1	Occurrence and Formation of Disinfection By-Products in the Swimming Pool Environment: A
2	Critical Review
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#### 8 Abstract

Disinfection of water for human use is essential to protect against microbial disease; however, 9 disinfection also leads to formation of disinfection by-products (DBPs), some of which are of health 10 concern. From a chemical perspective, swimming pools are a complex matrix, with continual addition of 11 a wide range of natural and anthropogenic chemicals via filling waters, disinfectant addition, 12 pharmaceuticals and personal care products and human body excretions. Natural organic matter, trace 13 amounts of DBPs and chlorine or chloramines may be introduced by the filling water, which is commonly 14 disinfected distributed drinking water. Chlorine and/or bromine is continually introduced via the addition 15 16 of chemical disinfectants to the pool. Human body excretions (sweat, urine and saliva) and pharmaceuticals and personal care products (sunscreens, cosmetics, hair products and lotions) are 17 introduced by swimmers. High addition of disinfectant leads to a high formation of DBPs from reaction 18 of some of the chemicals with the disinfectant. Swimming pool air is also of concern as volatile DBPs 19 20 partition into the air above the pool. The presence of bromine leads to the formation of a wide range of bromo- and bromo/chloro-DBPs, and Br-DBPs are more toxic than their chlorinated analogues. This is 21 22 particularly important for seawater filled pools or pools using a bromine-based disinfectant. This review summarises chemical contaminants and DBPs in swimming pool waters, as well as in the air above pools. 23 Factors that have been found to affect DBP formation in pools are discussed. The impact of the 24 25 swimming pool environment on human health is reviewed.

26 Keywords: disinfection by-products, disinfection, swimming pool, spa, water quality, health effects

# 27 1. Introduction

Swimming pool chemical water quality is currently a topic of interest, with many studies occurring in both the United States and Europe. Swimming pool chemical water quality is of possible public health concern due to the formation of disinfection by-products (DBPs), where total DBP concentrations have been shown to progressively increase in pools and spas (up to 610% and 900%, respectively) compared to their respective filling waters (Daiber et al., 2016). Swimming pool DBPs are unwanted consequences 33 from the reactions of components of the swimming pool water and the disinfectant, during the swimming 34 pool disinfection process. There is an increased potential risk to babies and small children where the health effects of DBPs may be more pronounced. Uptake of DBPs are likely increased in children 35 compared to adults due to higher breathing rates of children (up to twice those of adults) and their lesser 36 developed gastrointestinal tracts and blood brain barriers possibly leading to higher absorption of DBPs 37 (Thompson, 2004). Additionally, children's organs are not fully developed, particularly the liver and 38 39 kidneys which have been shown to be two to nine times slower in the breakdown of chemical compounds 40 compared to adults, and, in combination with immature metabolite breakdown mechanisms, may not be able to metabolise and remove DBPs sufficiently (Thompson, 2004). DBPs in swimming pools have been 41 potentially linked to several health issues, including asthma, bladder cancer, liver and kidney issues 42 43 (Villanueva et al., 2007; Villanueva and Font-Ribera, 2012). Swimming pool waters have shown 44 increased genomic DNA damage effects on Chinese hamster ovary cells than the corresponding filling water (Liviac et al., 2010b), which is likely due to more than one mutagen (Honer et al., 1980). 45 Respiratory issues, such as asthma, wheeze, cough and lower respiratory tract infections, have been 46 correlated with swimming pool attendance, which is likely due to chlorinated volatile DBPs, such as 47 48 chloramines (Bernard et al., 2006; Ferrari et al., 2011; Jacobs et al., 2007; Kaydos-Daniels et al., 2008; Rosenman et al., 2015; Uyan et al., 2009). However, these studies are not conclusive and Goodman and 49 50 Hays (2008) suggested that "it is premature to draw conclusions about the causal link between swimming and asthma", warranting further investigation of the health effects of the swimming pool environment. 51

Indoor swimming pools are of particular concern since they may be more regularly used all year round, and volatile DBPs can become trapped within the environmental air of indoor swimming pool complexes. The higher the concentration of these volatile DBPs in the swimming pool water, the higher their concentration in the air above the pool. Volatile compounds of potential health concern in the air pose a risk not only to regular swimmers, but also to regular non-swimmers, such as swimming pool workers and non-swimming visitors.

Disinfection is essential to protect against the microbial disease risk in pools (Montgomery, 1985). 58 59 Studies of comparison of microbial disease and DBP risks in pools are limited, but, in drinking waters, the risk of death or illness from pathogens is much higher than the risk of cancer from DBPs (Ashbolt, 60 2004; WHO, 2000). Although chlorine based disinfectants, calcium or sodium hypochlorite and chlorine 61 62 gas, are more commonly used (Montgomery, 1985), other disinfectants including chlorine dioxide (ClO<sub>2</sub>), chloroisocyanurates or their acid counterparts, bromine gas, sodium bromide (in combination with a 63 chlorine oxidiser), bromochlorodimethylhydantoin (BCDMH) or electrochemically generated mixed 64 oxidant (EGMO) can be employed for swimming pool disinfection. 65

66 Chlorine based disinfectants result in the formation of hypochlorous acid (HOCl), whilst bromine 67 based disinfectants predominantly produce hypobromous acid (HOBr). These species react further, 68 producing additional 'active' oxidising species, hypochlorite (<sup>-</sup>OCl) and hypobromite (<sup>-</sup>OBr). All active species (the acids (HOCl/HOBr) and the ions (OCl/OBr)) have the ability to inactivate microorganisms 69 and react with organic matter, leading to the formation of organic DBPs, chloride (Cl<sup>-</sup>) and bromide (Br<sup>-</sup>). 70 Hypochlorous acid is approximately 100 times more effective than the hypochlorite ion, whilst HOBr is 71 the stronger oxidising species (Chow et al., 2014). These reactions, and hence disinfectant speciation, are 72 both pH and chloride dependent (E et al., 2016; Hansen et al., 2012b), and care should be taken to 73 maximise the dominance of the more powerful oxidant species to ensure maximum disinfection power, 74 although DBP formation rates and the behaviour of DBP precursors will also be influenced by these more 75 reactive disinfectant species. Unlike other chlorine containing disinfectants, ClO<sub>2</sub> does not produce 76 HOCI: ClO<sub>2</sub> does not hydrolyse in water, rather it remains as a dissolved gas, with oxidation occurring 77 78 via electron exchange mechanisms (NRC, 1980). The other oxidants, BCDMH or EGMO (the production of oxidants via the electrolysis of waters rich in sodium chloride), are also used as disinfectants in 79 swimming pool waters, however their chemistry is not as straightforward. BCDMH results in both HOCl 80 and HOBr (Elsmore, 1994), whilst EGMO leads to the presence of several oxidising species: HOCl, 81 HOBr, ozone and hydrogen peroxide (Kraft et al., 1999; Patermarakis and Fountoukidis, 1990), with 82 HOBr and HOCl being the dominating species for BCDMH and EGMO, respectively. A detailed 83 discussion of the chemistry of swimming pool disinfectants is provided in Section 2 below. 84

