, J. & van Dijk, J. 2012 Definition and quantification of initial anthropogenic pollutant release in swimming pools. *Water Res.* **46** (11), 3682–3692.
- Keuten, M., Peters, M., Daanen, H., de Kreuk, M., Rietveld, L. & van Dijk, J. 2014 Quantification of continual anthropogenic pollutants released in swimming pools. *Water Res.* **53**, 259–270.
- Kim, H. 1997 Human Exposure to Dichloroacetic Acid and Trichloroacetic Acid From Chlorinated Water During Household use and Swimming. PhD Dissertation, The State University of New Jersey and University of medicine and Dentistry of New Jersey, Rutgers.
- Kim, H. & Han, K. 2011 Swimmers contribute to additional formation of N-nitrosamines in chlorinated pool water. *Toxicol. Environ. Health Sci.* **3** (3), 168–174.
- Kim, H., Shim, J. & Lee, S. 2002 Formation of disinfection by-products in chlorinated swimming pool water. *Chemosphere* **46** (1), 123–130.
- Kogevinas, M., Villanueva, C. M., Font-Ribera, L., Liviach, D., Bustamante, M. & Espinoza, F. 2010 Genotoxic effects in swimmers exposed to disinfection by-products in indoor swimming pools. *Environ. Health Perspect.* **118** (11), 1531–1537.
- Korich, D., Mead, J. R., Madore, M. S., Sinclair, N. A. & Sterling, C. R. 1990 Effects of ozone, chlorine dioxide, chlorine, and monochloramine on *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* **56** (5), 1423–1428.
- Koudjonou, B. K. & LeBel, G. L. 2006 Halogenated acetaldehydes: analysis, stability and fate in drinking water. *Chemosphere* **64**, 795–802.
- Kramer, M., Hübner, I., Rörden, O. & Schmidt, C. 2009 Haloacetonitriles-another important group of disinfection byproducts in swimming pool water. In: *Swimming Pool & Spa International Conference London*.
- Kristensen, G. H., Klausen, M. M., Andersen, H. R., Erdinger, L., Lauritsen, F. R., Arvin, E. & Albrechtsen, H.-J. 2009 Full scale test of UV-based water treatment technologies at Gladsaxe Sport centre – with and without advanced oxidation mechanisms. In: *The Third International Swimming Pool and Spa Conference*, March, London.
- Lahl, U., Batjer, K., Duszeln, J., Gabel, B., Stachel, B. & Thiemann, W. 1981 Distribution and balance of volatile halogenated hydrocarbons in the water and air of covered swimming pools using chlorine for water disinfection. *Water Res.* **15** (7), 803–814.
- Lee, J., Ha, K.-T. & Zoh, K.-D. 2009 Characteristics of trihalomethane (THM) production and associated health risk assessment in swimming pool waters treated with different disinfection methods. *Sci. Total Environ.* **407** (6), 1990–1997.
- Lee, J., Jun, M., Lee, M., Lee, M., Eom, S. & Zoh, K.-D. 2010 Production of various disinfection byproducts in indoor swimming pool waters treated with different disinfection methods. *Int. J. Hyg. Environ. Health.* **213**, 465–474.
- Li, J. & Blatchley III, E. R. 2007 Volatile disinfection byproduct formation resulting from chlorination of organic-nitrogen precursors in swimming pools. *Environ. Sci. Technol.* **41** (19), 6732–6739.
- Li, J. & Blatchley III, E. R. 2009 UV photodegradation of inorganic chloramines. *Environ. Sci. Technol.* **43** (1), 60–65.
- Liang, L. & Singer, P. C. 2003 Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environ. Sci. Technol.* **37**, 2920–2928.
- Lifongo, L. L., Bowden, D. J. & Brimblecombe, P. 2010 Thermal degradation of haloacetic acids in water. *Int. J. Phys. Sci.* **5** (6), 738–747.
- Loos, R. & Barceló, D. 2001 Determination of haloacetic acids in aqueous environments by solid-phase extraction followed by ion-pair liquid chromatography–electrospray ionization mass spectrometric detection. *J. Chromatogr. A.* **938** (1), 45–55.
- Lourencetti, C., Grimalt, J. O., Marco, E., Fernandez, P., Font-Ribera, L., Villanueva, C. M. & Kogevinas, M. 2012 Trihalomethanes in chlorine and bromine disinfected swimming pools: air-water distributions and human exposure. *Environ. Int.* **45**, 59–67.

