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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. The 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 ± 437 and $326 \pm 517 \,\mu g \, L^{-1}$, respectively, which most often surpassed the WHO guidelines. Similarly, more than half of the examined pools had higher values of chloral hydrate ($102 \pm 128 \,\mu g \, L^{-1}$). The concentration of total chloramines ($650 \pm 490 \,\mu g \, L^{-1}$) 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 ($134 \pm 160 \,\mu g \, L^{-1}$), dichloroacetonitrile ($12 \pm 12 \,\mu g \, L^{-1}$) and dibromoacetonitrile ($12 \pm 12 \,\mu g \, L^{-1}$) and dibromoacetonitrile ($12 \pm 12 \,\mu g \, L^{-1}$). Total organic carbon, free residual chlorine, temperature, pH, total nitrogen and bromide ions play a 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 essential to maintain 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 to 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-organisms such as Cryptosporidium parvum and Giardia lambia 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 reported the use of brominebased 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 (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 (O₃) (Hang et al. 2016; Hansen et al. 2016), UV-based advanced oxidation processes (AOPs) such as UV/hydrogen peroxide (H₂O₂) (Spiliotopoulou et al. 2015), and ozone-based AOPs such as O₃/UV and O₃/H₂O₂ (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 (Ilvas 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 (μ g L ⁻¹) (WHO 2006, 2017) ^a
Chloroform	B2	300
Bromodichloromethane	B2	60
Dibromochloromethane	C	100
Bromoform	B2	100
Total trihalomethanes	-	100
Monochloracetic 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 ^aThe 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, available with the online version of this paper). The suggested limits by six European countries for total THMs (tTHMs) for swimming pool water were in the range of $20-100 \,\mu g \, L^{-1}$. 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- $1,000 \,\mu g \, L^{-1}$ 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 $100 \,\mu g \, L^{-1}$ 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- 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 of 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 to validating the nature and strength of such relationships, and where possible develop predictive models (e.g. regression equations and processbased 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.

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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⁻) 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⁻?
 - o 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 a 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 on 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, available with the online version of this paper). 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-), source water (e.g. fresh and sea), pool location (indoor and outdoor) and disinfection and detection methods.

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 ± 140 , 58 ± 152 and $134 \pm$ 160 μ g L⁻¹, respectively.

HAAs

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

Table 2 | Types and species of DBPs

DBP type	DBPs species	Abbreviation	Chemical formula
Trihalomethanes (THMs)	Trichloromethane (chloroform) Bromodichloromethane Dibromochloromethane Tribromomethane (bromoform)	TCM BDCM DBCM TBM	CHCl ₃ CHBrCl ₂ CHBr ₂ Cl CHBr ₃
Haloacetic acids (HAAs)	Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Monobromoacetic acid Dibromoacetic acid Bromochloroacetic acid Bromodichloroacetic acid Dibromochloroacetic acid Tribromoacetic acid	MCAA DCAA TCAA MBAA DBAA BCAA BDCAA DBCAA TBAA	CH ₂ ClCOOH CHCl ₂ COOH CCl ₃ COOH CH ₂ BrCOOH CHBr ₂ COOH CHBrClCOOH CBrCl ₂ COOH CBr ₂ ClCOOH CBr ₃ COOH
Haloacetonitriles (HANs)	Dichloroacetonitrile Trichloroacetonitrile Bromochloroacetonitrile Dibromoacetonitrile Chloroacetonitrile Bromoacetonitrile	DCAN TCAN BCAN DBAN CAN BAN	CHCl ₂ CN CCl ₃ CN CHBrClCN CHBr ₂ CN CH ₂ ClCN CH ₂ BrCN
Trihaloacetaldehydes (THAs)	Chloral hydrate Bromal hydrate	CH BH	CCl ₃ CH(OH) ₂ or C ₂ H ₃ Cl ₃ O ₂ CBr ₃ CH(OH) ₂ or C ₂ H ₃ Br ₃ O ₂
Chloramines (CAMs)	Monochloramine Dichloramine Trichloramine	MCAM DCAM TCAM	NH ₂ Cl NHCl ₂ 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 ± 437 and $326 \pm 517 \,\mu g \, L^{-1}$, 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 ± 145 and $51 \pm 86 \,\mu g \, L^{-1}$, 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 ± 12 and $8 \pm 11 \,\mu g \, L^{-1}$, 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 a 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 Laat 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 $0.1-12 \,\mu g \, L^{-1}$, with means and standard deviations of 102 ± 128 and $5.0 \pm 5.0 \,\mu g \, L^{-1}$, 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 mol L⁻¹, 25 °C, pH 1.0-10), therefore, its concentrations above this limit volatize 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 ug 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 $\mu g m^{-3}$ for indoor pools in Switzerland. Therefore, they strongly suggest fixing the TCAM occupational exposure limit at $300 \, \mu g \, m^{-3}$. The reported concentration of TCAM and tCAMs in pool water was 149 ± 136 and $650 \pm 490 \,\mu g \, L^{-1}$, respectively and TCAM in air was $216 \pm 76 \,\mu g \, m^{-3}$.