85 There is currently no international standard for the treatment of swimming pools, with regulations often provided by state or local governing bodies. For example, the USA's Centre for Disease Control 86 (CDC) have released the 'Model Aquatic Health Code' (MAHC) which other governing bodies are 87 encouraged to adopt (CDC, 2016). Similarly, the Australian National Health and Medical Research 88 89 Centre (NHMRC) encourages Australian pool operators to adopt their 'Guidelines for managing Risks in Recreational Waters' (NHMRC, 2008), whilst the DIN 19643 is regulation in Germany (German Institute 90 91 for Standardization, 2012). Other bodies such as the Pool Water Treatment Advisory Group (PWTAG) or 92 the World Health Organisation (WHO) have produced guidelines which have been adopted by various 93 other countries, including the United Kingdom (PWTAG, 2003). The minimum free chlorine equivalent 94 concentrations recommended by the aforementioned organisations are presented as examples in Table 1. 95 It is evident that recommended guidelines can differ among regulators, suggesting a more complete understanding of treatment methods is required. Development of international swimming pool guideline 96 recommendations, similar to the World Health Organisation's "Guidelines for Drinking Water Quality", 97 would be beneficial in assisting governing bodies worldwide to develop local guidelines based on their 98 local requirements. Since the required free chlorine equivalent residual in swimming pools is higher than 99 that reported in drinking water distribution systems (e.g. minimum 0.2 mg/L, Chow et al., 2014) and there 100 is a build-up of organic compounds in swimming pool waters such that the total organic carbon content is 101 102 usually much higher (e.g. <33 mg/L, Plewa et al., 2011) than that detected in drinking waters (e.g. 1.8 to

3.6 mg/L, McDonald et al., 2013), DBP formation is a magnified issue in swimming pool waters
compared to drinking waters.

Swimming pools have a wide variety of uses and therefore the swimming pool water matrix is 105 quite unique. Not only does the type of swimming pool affect the water matrix, but other factors, 106 including temperature, climate, location and swimming habits, particularly swimmer hygiene, all have an 107 impact. Both organic and inorganic compounds may enter a swimming pool in a variety of ways, as 108 illustrated in Figure 1. The filling water, or water used to fill the swimming pool, is commonly 109 disinfected distributed drinking water (freshwater swimming pools), although seawater is sometimes 110 used, and the filling water can introduce species such as natural organic matter (NOM), trace amounts of 111 DBPs and chlorine or chloramines. Compounds introduced in the filling water are highly dependent on 112 113 the disinfection method used for the distributed water. Due to the constant addition of a disinfectant to the pool, chlorine and/or bromine are introduced. Personal care products, such as sunscreens, hair products, 114 lotions/soaps and cosmetics, as well as human body excretions (sweat, urine, saliva and body cells), are 115 also introduced into the swimming pool water, with urea being detected up to 3.7 mg/L (De Laat et al., 116 2011). These two categories together have been termed bather load as they are introduced by swimmers 117 or 'bathers'. The continual use of the swimming pool, input from bather load, continual addition of a 118 disinfectant, combined with minimal freshwater input and continual recirculation of the same water, can 119 120 cause these contaminants to become highly concentrated within swimming pool waters.

Swimming pool waters are commonly subject to filtration by either sand, diatomaceous earth or 121 membrane filters, however this predominantly removes the physical contaminants, such as hair and lint, 122 123 rather than the chemical contaminants, although some dissolved compounds (e.g. DBPs and their 124 precursors) may be adsorbed. Filter media have also shown potential to form some DBPs (Hansen et al., 2012b) and proper operation of filters should seek to minimise them as a source of DBPs in swimming 125 pool waters. Some swimming pools employ additional treatment to improve microbiological inactivation, 126 such as ozone or ultraviolet (UV) irradiation, however, while these methods commonly decrease some 127 chemical contaminants, they can increase the formation of others. For example, UV followed by post-128 chlorination of swimming pool water has been shown to decrease chloramine concentrations, however the 129 formation of trihalomethanes increased (Cimetiere and De Laat, 2014). Other studies have reported 130 contradictory findings (discussed in more detail in Section 5.1), highlighting the complex nature of the 131 132 chemistry involved in secondary treatment of swimming pools.

There are three DBP uptake mechanisms applicable to the swimming pool environment: ingestion, absorption and inhalation. Ingestion and absorption both occur during swimming activities as some water is often accidentally swallowed and DBPs may be absorbed through the skin. For example, Dufour et al. (2006) found the average volume of water ingested by adults during a 45 minute swim was 16 mL (21 mL/hour), with non-adults (<18 years) swallowing twice as much as adults. A recent study, however, 138 reported that previous investigations of swimming pool water ingestion may be underestimated by up to 139 15% (Sinclair et al., 2016). The skin permeability of some DBPs has been studied. Xu et al. (2002) investigated trihalomethanes (THMs), haloketones (HKs) and haloacetic acids (HAAs), reporting that 140 THMs had the highest skin permeability, with brominated THMs being more permeable than chlorinated 141 THMs. HKs were reported to be less permeable to human skin than THMs, but more permeable than 142 HAAs, which showed almost no permeability (Xu et al., 2002). Haloacetonitriles (HANs) were 143 investigated by Trabaris et al. (2012), with dibromoacetonitrile being found to have the highest 144 permeability to human skin, whilst chloroacetonitrile had the least. HANs were shown to be less 145 permeable to human skin than chloral hydrate (Trabaris et al., 2012). Both studies correlated an increase 146 in temperature to increased human skin permeability of selected DBPs (Trabaris et al., 2012; Xu et al., 147 2002). Inhalation is particularly important for volatile DBPs and has been reported to be the major route 148 149 of human exposure of DBPs in the swimming pool environment (Aggazzotti et al., 1998; Aprea et al., 2010; Chen et al., 2011; Erdinger et al., 2004). In the swimming pool environment, THM uptake via 150 inhalation has been estimated to have a higher associated cancer risk than uptake via ingestion or dermal 151 routes (Lee et al. 2009), where estimations were calculated using the US EPA guidelines for carcinogen 152 153 risk assessment and the Swimmer Exposure Assessment Model using standard values from the US EPA Exposure Factors Handbook. Similar results were reported by Chen et al. (2011), who found that 99% of 154 the risk arising from THM exposure was due to inhalation of chloroform. . An increase in water 155 temperature, swimming activity and blowers/jets causes an increased volatilization rate of volatile DBPs 156 and hence this inhalation uptake mechanism can become of high importance, particularly for indoor 157 158 heated swimming pools (Aggazzotti et al., 1998; Kristensen et al., 2010; Marco et al., 2015).