- Mah, D. J. & Heacock, H. 2014 The effectiveness of ozone-chlorine treatment for reducing chloramine concentration compared to chlorine treatment in swimming pools and whirlpools. *BCIT Environ. Health J.* Available from: [www.nceh.ca/sites/default/files/BCIT-Mah-2014.pdf](http://www.nceh.ca/sites/default/files/BCIT-Mah-2014.pdf) (date accessed 10 September, 2017).
- Maia, R., Correia, M., Pereira, I. M. B. & Belezza, V. M. 2014 Optimization of HS-SPME analytical conditions using factorial design for trihalomethanes determination in swimming pool water samples. *Microchem. J.* **112**, 164–171.
- Mallika, P., Sarisak, S. & Pongsri, P. 2008 Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water. *J. Environ. Sci.* **20** (3), 372–378.
- Manasfi, T., Méo, M. D., Coulomb, B., Giorgio, C. D. & Boudenne, J.-L. 2016 Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity. *Environ. Int.* **88**, 94–102.
- Manasfi, T., Coulomb, B. & Boudenne, J. L. 2017a Occurrence, origin, and toxicity of disinfection byproducts in chlorinated swimming pools: an overview. *Int. J. Hyg. Environ. Health.* **220**, 591–603.
- Manasfi, T., Méo, M. D., Giorgio, C. D., Coulomb, B. & Boudenne, J.-L. 2017b Assessing the genotoxicity of two commonly occurring byproducts of water disinfection: chloral hydrate and bromal hydrate. *Mut. Res. Genet. Toxicol. Environ. Mutagen.* **813**, 37–44.
- Manasfi, T., Temime-Roussel, B., Coulomb, B., Vassalo, L. & Boudenne, J.-L. 2017c Occurrence of brominated disinfection by-products in the air and water of chlorinated seawater swimming pools. *Int. J. Hyg. Environ. Health.* **220** (3), 583–590.
- Moore, R. M., Geen, C. E. & Tait, V. K. 1995 Determination of Henry's law constants for a suite of naturally occurring halogenated methanes in seawater. *Chemosphere* **30** (6), 1183–1191.
- Muellner, M. G., Wagner, E. D., McCalla, K., Richardson, S. D., Woo, Y. T. & Plewa, M. J. 2007 Haloacetoneitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic? *Environ. Sci. Technol.* **41** (2), 645–651.
- Nsubuga, H. & Basheer, C. 2013 Determination of haloacetic acids in swimming pool waters by membrane-protected micro-solid phase extraction. *J. Chromatogr. A* **1315**, 47–52.
- Parinet, J., Tabaries, S., Coulomb, B., Vassalo, L. & Boudenne, J. L. 2012 Exposure levels to brominated compounds in seawater swimming pools treated with chlorine. *Water Res.* **46** (3), 828–836.
- Parrat, J., Donzé, G., Iseli, C., Perret, D., Tomcic, C. & Schenk, O. 2012 Assessment of occupational and public exposure to trichloramine in Swiss indoor swimming pools: a proposal for an occupational exposure limit. *Ann. Occup. Hyg.* **56** (3), 264–277.
- Peng, D., Saravia, F., Abbt-Braun, G. & Horn, H. 2016 Occurrence and simulation of trihalomethanes in swimming pool water: a simple prediction method based on DOC and mass balance. *Water Res.* **88**, 634–642.
- Plewa, M. J., Kargalioglu, Y., Vanker, D., Minear, R. A. & Wagner, E. D. 2002 Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products. *Environ. Mol. Mutagen.* **40** (2), 134–142.
- Plewa, M. J., Wagner, E. D., Muellner, M. G., Hsu, K. M. & Richardson, S. D. 2008 Comparative mammalian cell toxicity of N-DBPs and C-DBPs. In: *Disinfection By-Products in Drinking Water: Occurrence, Formation, Health Effects, and Control* (T. Karanfil, S. W. Krasner & Y. Xie eds). American Chemical Society, Washington, DC, pp. 36–50.
- Pozzi, R., Bocchini, P., Pinelli, F. & Galletti, G. C. 2011 Determination of nitrosamines in water by gas chromatography/chemical ionization/selective ion trapping mass spectrometry. *J. Chromatogr. A* **1218** (14), 1808–1814.