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 analysis was conducted on water quality parameters (temperature, pH, FRC TOC, TN and 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 (118-657 μg L⁻¹) in outdoor pools (Table S1). Similarly, Simard et al. (2013) observed a higher level of tTHMs (up to 311 µg L⁻¹) in outdoor pools compared with indoor pools (up to $114 \,\mu g \, L^{-1}$). 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 μ 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 µg L⁻¹ in indoor and outdoor pools, respectively.

The concentration of tCAMs was less in outdoor pools $(8.0-854 \,\mu g \,L^{-1})$ 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 et al. (2012); Simard et al. (2013)
	HAAs	Increase	Kanan (2010); Hansen et al. (2012); Simard et al. (2013)
	HANs	Increase	Kanan (2010); Hansen <i>et al.</i> (2012)
	CAMs	Decrease	Simard et al. (2013)
pH	THMs	Increase	Kanan (2010); Hansen et al. (2012)
	HAAs	Increase/No change	Kanan (2010); Hansen et al. (2012)
	HANs	Decrease	Kanan (2010); Lee et al. (2010); Hansen et al. (2012)
	CAMs	Decrease	Schmalz et al. (2011); (Hansen et al. (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 et al. (2010); Parinet et al. (2012); Simard et al. (2013); Hang et al. (2016)
	HAN	Increase	Kanan (2010); Lee et al. (2010); Hang et al. (2016)
	CH	Increase	Lee et al. (2010)
Free residual chlorine	THMs	Increase	Hansen et al. (2012); Simard et al. (2013); Hang et al. (2016)
	HAAs	Increase	Hansen et al. (2012); Wang et al. (2014); Hang et al. (2016)
	HANs	Increase/decrease	Hang et al. (2016)/Weng et al. 2012; Hansen et al. (2013)
	CAMs	Decrease	Li & Blatchley III (2009)
Total nitrogen			
Urea and ammonia	THMs	Decrease	Judd & Jeffrey (1995); Kim et al. (2002); Yang et al. (2016)
Amino acids	HAAs	Increase	Kanan (2010); Kanan & Karanfil (2011); Parinet et al. (2012)
Amino acids	HANs	Increase	Kim et al. (2002); Li & Blatchley (2007); Weaver et al. (2009); Weng et al. (2012)
Urea and ammonia	CAMs	Increase	Li & Blatchley III (2007); Schmalz et al. (20п)
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

tatistics Temperatur		рН	FRC	тос	TN	Br ⁻
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-, bromide ion.