Currently, few guidelines appear to exist worldwide for the concentrations of DBPs specifically in 159 the swimming pool environment. DBPs are regulated in drinking waters; however, due to the uptake 160 mechanism ratio shift from ingestion (drinking waters) to inhalation (swimming pool waters), the 161 drinking water DBP guidelines may not be directly applicable to assess the health risk associated with 162 DBPs in swimming pool waters. Drinking water guidelines may, however, act as an indicative health 163 guideline value where no swimming pool specific guideline value exists. Current swimming pool specific 164 regulations mainly provide health guidelines for chloramines (measured as combined chlorine), which are 165 encouraged to be no greater than half that of the free chlorine equivalent concentrations in pool water, 166 although lower ideal concentrations (less than 0.2 to 0.4 mg/L) have been suggested (CDC, 2016; WHO, 167 2006). Trichloramine in the swimming pool air has also been regulated, with WHO (2006) recommending 168 maximum concentrations of  $0.5 \text{ mg/m}^3$ , although some European countries propose a lower guideline for 169 trichloramine in the air of indoor swimming pool complexes, 0.2 to 0.3 mg/m<sup>3</sup> (Cassan et al., 2011; 170 Umweltbundesamtes, 2011). THMs are the only organic DBP class known to be regulated in swimming 171 pool waters. For the total THM concentrations (sum of trichloro-, bromodichloro-, dibromochloro- and 172 tribromo-methane), the German standard DIN 19643 suggests a guideline value of 20 µg/L in swimming 173

pool waters (German Institute for Standardization, 2012), whilst Denmark's Statutoy Order no 623 recommends total THM concentrations do not exceed 25  $\mu$ g/L in pool waters (Lovtidende, 2012).

This critical review summarises chemical contaminants and DBPs reported in swimming pool waters, as well as in air above swimming pools. Factors that have been found to affect DBP formation in pools are also discussed. The impact of the swimming pool environment on human health is reviewed.

#### 179 2. Disinfectants and their Associated Chemistry in Swimming Pools and Spas

Although many oxidants can form by the addition of one disinfectant to water, the type of the 180 disinfectant (chlorine or bromine based) refers to the most dominant species. Although specific 181 disinfectants will be provided in some examples, for the purpose of this review, chlorination (treated by 182 chlorine) refers to the use of disinfectants where HOCl is the primary oxidant (sodium hypochlorite 183 (NaOCl), calcium hypochlorite (Ca(OCl)<sub>2</sub>), chlorine gas (Cl<sub>2</sub>), sodium dichloroisocyanurate (SDCIC), 184 chloroisocyanurate (CIC), dichloroisocyanuric acid (DCICA) or trichloroisocyanuric acid (TCICA)), 185 whilst bromination (treated by bromine) refers to the use of disinfectants where HOBr is the primary 186 oxidant, the main examples being bromochlorodimethylhydantoin (BCDMH) and sodium bromide 187 (NaBr) in the presence of an oxidant. EGMO and ClO<sub>2</sub> will be discussed separately to other disinfectants, 188 where possible. Waters which are treated in combination with a secondary treatment (e.g. UV or ozone) 189 will be distinguished from those treated solely by disinfectants. 190

# 191 **2.1. Chlorine Based Disinfectants**

192 The addition of the major chlorine based disinfectants (chlorine gas, sodium and calcium 193 hypochlorite) to water results in the formation of hypochlorous acid (HOCl) as per **Equations (i)**, (**ii**) and 194 (**iii**), respectively.

195

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
 Equation (i)

196 
$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-$$
 Equation (ii)

197 
$$Ca(OCl)_2 + H_2O \rightarrow 2HOCl + Ca^{2+} + 2OH^-$$
 Equation (iii)

198 HOCl further dissociates in water producing hypochlorite as per **Equation** (iv).

199 
$$HOCl \rightleftharpoons OCl^- + H^+$$
 Equation (iv)

Both HOCl and OCl<sup>-</sup> have the ability to inactivate microorganisms (disinfect), as well as react with organic matter leading to the formation of Cl-DBPs and oxidised organic matter/ chloride. Although the predominant chlorine species is HOCl, the highly reactive, but less abundant, electrophiles, Cl<sub>2</sub>O and Cl<sub>2</sub>, may also be present in swimming pool waters and, due to their higher reactivity compared to HOCl (De La Mare et al., 1975), may be responsible for the formation of some Cl-DBPs. In a study of aromatic ethers, (Sivey and Roberts, 2012),. Although unexplored specifically in swimming pools, Cl<sub>2</sub>O and Cl<sub>2</sub>
were shown to be important species in generation of DBPs from aromatic ether DBP precursors of
moderate reactivity (Sivey and Roberts, 2012).

Cyanurates and their acids all result in the formation of HOCl (and hence OCl<sup>-</sup>), via twelve simultaneous chemical equilibrium reactions (dissociation or chlorination) of the cyanurates, their acids, and their chlorinated counterparts. In the case of chlorinated cyanuric acids, the most commonly used in pools are trichloro- and dichloro-isocyanuric acid (TCICA and DCICA), which are often added as their salt form; in these cases, HOCl will be formed directly via dissociation in water, as shown in **Figure 2** (a) and (b) where DCICA and TCICA are used as examples, respectively.

In pools, the majority of chlorine (97%) is bound to the cyanurates which are poor oxidants compared to HOCl, but despite this and due to the equilibrium, as HOCl is depleted, chlorinated cyanurates 'release' chlorine to reform HOCl, and hence maintain the desired free chlorine residual. These types of chemicals are referred to as chlorine stabilisers, as cyanurates are less susceptible to solar degradation than HOCl itself. This lower chlorine decay observed is seen as stabilisation of the chlorine, hence the name chlorine stabiliser. Stabilised chlorine may also be formed by the addition of cyanurate to swimming pools that use chlorine based disinfectants, as in the reverse reactions of **Figure 2**.

### 221 **2.2. Bromine Based Disinfectants**

Similar to the formation of HOCl and OCl<sup>-</sup> via chlorine based disinfectants, bromine based disinfectants result in the formation of HOBr, which further dissociates to OBr<sup>-</sup> as per **Equations** (v) and (vi).

225 
$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$$
 Equation (v)

$$HOBr \rightleftharpoons OBr^- + H^+$$
 Equation (vi)

Unlike Cl<sub>2</sub>, bromine gas is rarely used as a disinfectant, instead HOBr may be formed by combining sodium bromide (NaBr) with an oxidant (usually chlorine based, although ozone is often used), as per **Equation (vii).** 

230

 $NaBr + HOCl \rightarrow HOBr + Na^{+} + Cl^{-}$  Equation (vii)

Analogous to HOCl, both HOBr and OBr<sup>-</sup> have the ability to inactivate microorganisms (disinfect), as well as react with organic matter leading to the formation of Br-DBPs and oxidised organic matter / bromide (Br<sup>-</sup>).

The most common bromine based disinfectant is BCDMH, which forms both HOBr and HOCl in the presence of water, as shown in **Figure 3**. HOCl and HOBr further dissociate as per **Equations** (iv) and (vi), respectively. Despite the formation of HOCl, BCDMH is considered a bromine based disinfectant as (i) HOBr is a stronger oxidising agent than HOCl and (ii) the HOCl is mainly associated with the bromide recycling reaction, that is, the regeneration of HOBr via oxidation of bromide as demonstrated in **Equation** (viii); HOCl still has the ability to inactivate microorganisms and form Cl-DBPs, although these are minor reactions in comparison to those involving HOBr (Black & Veatch Corporation, 2010).

242

$$Br^- + HOCl \rightarrow HOBr + Cl^-$$
 Equation (viii)

#### 243 **2.3. Chlorine Dioxide**

Although not as commonly used as other chlorine based disinfectants, chlorine dioxide may be used in swimming pools or spas, however, unlike other chlorine containing disinfectants,  $ClO_2$  does not produce HOCl as it does not hydrolyse in water.  $ClO_2$  remains as a stable free radical ( $ClO_2^{-}$ ), where it reacts by radical mechanisms with electron rich moieties following **Equation** (**ix**), where the source of the e<sup>-</sup> is electron rich moieties (e.g. lone electron pairs on amines or phenolates) present in organic matter, and leads to the formation of chlorite ( $ClO_2^{-}$ ).