- Prieto-Blanco, M., Alpendurada, M., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., Machado, S. & Gonçalves, C. 2012 Improving methodological aspects of the analysis of five regulated haloacetic acids in water samples by solid-phase extraction, ion-pair liquid chromatography and electrospray tandem mass spectrometry. *Talanta* **94**, 90–98.
- Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R. & DeMarini, D. M. 2007 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res.* **636**, 178–242.
- Richardson, S. D., DeMarini, D. M., Kogevinas, M., Fernandez, P., Marco, E., Lourencetti, C., Balleste, C., Heederik, D., Meliefste, K., McKague, A. B., Marcos, R., Font-Ribera, L., Grimalt, J. O. & Villanueva, C. M. 2010 What's in the pool? A comprehensive identification of disinfection by products and assessment of mutagenicity of chlorinated and brominated swimming pool water. *Environ. Health Perspect.* **118** (11), 1523–1530.
- Sarrión, M., Santos, F. & Galceran, M. 2000 Insituderivatization /solid-phase micro-extraction for the determination of haloacetic acids in water. *Anal. Chem.* **72** (20), 4865–4873.
- Schmalz, C., Frimmel, F. H. & Zwiener, C. 2011 Trichloramine in swimming pools-Formation and mass transfer. *Water Res.* **45**, 2681–2690.
- Shah, A. D. & Mitch, W. A. 2011 Halonitroalkanes, halonitriles, haloamides, and Nnitrosamines: a critical review of nitrogenous disinfection byproduct formation pathways. *Environ. Sci. Technol.* **46** (1), 119–131.
- Simard, S., Tardif, R. & Rodriguez, M. J. 2013 Variability of chlorination by-product occurrence in water of indoor and outdoor swimming pools. *Water Res.* **47**, 1763–1772.
- Singer, P. C. 1994 Control of disinfection by-products in drinking water. *J. Environ. Eng.* **120**, 727–744.
- Soltermann, F., Widler, T., Canonica, S. & von Gunten, U. 2014 Photolysis of inorganic chloramines and efficiency of trichloramine abatement by UV treatment of swimming pool water. *Water Res.* **56**, 280–291.
- Spiliotopoulou, A., Hansen, K. M. S. & Andersen, H. R. 2015 Secondary formation of disinfection by-products by UV



- treatment of swimming pool water. *Sci. Total Environ.* **520**, 96–105.
- Takahashi, Y., Onodera, S., Morita, M. & Terao, Y. 2003 A problem in the determination of trihalomethane by headspace-gas chromatography/mass spectrometry. *J. Health Sci.* **49** (1), 1–7.
- Tardif, R., Catto, C., Haddad, S., Simard, S. & Rodriguez, M. 2016 Assessment of air and water contamination by disinfection by-products at 41 indoor swimming pools. *Environ. Res.* **148**, 411–420.
- Teo, T. L. L., Coleman, H. M. & Khan, S. J. 2015 Chemical contaminants in swimming pools: occurrence, implications and control. *Environ. Int.* **76**, 16–31.
- Thacker, N. P. & Nitnaware, V. 2003 Factors influencing formation of trihalomethanes in swimming pool water. *Bull. Environ. Contam. Toxicol.* **71** (3), 633–640.
- Tian, C., Liu, R., Guo, T., Liu, H., Luo, Q. & Qu, J. 2013 Chlorination and chloramination of high-bromide natural water: DBPs species transformation. *Separ. Purif. Technol.* **102**, 86–93.
- US EPA Integrated Risk Information System (IRIS). Available from: <https://cfpub.epa.gov/ncea/iris2/atoz.cfm> (date accessed 15 September, 2017).
- Uyak, V. & Toroz, I. 2007 Investigation of bromide ion effects on disinfection by-products formation and speciation in an istanbul water supply. *J. Hazard. Mater.* **149**, 445–451.
- Villanueva, C. M., Gagniere, B., Monfort, C., Nieuwenhuijsen, M. J. & Cordier, S. 2007 Sources of variability in levels and exposure to trihalomethanes. *Environ. Res.* **103** (2), 211–220.
- Vlaanderen, J., Veldhoven, K., Font-Ribera, L., Villanueva, C. M., Hyam, M. C., Portengen, L., Grimalt, J. O., Zwiener, C., Heederik, D., Zhang, X., Vineis, P., Kogevinas, M. & Roel Vermeulen, R. 2017 Acute changes in serum immune markers due to swimming in a chlorinated pool. *Environ. Int.* **105**, 1–11.