indoor pools (311–1,723 μ g L⁻¹) (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⁻³, which indicates that indoor pools need better ventilation systems (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 by 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 ($<0.4 \,\mu g \, L^{-1}$). 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 NH₄⁺-N in source tap water may be a nitrogen source for the formation of HANs (Hang et al. 2016). Seawater contains 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 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 $\mu g L^{-1}$) 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 $380 \, \mu g \, L^{-1}$ (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 $(230 \,\mu g \, L^{-1})$ in seawater swimming pools compared with the level of BH $(0.4-12 \mu g L^{-1})$ 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 $(190 \,\mathrm{ug}\,\mathrm{L}^{-1})$ 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 μ g L⁻¹), corresponding alone to 70% of tHAAs $(35-747 \mu g L^{-1})$ and Manasfi et al. (2016) found the concentration of TCAA (461 μ g L⁻¹), corresponding alone to 92% of tHAAs (498 μ g L⁻¹) (Table S2). Similarly, in the case of bromination, Yang et al. (2016) observed the predominance of TBAA (17–22 μ g L⁻¹) over DBAA (8.9–10 μ g L⁻¹). However, Daiber *et al.* (2016) reported the predominance of DBAA (115–131 μ g L⁻¹) over TBAA (50-93 µg 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). Conversely, in the comparative studies of chlorination and bromination, the predominance of TCAN (2.9–7.2 μ g L⁻¹) over DCAN $(0.1-1.1 \,\mu g \, L^{-1})$ 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 by 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 $630 \,\mu g \, m^{-3}$ (Jacobs *et al.* 2007) and $20-1,260 \,\mu g \, m^{-3}$ (Bessonneau et al. 2011). In swimming pool water a 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 the 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 their reported concentrations 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 the 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 the 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 & Blatchlev III 2011). Some other studies reported similar results with the MIMS method of detection (Li & Blatchley III 2007; Weaver et al. 2009; Afifi & 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 $<100 \text{ ug L}^{-1}$, respectively) compared with bromination (240–300, <10 and $<100 \,\mu g L^{-1}$, 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 $674 \,\mu g \, L^{-1}$) 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 µg L⁻¹) was observed in heated outdoor pools compared with unheated pools (up to 150 μ 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 $800-1,200 \,\mu g \, L^{-1}$) was observed in heated outdoor pools compared with unheated pools (in the range of 250–1,260 μ 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 $\mu g L^{-1}$) compared with the level of BH (0.1–12 $\mu g L^{-1}$) 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 the rate of volatility of CAMs increases in warmer water (Simard et al. 2013).

Effect of pH

The research shows divergent 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 & Nitnaware 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 by 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 possible ability to decompose 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 $(230 \,\mu g \, L^{-1})$ in seawater swimming pools compared with the low level of BH (0.1-12 µg 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 $(3,615 \,\mu g \, L^{-1})$ was detected at a pH value of 6.0 and it decreased continuously with increasing pH value. It was measured at 241 µg 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 (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 mg L^{-1}) compared with the level recommended by WHO (2006) in swimming pool water (1.2 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 1.5-5.8 mg L⁻¹ the level of HANs was in the range of $< 0.56-42 \,\mu g \, L^{-1}$ (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, 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), Nnitrosopyrrolidine (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 a probable human carcinogen (US EPA, IRIS), WHO (2017) recommended a guideline value of $0.1 \, \text{ug L}^{-1}$ for NDMA in drinking water.

Effect of TOC

The high levels of TOC trigger higher chlorine demand, which consequently favors 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 mg L⁻¹) in outdoor pools, which was almost twice the TOC level in the indoor pool (8.7 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 mg L^{-1}) and consequently, the level of TCM and BDCM was 220 and 202 µg L⁻¹. Chu &

Nieuwenhuijsen (2002) observed that DOC significantly increased with the number of swimmers, ranging from 3.3 to 13 mg L^{-1} . 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 a 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^{-1}) in indoor pools compared with the level in outdoor pools (up to 13 mg L^{-1}) 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 Laat 2014; Manasfi et al. 2016) and the levels reached up to 380 µg L⁻¹ (e.g. Cimetiere & De Laat 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 Laat (2014) and Manasfi et al. (2016) was 5.5 and 12 mg L^{-1} , respectively (Table S4).

Effect of TN

Human body fluid discharges 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)

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

Sweat			Urine	By swimmers		
Nitrogen-containing compounds	Mean content (mg L ⁻¹)	Portion of TN (%)	Mean content (mg L ⁻¹)	Portion of TN (%)	estimated range of input (mg)	
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	

(De 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 μ g L⁻¹) to a high level of TN (7.7 mg L^{-1}) in the seawater pool (Table S2).

H. Ilyas et al. | Disinfection by-products formation in chlorinated swimming pool water

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 Br⁻ are both present in chlorinated pool water, then FRC reacts simultaneously with ammonia to form CAMs and with Br to form HOBr, which favors the formation of Br-DBPs.