250 
$$ClO_2 + e^- \rightarrow ClO_2^-$$
 Equation (ix)

This reaction leads to the formation of highly reactive organic radical moieties which may be further oxidised by  $ClO_2$  or react with other organic moieties. Although chlorite is relatively stable in conditions commonly used in swimming pools, it may lead to the formation of chloride and chlorate as per **Equations** (**x**) and (**xi**).

255 
$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O$$
 Equation (x)  
256 
$$ClO_2^- + Cl_2 + H_2O \rightarrow ClO_3^- + 2Cl^- + 2H^+$$
 Equation (xi)

## 257 2.4. Electrochemically Generated Mixed Oxidant

Electrochemically generated mixed oxidant (EGMO) disinfection is achieved by applying an electric current to water with a high chloride content and, despite the production of several oxidising species, the predominant species formed is Cl<sub>2</sub>. Electrolysis of water involves an anodic reaction (**Equation xii**) and a cathodic reaction (**Equation xiii**), where the overall process is shown in **Equation xiv**.

262  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$  Equation (xii)

263 
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 Equation (xiii)

264 
$$2H_2O \rightarrow O_2 + 2H_2$$
 Equation (xiv)

Disinfection is achieved by the production of  $Cl_2$ , which is formed as a secondary reaction at the anode (**Equation xv**), where **Equation xvi** represents the overall equation.

267 
$$2Cl^2 \rightarrow Cl_2 + 2e^2$$
 Equation (xv)

268 
$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$
 Equation (xvi)

In conjunction with **Equation** (i), HOCl may be formed as per **Equation** (**xvii**). The reformation of chloride allows the EGMO process to repeat as long as an electric current is applied.

271 
$$Cl_2 + NaOH \rightarrow OCl^- + NaCl + H^+$$
 Equation (xvii)

Ozone and hydrogen peroxide are also formed during EGMO disinfection, although to a much smaller extent than the formation of Cl<sub>2</sub>, as per **Equations xviii** and **xix**, respectively. Furthermore, if bromide is present, HOBr may be produced as per **Equation viii**.

275 
$$3H_2O \rightarrow O_3 + 6e^- + 6H^+$$
 Equation (xviii)

276

 $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$  Equation (xix)

# 277 3. <u>Disinfection By-Products: Occurrence in Swimming Pool and Spa Waters and the Ambient Air</u> 278 <u>Above Pools</u>

279 Many studies have investigated the occurrence of DBPs and other chemical contaminants in both drinking waters and wastewaters, with fewer studies of swimming pool waters being available. Arguably 280 the most comprehensive study of DBPs in swimming pools was that of Richardson et al. (2010), who 281 282 identified over 100 DBPs (including 8 haloalkanes, 9 haloacetic acids, 22 other haloacids, 9 halodiacids, 8 haloaldehydes, 24 halonitriles, 6 haloamides, 18 haloalcohols and 7 non-halogenated DBPs) in their 283 investigation of five chlorinated and two brominated public swimming pools in Spain. Similarly, Daiber 284 et al (2016) identified over 100 DBPs (iodo-THMs, bromoimidazoles, bromoanilines, haloacids, 285 halonitriles, haloamides, halonitromethanes, haloketones, haloaldehydes, halophenols, halobenzenes, 286 halobenzenediols, bromomethanesulfenic acid esters, aldehydes, ketones, and an organic chloramine), 287 including a range of newly reported DBPs (bromoimidazoles, bromoanilines, bromomethanesulfenic acid 288 esters), in a range of swimming pools and spas treated by either chlorine or bromine based disinfectants. 289 Although many different types of swimming pools exist, the majority of studies have primarily focused 290 on chlorinated swimming pools, particularly those located indoors. Similarly, the ambient air of indoor 291 292 swimming pool complexes has received some attention. Due to the vast numbers of reports of some DBPs (particularly trihalomethanes, haloacetic acids, chloramines and haloacetonitriles), this review will 293 discuss overall trends for the occurrence of DBPs in the swimming pool environment: both swimming 294 pool water and the ambient air of indoor swimming pool complexes. Table 2 summarises the range of 295 average concentrations for selected DBPs in swimming pool waters, with Tables S1-S11 providing a 296

complete summary. Similarly, **Tables S12** and **S13** provide a summary of THM and trichloramine
concentrations reported in the ambient air of indoor swimming pool complexes.

## **3.1. Occurrence in Swimming Pool and Spa Waters**

# 300 **3.1.1. Trihalomethanes**

Rook (1974) was the first to investigate trihalomethanes (THMs) in drinking water, with attention turning to swimming pool waters less than 6 years later (Beech et al., 1980; Norin and Renberg, 1980). To date, THMs, along with HAAs (discussed in **Section 3.1.2**), are the most commonly reported class of DBPs in the swimming pool environment. **Table 2** summarises the average occurrence of brominated and chlorinated THMs in a variety of swimming pool waters, with **Table S1** providing a more complete summary.

As opposed to reporting individual THM species, a value known as TTHM is often presented and 307 refers to the sum of trichloro-, bromodichloro-, dibromochloro- and tribromo-methane. TTHM 308 concentrations were generally lower in chlorinated pools that employ ozone compared to those reported 309 310 in pools treated solely by chlorination (Kelsall and Sim, 2001; Zhang et al., 2015), whilst chlorinated pools filled with salt water contained on average the highest TTHMs concentrations (Beech et al., 1980; 311 312 Chowdhury et al., 2016; Manasfi et al., 2016; Parinet et al., 2012). Similarly, lower TTHM concentrations (12 to 311 µg/L; Glauner et al., 2005, Manasfi et al., 2016, Panyakapo et al., 2008, Simard et al., 2013, 313 Tang and Xie, 2016, Yang et al., 2016, Zhang et al., 2015) were reported for outdoor pools treated by 314 chlorination compared to chlorinated pools located indoors, which is likely due to the increased 315 volatilisation and UV degradation in outdoor pools, which is discussed further in Sections 5.1 and 5.3. 316

Considering individual THMs, chloroform and bromoform were the most abundant THMs in 317 pools treated with chlorine and bromine, respectively, with concentrations of up to 520 and 400 µg/L 318 reported in these pools for chloroform and bromoform, respectively (Norin and Renberg, 1980; Sa et al., 319 2012). On average, chlorinated pools had higher concentrations of bromodichloro- and dibromochloro-320 methane than pools treated with bromine. Pools where ozone in addition to chlorine was employed 321 generally reported lower average concentrations of THMs compared to pools where only chlorination was 322 employed. Whilst the average concentrations of THMs were lower compared to chlorinated pools, pools 323 324 where EGMO was employed reported a higher ratio of bromo- and mixed bromochloro-THMs, which is 325 likely due to the higher bromide content, which, as discussed in Section 4.2, is likely added as an impurity in the added salt. A similar trend was observed for seawater filled pools treated by chlorination, 326 which is likely due to the higher bromide content of the filling water, as discussed in Section 4.1. Spas 327 treated with chlorine generally had lower concentrations of THMs than chlorinated pools, whilst bromine 328 treated spas contained higher levels of THMs than those reported in brominated pools. These observations 329 are likely due to (i) the increased formation of THMs at the higher temperatures of spas compared to 330

331 pools, and (ii) the increased partitioning of THMs into the air above the pool as a result of the higher 332 temperature and water agitation in spas, which would have an increased effect on chlorinated THMs due 333 to their higher volatility.