- Walse, S. S. & Mitch, W. A. 2008 Nitrosamine carcinogens also swim in chlorinated pools. *Environ. Sci. Technol.* **42** (4), 1032–1037.
- Wang, X., Leal, M. G., Zhang, X., Yang, H. & Xie, Y. 2014 Haloacetic acids in swimming pool and spa water in the United States and China. *Front. Environ. Sci. Eng.* **8** (6), 820–824.
- Weaver, W. A., Li, J., Wen, Y., Johnston, J., Blatchley, M. R. & Blatchley III, E. R. 2009 Volatile disinfection by-product analysis from chlorinated indoor swimming pools. *Water Res.* **43**, 3308–3318.
- Weisel, C. P., Richardson, S. D., Nemery, B., Aggazzotti, G., Baraldi, E., Blatchley, E. R., Blount, B. C., Carlsen, K. H., Eggleston, P. A., Frimmel, F. H., Goodman, M., Gordon, G., Grinshpun, S. A., Heederik, D., Kogevinas, M., LaKind, J. S., Nieuwenhuijsen, M. J., Piper, F. C. & Sattar, S. A. 2009 Childhood asthma and environmental exposures at swimming pools: state of the science and research recommendations. *Environ. Health Perspect.* **117** (4), 500–507.
- Weng, S. & Blatchley III, E. R. 2011 Disinfection by-product dynamics in a chlorinated, indoor swimming pool under conditions of heavy use: national swimming competition. *Water Res.* **45** (16), 5241–5248.
- Weng, S. C., Li, J. & Blatchley III, E. R. 2012 Effects of UV<sub>254</sub> irradiation on residual chlorine and DBPs in chlorination of model organic-N precursors in swimming pools. *Water Res.* **46**, 2674–2682.
- Westerhoff, P., Chao, P. & Mash, H. 2004 Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Res.* **38**, 1502–1513.
- White, G. C. 1992 *Handbook of Chlorination and Alternative Disinfectants*, 3rd edn. Van Nostrand Reinhold, New York.
- World Health Organization (WHO) 2006 *Guidelines for Safe Recreational Water Environments*, Vol. 2. Swimming Pools and Similar Environments. Available from: [http://apps.who.int/iris/bitstream/10665/43336/1/9241546808\\_eng.pdf](http://apps.who.int/iris/bitstream/10665/43336/1/9241546808_eng.pdf) (date accessed 15 September, 2017).
- World Health Organization (WHO) 2017 *Guidelines for Drinking-Water Quality*, 4th edn. Incorporating the First Addendum. Available from: <http://apps.who.int/iris/bitstream/10665/254637/1/9789241549950-eng.pdf> (date accessed 15 September, 2017).
- Xiao, F., Zhang, X., Zhai, H., Lo, I. M. C., Tipoe, G. L., Yang, M., Pan, Y. & Chen, G. 2012 New halogenated disinfection byproducts in swimming pool water and their permeability across skin. *Environ. Sci. Technol.* **46** (13), 7112–7119.
- Yang, M. & Zhang, X. 2013 Comparative developmental toxicity of new aromatic halogenated DBPs in a chlorinated saline sewage effluent to the marine polychaete *Platynereis dumerilii*. *Environ. Sci. Technol.* **47** (19), 10868–10876.
- Yang, L., Schmalz, C., Zhou, J., Zwiener, C., Chang, V. W. C., Ge, L. & Wan, M. P. 2016 An insight of disinfection by-product (DBP) formation by alternative disinfectants for swimming pool disinfection under tropical conditions. *Water Res.* **101**, 535–546.
- Yeh, R. Y., Farré, M. J., Stalter, D., Tang, J. Y., Molendijk, J. & Escher, B. I. 2014 Bioanalytical and chemical evaluation of disinfection by-products in swimming pool water. *Water Res.* **59**, 172–184.
- Yilmaz, I., Yanardag, M., Birkan, B. & Bumin, G. 2004 Effects of swimming training on physical fitness and water orientation in autism. *Pediatr. Int.* **46**, 624–626.
- Zhang, X. & Minear, R. A. 2002 Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. *Water Res.* **36**, 3665–3675.
- Zwiener, C., Richardson, S. D., De Marini, D. M., Grummt, T., Glauner, T. & Frimmel, F. H. 2007 Drowning in disinfection byproducts? assessing swimming pool water. *Environ. Sci. Technol.* **41** (2), 363–372.

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