Therefore, TN is a crucial parameter that increases 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 $mg L^{-1}$, 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 Br

The bromination of freshwater pools 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 Br and part reacted with organic matter and was transformed to Br-DBPs. Further, the hydrolyzed product HOCl reacts with 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 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 Br present in the seawater to form HOBr and hypobromite ion (BrO⁻) (Heeb et al. 2014; Manasfi et al. 2016, 2017c). Most of the HOBr is rapidly reduced to 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; Fabbricino & 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 Br⁻ is oxidized by HOCl to form HOBr, bromine substitution into organic compounds is favored (Uyak & Toroz 2007). Consequently, if 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 Br⁻ (Mallika et al. 2008; Kanan 2010; Kanan & Karanfil 2011; Yeh et al. 2014; Hang et al. 2016), though the level of Br was relatively low in tap water $(0.1-7.3 \text{ mg L}^{-1})$ 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 Br⁻ (2.2 mg L⁻¹) in the ground water (Mallika et al. 2008; Kanan 2010) (Table S1). However, the level of Br- $(68-107 \text{ mg L}^{-1})$ 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 (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 (Cl⁻) by 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 Brwith DBPs formation

The Pearson correlation analysis of temperature, pH. FRC. TOC, TN and 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 Br is discussed in this section. It is evident from Figure 1 that temperature, pH,

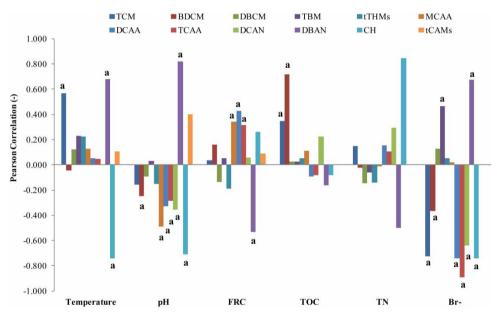


Figure 1 | Correlation statistics among the studied factors and DBPs, established using data of all types of studied pools with all types of fresh and seawater as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature 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 Br the number of observations were 30, 27, 30, 30, 24, 15, 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.

FRC, TOC, TN and 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, DBCM, 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, DBCM, tTHMs, MCAA, DCAA, TCAA, DCAN and CH, although there is a significant correlation 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 Br⁻, the formation of DBAN is promoted.

TOC shows a positive correlation with TCM, BDCM, DBCM, 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 a 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).

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 Br is evident due to a positive correlation with DBCM, 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, DBCM, 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 Br⁻ is not made (Figure 3).

The correlation of TCM, DBCM, 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, DBCM, 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, DBCM, DCAA and TCAA with FRC is analogous to all types of pools and all sources of water, although there is significant correlation 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 in the formation of DBPs, which is clear from the positive correlation of TOC with TCM, BDCM, DBCM, tTHMs and DCAN, which was significant with TCM, BDCM, DBCM and tTHMs (Figures 3 and 4(c) and 4(d)). The correlation of tTHMs and DCAN with TN 878

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 Br-; (f) DBAN and Br-.

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 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

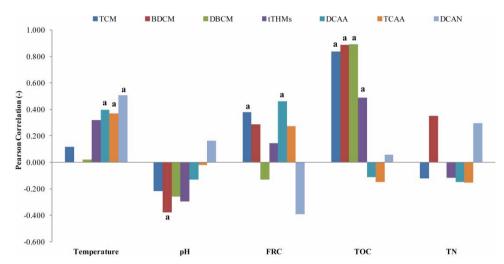


Figure 3 | Correlation statistics among the studied factors and DBPs, established using data of studied indoor pools with tap water as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature were 26, 22, 22, 17, 22, 22 and 16 for TCM, BDCM, 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.

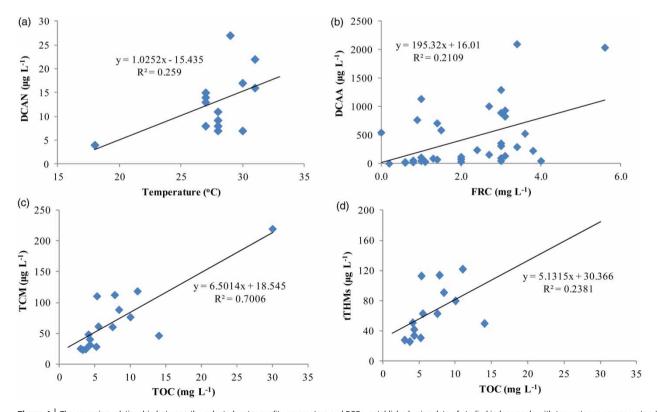


Figure 4 | The emerging relationship between the selected water quality parameters and DBPs, established using data of studied indoor pools with tap water as source water: (a) DCAN and temperature; (b) DCAA and FRC; (c) TCM and TOC; (d) tTHMs and TOC.