Only two published studies have investigated iodinated THMs (I-THMs), where individual concentrations up to 17 and 8.5  $\mu$ g/L were reported for chlorinated pools and a spa, respectively (Carter et al., 2015; Yeh et al., 2014).

# 337 **3.1.2. Haloacetic Acids**

Haloacetic acids (HAAs) have been extensively studied in drinking water, however studies investigating their occurrence in swimming pool waters only began to be published in 1999 (Martínez et al., 1999). Early studies investigated only chlorinated HAAs, but attention quickly expanded to the brominated and mixed chlorinated/brominated analogues. As presented in **Table 2**, the average concentrations of HAAs will be the focus of discussion in this section, whilst **Table S2** provides a more complete summary of the occurrence of HAAs in a variety of swimming pool and spa waters.

Excluding bromine treated or seawater filled pools and spas, the most abundant of the HAAs are 344 dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), where concentrations of up to 2400 and 345 2600 µg/L have been reported, respectively (Yeh et al., 2014). As observed with THMs and presented in 346 Table 2, for chlorinated pools, HAA concentrations generally decrease as bromine substitution increases, 347 348 which is likely a result of the low bromide concentrations in chlorinated pools. Likewise, for bromine treated pools, brominated HAAs generally increase in concentration as bromine substitution increase, 349 350 with dibromo- and tribromo-acetic acid the dominant species. Chlorinated pools where ozone is employed contained lower HAAs on average than those treated solely by chlorine, whilst EGMO treated pools 351 352 generally contained the lowest concentrations of HAAs.

Chlorinated spas generally contained similar or lower concentrations of HAAs compared to chlorinated pools, excluding TCAA where concentrations were approximately double, whilst brominated spas were reported to generally contain higher concentrations of HAAs than brominated pools. As discussed in **Sections 5.4** and **5.5**, factors including water agitation and temperature are likely to affect the formation of HAAs.

## 358 **3.1.3. Inorganic Halamines**

Chloramines have been investigated in swimming pools and spas, with their average occurrence summarised in **Table 2** and a more complete summary provided in **Table S3**. Regardless of pool type or treatment method, trichloramine was generally the dominant chloramine, followed by di- and monochloramine, although, as discussed in **Section 5.5**, pH plays an important role in DBP occurrence, particularly for chloramines. On average, chloramines were detected at higher concentrations in 364 chlorinated pools filled with fresh water compared to those filled with seawater, where maximum 365 concentrations of between 11 to 3412 µg/L and between 110 to 490 µg/L have been reported, respectively (Chowdhury et al., 2016; Wang et al., 2014; Weaver et al., 2009). Generally (Table 2), brominated pools 366 had lower concentrations of chloramines compared to chlorinated pools, where maximum concentrations 367 between 18 and 300 µg/L have been reported (Daiber et al., 2016; Richardson et al., 2010). Brominated 368 spas contained slightly higher concentrations of chloramines than brominated pools, up to 363 µg/L 369 (Daiber et al., 2016), which is likely due to the higher release of human derived chloramine precursors 370 and an increased formation due to the higher operating temperature used in spas, as discussed in Section 371 5.5. 372

Bromamines are known to form in the presence of ammonia in chlorinated waters (NRC, 1980). Despite the possibility that other halamines (e.g. bromamines, mixed bromochloramines) may be present in the swimming pool environment, their occurrence has yet to be investigated due to the lack of suitable analytical methods. Further work is required to develop such analytical methods in order to fully understand halamines in the swimming pool environment.

#### 378 **3.1.4. Haloacetonitriles**

379 Few studies investigating haloacetonitriles (HANs) in swimming pool waters and spas have been reported to date and they have mainly focused on bromochloro-, dibromo-, dichloro- and trichloro-380 381 acetonitrile (BCAN, DBAN, DCAN and TCAN, respectively), as summarised in Tables 2 and S4. Chlorinated and brominated species dominated pools treated with chlorine and bromine, respectively, 382 383 with BCAN concentrations reported higher in chlorinated pools compared to those treated with bromine. Of the HANs investigated, DCAN and DBAN were generally the most abundant in pools treated with 384 385 chlorine and bromine, respectively, with maximum concentrations of 89 and 39 µg/L being reported (Daiber et al., 2016; Hang et al., 2016). Where disinfection was achieved by bromine, Daiber et al. (2016) 386 387 reported a higher concentration of DBAN in spas compared to pools, which is likely due to the higher release of nitrogen containing anthropogenic chemicals due to the elevated temperatures, as discussed in 388 Section 5.5. As shown in Table S4, limited reports of other HANs have been published, although 389 concentrations are much lower, up to 3.0 µg/L (Carter et al., 2015; Kanan, 2010), compared to those 390 discussed above. 391

#### 392 **3.1.5**.*N*-Nitrosamines

Few studies have investigated the occurrence of *N*-nitrosamines in swimming pool waters, as summarised in **Table 2**, with a more complete summary of the studies provided in **Table S4**. Walse and Mitch (2008) were the first researchers to investigate *N*-nitrosamines in chlorinated swimming pool waters, reporting maximum concentrations of *N*-nitrosodimethylamine (NDMA) of 44, 6.9 and 429 ng L<sup>-1</sup> in indoor pools, outdoor pools and a heated spa, respectively. Considering average concentrations, NDMA is generally 398 higher in chlorinated spas than chlorinated pools, which is likely due to the increased release of anthropogenic NDMA precursors from swimmers due to the higher water temperature (discussed further 399 in Section 5.5). Although similar average concentrations have been reported for NDMA, maximum 400 concentrations have been reported between 6.9 and 208 ng/L for pools treated by chlorination (Kim and 401 Han, 2011; Wang et al., 2011). Other nitrosamines, N-nitrosodiethylamine, N-nitrosomorpholine and N-402 nitrosoethylmethylamine have been detected in chlorinated pools at concentrations up to 72, 34 and 26 403 ng/L, respectively (Kim and Han, 2011; Wang et al., 2011), with N-nitrosopyrrolidine reported at 404 concentrations up to 127 ng/L (Pozzi et al., 2011), although information regarding pool type or treatment 405 method was not presented. 406

## 407 **3.1.6. Haloacetaldehydes**

Very limited information exists on haloacetaldehydes (HALs) in swimming pool waters, as summarised 408 in Tables 2 and S6. Chloral hydrate (CH), the monohydrate of trichloroacetaldehyde, has been the most 409 commonly investigated, with concentrations of up to 400, 190, 10 and 23 µg/L in chlorinated indoor, 410 chlorinated outdoor, chlorinated with ozone and EGMO treated swimming pools, respectively (Carter et 411 al., 2015; Lee et al., 2010; Manasfi et al., 2016). CH was not detected in seawater filled or brominated 412 pools and was detected at lower concentrations in brominated spas compared to those that were 413 chlorinated, up to 2.9 and 405 µg/L, respectively (Carter et al., 2015; Daiber et al., 2016; Manasfi et al., 414 2016), which is likely due to the higher availability and reactivity of bromine based disinfectants present 415 in these waters. Dichloroacetaldehyde (up to 23 µg/L) has been reported in one study, although pool type 416 and treatment method were not presented (Serrano et al., 2011). Although at much lower concentrations 417 (0.3 to 2.4 µg/L), a few studies have reported the occurrence of other HALs (dibromo-, dibromochloro-418 and tribromo-acetaldehyde) in swimming pool waters (Carter et al., 2015; Manasfi et al., 2016). 419

# 420 **3.1.7. Haloketones**

Little is known about haloketones (HKs) in swimming pool or spa waters, with their known occurrence 421 summarised in Tables 2 and S7. The majority of researchers have investigated chlorinated pools, 422 reporting 1,1-dichloro- and 1,1,1-trichloro-propanone at concentrations up to 7.7 and 15 µg/L, 423 respectively (Hang et al., 2016), although 1,1,1-trichloropropanone was reported at significantly higher 424 concentrations (up to 180 µg/L; Hang et al. (2016)) in some pools. Carter et al. (2015) was the only 425 426 known study to investigate other HKs, 1,2-dichloro- and chloro-acetone, where concentrations up to 1.8 µg/L were reported. Only one study has investigated HKs in brominated (treated with BCDMH or sodium 427 bromide in combination with TCICA) pools or spas, although both 1,1,1-trichloro- and 1,2-dichloro-428 propanone were below detection limits in all cases (Daiber et al., 2016). No studies have reported the 429 occurrence of brominated ketones, despite their likely occurrence in pools treated with bromine. 430

# 431 **3.1.8. Halonitromethanes**

As summarised in **Tables 2** and **S8**, few studies have investigated halonitromethanes (HNMs) in pool or spa waters. Trichloronitromethane (TCNM) is the most investigated HNM, where concentrations up to 5  $\mu$ g/L have been reported for chlorinated pools (Tardif et al., 2015). Daiber et al. (2016) is the only known study of HNMs in spas or brominated pools, although TCNM was not detected in any waters investigated. Several other HNMs (tribromo-, bromochloro- and bromo-nitromethane) have been investigated, where maximum concentrations between 1.2 and 11  $\mu$ g/L were reported (Kanan, 2010; Yeh et al., 2014).

## 438 **3.1.9. Haloacetamides**

Haloacetamides (HAAms) are an almost unexplored DBP class in swimming pool waters, with only two publications to date. Not all investigated HAAms were detected, and as summarised in **Tables 2** and **S9**, on average dibromo-, dichloro- and trichloro-acetamide were reported at similar concentrations in the investigated chlorinated pools, where maximum concentrations between 2 and 3.1  $\mu$ g/L were reported (Carter et al., 2015; Yeh et al., 2014).

## 444 3.1.10. Inorganic Anions

A few studies have investigated the occurrence of inorganic anions which are DBPs in swimming pool waters. The relevant results from these studies are summarised in **Table S10**, with a simplified summary provided in **Table 2**. The inorganic anions bromide and chloride play multiple roles in disinfected water systems and these roles will be discussed in **Sections 4.14.1**, **4.2 and 5.25.2**. Additionally, although measured in swimming pool waters, fluoride, sulfate and phosphate have been excluded from this review as they are unlikely to directly take part in DBP formation under the conditions commonly found in swimming pool waters.

The occurrence of bromate has been limited to pools where ozone was employed as a secondary 452 treatment, with concentrations below detection in all other investigated pools (Kelsall and Sim, 2001; 453 Michalski and Mathews, 2007). As bromide was not detected in the pools treated with ozone, but was 454 present in the chlorinated swimming pools in the study by Michalski and Mathews (2007), bromide was 455 likely oxidised to bromate in the presence of ozone, as observed in bromide containing waters (von 456 Gunten and Hoigne, 1994). Where bromide is limited, the bromide to bromate oxidation likely goes to 457 completion. However, where there is a continual input of bromide (e.g. via bromine based disinfectant), 458 459 the oxidation process may not go to completion and both bromide and bromate may exist. It is evident 460 that both the bromide availability and treatment process have an effect on the chemical water quality of pools, particularly the occurrence of bromide and bromate, with further investigations required to fully 461 462 understand their implications (discussed further in Sections 4.1, 4.2, 5.1 and 5.2).

Although reported at higher concentrations in pools treated with ozone, chlorate has also been detected in pools where ozone was not employed as a secondary treatment. For example, Michalski and Mathews (2007) reported the occurrence of chlorate ( $ClO_3^{-}$ ) in two pools treated with ozone (2.1 to 3.2 466 mg/L), three pools treated with chlorine dioxide (22 to 23 mg/L) and at even higher concentrations in two 467 pools treated with sodium hypochlorite (29 to 32 mg/L), where all pools were located indoors. The occurrence of chlorate in pools can be explained by (i) the direct addition as a DBP in pre-treated filling 468 water, (ii) the direct addition as a degradation product of hypochlorite stock solutions (Garcia-Villanova 469 et al., 2010), (iii) formation in pools due to the degradation of hypochlorite which has been shown to 470 increase in the presence of metal oxides (Liu et al., 2012), (iv) or in cases where ozone is employed as 471 secondary treatment, formation due to oxidation of hypochlorite by ozone and hydroxyl radicals via a 472 several step mechanism (Von Gunten, 2003). Similarly, chlorite has been detected in pools treated with 473 chlorine and chlorine dioxide, where concentrations up to 2.5 mg/L have been reported (Michalski and 474 Mathews, 2007). 475

## 476 **3.1.11. Total Organic Halogen**

The structures of many DBPs in swimming pool waters remain unknown and, therefore, not all 477 DBPs can be individually identified. However, the bulk parameter, total organic halogen (TOX), 478 sometimes referred to as adsorbable organic halogen (AOX), can be used as a measure of all halogenated 479 480 organic compounds in a water sample. As a bulk measurement of halogen, TOX is reported as a chloride equivalent concentration (Kristiana et al., 2015). Furthermore, individual measurement of chlorine, 481 bromine and iodine incorporated into NOM can be carried out, known as total organic chlorine (TOCl), 482 483 total organic bromine (TOBr) and total organic iodine (TOI), respectively. TOCl, TOBr and TOI are reported as chloride, bromide and iodide concentrations, respectively (Kristiana et al., 2015). Table S11 484 485 summarises the total TOX and individual TOCI, TOBr, and TOI concentrations previously reported in swimming pools and spas, with **Table 2** presenting a more simplified version. 486

487 Considering average concentrations (Table 2), TOCI dominated chlorinated pools, whilst TOBr was highest in pools treated with bromine, which is likely due to the higher availability of chlorine and 488 bromine in these waters, respectively. Brominated spas had significantly higher concentrations of TOBr 489 than those reported for brominated pools, indicating that larger concentrations of brominated organic 490 compounds exist in these spa waters, which is likely due to the higher release of anthropogenic precursors 491 and faster reaction rates as a result of the elevated temperatures, as discussed in Section 5.5. Only one 492 study has reported the occurrence of TOI, which was present in significantly lower concentrations 493 compared to TOCI or TOBr, attributable to the minimal availability of iodine in pools or spas (Yeh et al., 494 2014). 495

#### 496 **3.1.12. Cyanogen Halides**

A limited number of studies have investigated cyanogen halides in swimming pools or spas. All
known studies have focused on the two cyanogen halide species, cyanogen chloride (CNCl) and cyanogen
bromide (CNBr), as summarised in **Table 1**. As observed with other DBP classes, CNCl concentrations

were reported to be higher than CNBr in pools treated with chlorine, although Weaver et al. (2009) observed cyanogen bromide up to  $325 \ \mu g/L$  in a study of eleven indoor pools treated by chlorination. CNBr concentrations were higher in brominated spas compared to pools treated by bromine, with maximum concentrations reported to be 125 and 52  $\mu g/L$ , respectively (Daiber et al., 2016), and were comparable to CNCl concentrations in chlorinated pools (Afifi and Blatchley, 2015; Daiber et al., 2016; Lian et al., 2014; Weaver et al., 2009; Weng and Blatchley, 2011).