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

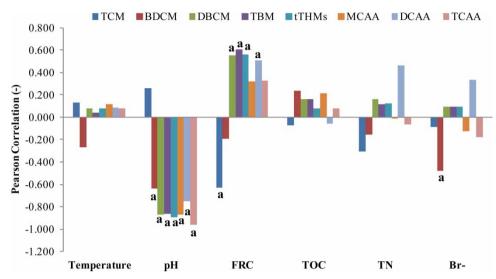


Figure 5 | Correlation statistics among the studied factors and DBPs, established using data of studied indoor pools with seawater as source water. Note: The number of studies reporting these parameters are different, thus the number of data points in the case of temperature, pH, FRC, TOC and Br were 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.

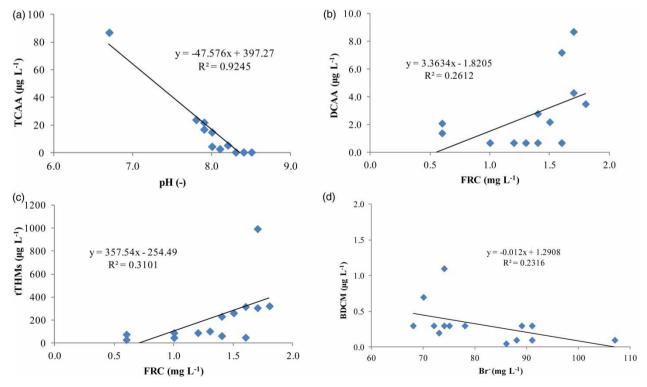


Figure 6 | The emerging relationship between the selected water quality parameters and DBPs, established using data of studied indoor pools with seawater as source water: (a) TCAA and pH; (b) DCAA and FRC; (c) tTHMs and FRC; (d) BDCM and Br-.

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 Bris 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 $(324-674 \,\mu g \, L^{-1})$ above the WHO standard (Table 1 and Table S1) and eight out of 66 (12%) reported elevated levels of TBM (101–931 μ 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 $(202 \mu g L^{-1})$. However, the level of tTHMs $(102-996 \mu g L^{-1})$ 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 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 (≥30 °C) and pH (≥7.8) also increase the level of THMs and was observed in 10 out

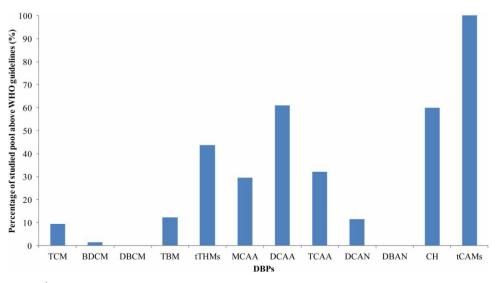


Figure 7 | Percentage of studied pools above WHO guidelines for drinking water quality for different DBPs species.

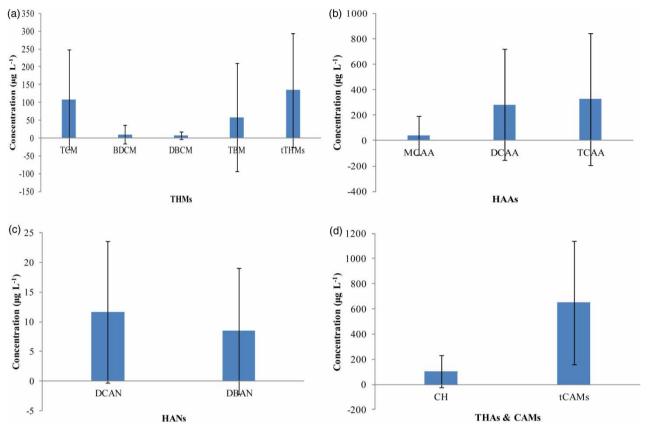


Figure 8 | Overall statistics (mean and standard deviation) of different DBPs species for which the guideline is set by WHO for drinking water quality.