# 506 3.2. Occurrence in the Ambient Air Above Swimming Pool and Spa Waters

## 507 3.2.1. Trihalomethanes

508 Several studies have investigated the occurrence of THMs in the ambient air of indoor swimming 509 pool facilities, with a summary provided in **Table S12**. Unless otherwise stated, all reports of THMs in 510 the ambient air were for swimming pools located indoors and treated by chlorination.

Trichloromethane (chloroform), the most investigated THM in the ambient air of swimming 511 pools, is generally reported to be between 12 and 320  $\mu$ g/m<sup>3</sup> (Aggazzotti et al., 1998; Aprea et al., 2010; 512 Cammann and Hübner, 1995; Caro and Gallego, 2008; Catto et al., 2012b; Lévesque et al., 2000; Silva et 513 al., 2012; Tardif et al., 2015, 2016), although other studies have reported significantly lower 514 concentrations (12 to 81 µg/m<sup>3</sup>) (Font-Ribera et al., 2010b; Lourencetti et al., 2012; Richardson et al., 515 2010: Thiriat et al., 2009). Compared to other reported studies, Aggazzotti et al. (1990) reported much 516 higher chloroform concentrations (66 to 650  $\mu$ g/m<sup>3</sup>), although these are consistent with concentrations 517 reported in their later investigations (16 to 853  $\mu$ g/m<sup>3</sup>) (Aggazzotti et al., 1995), as well as those reported 518 in a study of sixteen chlorinated whirlpool spas (4 to 750 µg/m<sup>3</sup>) (Benoit and Jackson, 1987). Other 519 THMs, bromodichloro-, dibromochloro- and tribromo-methane, have been reported in the ambient air 520 above indoor chlorinated swimming pools at concentrations of below detection to 24, below detection to 521 26 and 0.2 to 23 µg/m<sup>3</sup>, respectively (Aggazzotti et al., 1998; Cammann and Hübner, 1995; Caro and 522 Gallego, 2008; Catto et al., 2012b; Font-Ribera et al., 2010b; Lourencetti et al., 2012; Richardson et al., 523 2010), with a few studies reporting higher concentrations, up to 155, 205 and 103  $\mu$ g/m<sup>3</sup> for 524 bromodichloro-, dibromochloro- and tribromo-methane, respectively (Tardif et al., 2015, 2016). Lahl et 525 al. (1981) measured trichloro- and bromodichloro-methane in the ambient air above eight chlorinated 526 pools in concentrations between 10 to 384 and 0.1 to 39  $\mu$ g/m<sup>3</sup>, respectively, although whether the pools 527 were located indoors or outdoors was not specified. Similarly, trichloro-, bromodichloro-, dibromochloro-528 and tribromo-methane have been found in the ambient air of other indoor swimming pools in 529 concentrations of 11 to 13000, 8.7, 3.1 and 0.8  $\mu$ g/m<sup>3</sup>, respectively, although the disinfection methods of 530 these pools were not provided (Chen et al., 2011; Erdinger et al., 2004; Fantuzzi et al., 2001; Hsu et al., 531 2009; Lévesque et al., 1994). 532

533 To the best of our knowledge, only two studies have investigated THMs in the ambient air of 534 swimming pools treated with bromine based disinfectants. Lourencetti et al. (2012) reported concentrations of 1.8 to 6.9, 1.9 to 4.2, 6.4 to 8.7 and 55 to 928 µg/m<sup>3</sup> for trichloro-, bromodichloro-, 535 dibromochloro- and tribromo-methane, in the air above an indoor swimming pool treated by bromination. 536 Similarly, Richardson et al. (2010) found concentrations of 1.7 to 9.4, 1.7 to 4.8, 6.1 to 9.7 and 53 to 101 537  $\mu g/m^3$  for trichloro-, bromodichloro-, dibromochloro- and tribromo-methane, respectively, in their 538 investigation of an indoor swimming pool treated with BCDMH. As observed in swimming pool water 539 and discussed further in Sections 4 and 5, the speciation of THMs in the ambient air is influenced by the 540 water quality of the corresponding swimming pool, particularly by filling water composition and 541 disinfection practices. 542

## 543 **3.2.2. Inorganic Halamines**

A few studies have investigated halamines in the air above swimming pools, although, to date, 544 545 studies have focused on trichloramine in the air of indoor swimming pool complexes (summarised in 546 Table S13). Although not detected in all samples, trichloramine has been reported in the ambient air of indoor swimming pool complexes that employ chlorination, at concentrations between 20 and 1340 547  $\mu g/m^3$ , although on average concentrations are generally between 80 and 637  $\mu g/m^3$  (Afifi and Blatchley, 548 2015; Bernard et al., 2011; Bessonneau et al., 2011; Catto et al., 2012b; Chu et al., 2013; Font-Ribera et 549 al., 2016; Fornander et al., 2013; Jacobs et al., 2007; Lévesque et al., 2015; Parrat et al., 2012; Predieri 550 and Giacobazzi, 2012; Richardson et al., 2010; Schmalz et al., 2011a). Richardson et al. (2010) reported 551 an average trichloramine concentration of 80  $\mu$ g/m<sup>3</sup> in the air of an indoor swimming pool treated with 552 BCDMH, with concentrations varying (70 to  $100 \,\mu\text{g/m}^3$ ) over the twelve samples taken. Monochloramine 553 was investigated in the ambient air of forty-one indoor and chlorinated swimming pool complexes, with 554 concentrations of 70, 320 and 150  $\mu$ g/m<sup>3</sup> reported for the minimum, maximum and average, respectively 555 556 (Tardif et al., 2016).

# 557 4. Disinfection By-Products in Swimming Pools and Spas: Precursor Input and Implications

Compared to drinking waters, DBP formation in pools and spas is increased due to the higher 558 559 input of organic matter and constant addition of disinfectants. Whilst DBP formation has been extensively studied in many different waters (e.g. Richardson et al., 2007, 2010; Richardson, 2009; Richardson and 560 561 Kimura, 2016; Richardson and Ternes, 2014), and despite the efforts of the many pool and spa studies covered in this review, much is still unknown about DBP formation in the swimming pool environment. 562 Daiber et al. (2016) were the first to follow the water quality from source to pool, by investigating the 563 DBP occurrence and mutagenicity of the waters at each stage: in source, finished, tap, pool and spa 564 waters. Considering average total molar concentrations of DBPs, an increase of 610% was observed 565 between filling and pool waters, whilst a 900% increase was observed between filling and spa waters. 566 Where pools and spas were at the same location, spas contained approximately 140% more DBPs than 567

568 pools. Their results provide evidence that DBP formation is prominent in swimming pool and spa waters, 569 proposed to be mainly attributable to human input (human body excretions, pharmaceuticals and personal 570 care products) (Daiber et al., 2016). In addition to input via humans, two additional sources of 571 contaminants (and hence possible DBP precursors) have been identified: the filling water and the 572 chemicals (particularly the disinfectants) used during treatment.