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 in their formation. The level of tTHMs can also be increased when the level of brominated species increases due to higher levels of Br in seawater pools. Eight out of 27 studies used seawater as source water. The higher level of Br (>70 mg L⁻¹) was reported in seven out of eight studies. In the case of tap water, the presence of 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 (23-1,000 µg L⁻¹) above the WHO guidelines (Table 1 and Table S2). Similarly, DCAA (52- $2,100 \,\mu g \, L^{-1}$) and TCAA (106–2,970 $\mu g \, L^{-1}$) 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 ($\geq 500 \, \mu g \, L^{-1}$) 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 (≥30 °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 (≥5.0 mg L^{-1}) and low level of pH (≤ 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).

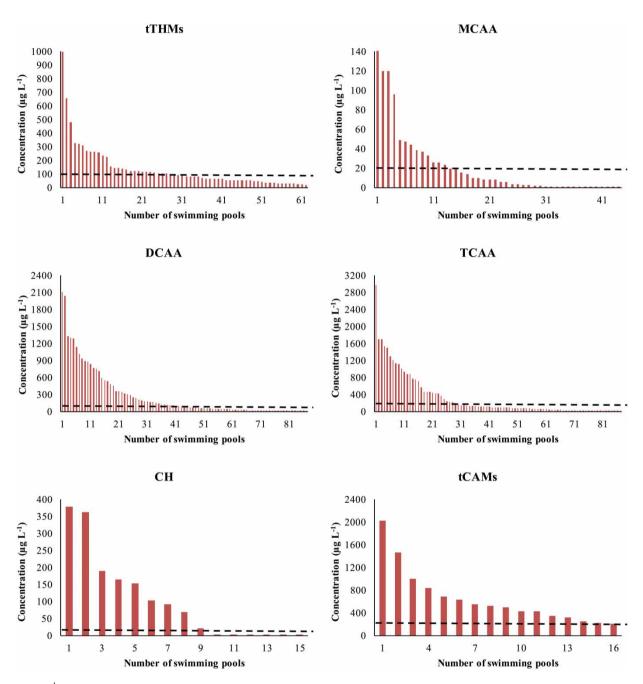


Figure 9 | A comparison of the concentrations of selected DBPs with WHO guidelines for drinking water. Note: The horizontal dash-line indicates the value of the WHO guideline for a given DBP.

Comparison for HANs

In chlorinated pools the level of DCAN (22–75 μ 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 (Table 1 and Table

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 (21–378 μ g L⁻¹) which were above the limits set by WHO (Figures 7, 8(d) and 9; Table 1 and Table S4). The higher level of CH may be due to the higher level of TOC (\geq 5.0 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 $mg L^{-1}$), but the concentration of combined chlorine should be as low as possible and preferably remain <200 μg 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 $(213-2,020 \,\mu g \, L^{-1})$ 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, the following best practices can be recommended.

Water quality parameters

Temperature: Pool temperature in the range of 24–28 °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 0.8–2.0 and 0.8–3.0 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 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 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 OCl-. HOCl is a much stronger, faster and oxidizing disinfectant compared with 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 chorine 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 Brcompared 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 Br in seawater ranges from 65 to over 80 mg L⁻¹, in freshwater from trace amounts to about 0.5 mg L^{-1} , and in desalinated waters up to 1.0 mg L^{-1} . In surface and ground water the level of 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 Br⁻) (WHO 2006; Parinet *et al.* 2012). Peng *et al.* (2016) acknowledged that the treatment process consisted of an inline flocculation, powdered activated

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

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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 (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 Br⁻. The seawater pools (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 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 ensuring 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 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 ensures 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 pools can be achieved by circulating pool water regularly through appropriate filtering systems, or by 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 m³ 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 $102 \pm 128 \,\mu g \, L^{-1}$, 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 μ g L⁻¹, respectively. The concentration of TCAM in the air was $216 \pm 76 \,\mu g \, m^{-3}$.
- 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 better 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

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- 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. O₃, 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.

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