As discussed in Section 3, due to the wide variety of DBPs and lack of suitable analytical 573 methods, not all individual DBPs and their precursors can be investigated in the swimming pool 574 environment. However, bulk parameters, like total organic carbon (TOC) and dissolved organic carbon 575 (DOC), are easily measured and are often used to assess the quality of the water, in terms of DBPs and 576 their precursors. TOC refers to the dissolved, particulate and colloidal organic matter contained within 577 578 water, whilst DOC refers to the soluble organic matter that cannot be removed by a 0.45 µm filter (US EPA, 2009). Table S14 summarises the occurrence of these bulk parameters in swimming pool and spa 579 580 waters to date.

For chlorinated indoor swimming pools, TOC concentrations are generally reported to be between 581 0.02 and 7.3 mg/L (Bessonneau et al., 2011; Carter et al., 2015; De Laat et al., 2011; Glauner et al., 2005; 582 Lee et al., 2010; Sa et al., 2011; Wang, 2011; Xiao et al., 2012), although some studies have reported 583 maximum concentrations of 16 to 71 mg/L (Kanan, 2010; Lee et al., 2009; Plewa et al., 2011; Wang et 584 al., 2013). Similar TOC concentrations have been reported for chlorinated pools located outdoors (0.02 to 585 33 mg/L) (Glauner et al., 2005; Manasfi et al., 2016; Plewa et al., 2011; Tang and Xie, 2016; Wang, 586 2011; Xiao et al., 2012; Yang et al., 2016; Yeh et al., 2014; Zhang et al., 2015). Where all pools were 587 588 located indoors, TOC concentrations have been measured for chlorinated pools additionally treated with 589 UV or ozone (5.2 to 18 and 0.7 to 27 mg/L, respectively), although a higher maximum concentration was reported in some ozonated pools (82 mg/L) (Lee et al., 2009, 2010; Plewa et al., 2011; Wang et al., 2013; 590 591 Zhang et al., 2015). TOC concentration has been measured in two studies of twenty-five and twenty-six indoor pools treated with EGMO, where concentrations of 0.4 to 12 and 1.9 to 5.8 mg/L were reported 592 (Lee et al., 2009, 2010). DOC concentration has been studied in several indoor swimming pools (1.3 to 593 39, 4.9 to 9.5 and 8.0 to 25 mg/L), where pools were treated by chlorination, chlorination with UV and 594 chlorination with ozone, respectively (Hang et al., 2016; Schmalz et al., 2011b; Tardif et al., 2016; Wang 595 et al., 2013). TOC and DOC concentrations have been presented in several other studies (below detection 596 597 to 27 and 0.6 to 1.5 mg/L, respectively), although not all pool details were provided (Chu and Nieuwenhuijsen, 2002; Font-Ribera et al., 2016; Maia et al., 2014; Panyakapo et al., 2008; Prieto-Blanco 598 et al., 2012; Spiliotopoulou et al., 2015; Wang et al., 2014). Generally, chlorinated spas reported higher 599 TOC concentrations (up to 155 mg/L) than those found in chlorinated swimming pools (Benoit and 600 Jackson, 1987; Carter et al., 2015; Plewa et al., 2011; Wang et al., 2014), which may be due to the higher 601 602 operation temperature of spas, promoting anthropogenic release of TOC from bathers, discussed further in **Section 5.5**. One study presented even higher concentrations for a whirlpool spas treated with bromine, up to 345 mg/L (Benoit and Jackson, 1987). Only one known study has provided TOC concentrations for indoor pools treated with bromine, where concentrations were generally higher than indoor pools treated with chlorine, being up to 125 mg/L (Plewa et al., 2011). Concentrations of DOC and TOC of 1.0 to 3.6 and 1.3 to 8.6 mg/L, respectively, were found in seawater filled, chlorinated swimming pools (Chowdhury, 2015; Parinet et al., 2012), with another study finding more elevated TOC concentrations (up to 12 mg/L) (Manasfi et al., 2016).

The following subsections present a review on current knowledge of the input of organic and inorganic matter in the swimming pool environment, with a particular focus on the impact on DBP formation.

#### 613 4.1. Filling Waters

One major factor that influences the occurrence of DBPs in swimming pool waters is the filling water, which can introduce a range of species, e.g. natural organic matter (NOM), trace amounts of DBPs chlorine and bromine, species that are dependent on both the quality and prior treatment of the filling water. The majority of swimming pools are filled with disinfected distributed drinking water (freshwater), however, the use of other natural waters, e.g. seawater, may become the norm in the future for some countries, where there is an increasing scarcity of freshwater.

620 Whilst TOC concentrations are often low in filling waters and not the major input of TOC for pools and spas (Daiber et al., 2016), filling waters may introduce bromide/bromine species, with bromide 621 reported at 65 to 80 and up to 0.5 mg/L, for sea and fresh water, respectively (WHO, 2009), which is 622 consistent with bromide levels reported in seawater filled swimming pools of 68 to 107 mg/L (Manasfi et 623 al., 2016; Parinet et al., 2012). Bromide can also be detected at higher concentrations in freshwaters, with 624 Heeb et al. (2014) detailing a concentration range of ~10 to >1000  $\mu$ g/L in their critical review of aqueous 625 reactions of bromine and concentrations up to 8.5 mg/L being measured in Western Australian 626 groundwaters (Gruchlik et al., 2014). 627

Although only studied in chlorinated pools, bromide (after quenching the oxidant residual) was reported at significantly lower concentrations than chloride, being below the detection limit in some studies (Cardador and Gallego, 2011; E et al., 2016) and ranging from 0.002 to 1.8 mg/L in other pools located indoors (Michalski and Mathews, 2007; Xiao et al., 2012). Similar results were reported for chlorinated swimming pools located outdoors, where bromide was below detection limits in some studies (Cardador and Gallego, 2011; Yeh et al., 2014) and 0.002 to 0.2 mg/L in others (Manasfi et al., 2016; Xiao et al., 2012). 635 As discussed in Section 2.2, the presence of bromide in swimming pools disinfected with chlorine 636 can lead to the formation of HOBr, as previously shown in Equation (viii), which is known to occur inpools treated by BCDMH, sodium bromide in combination with a chlorine based oxidant or EGMO. As 637 the reaction of HOBr with organic compounds in pools results in the formation of Br-DBPs which are 638 generally more toxic than their chlorinated counterparts (Plewa et al., 2004), increasing bromide 639 concentrations in swimming pools will increase the formation of Br-DBPs, an undesired consequence. 640 The predominance of the Br-DBPs despite the lower concentrations of bromine than chlorine is likely due 641 to the higher halogenation reactivity of bromine compared to chlorine, i.e., bromine is incorporated into 642 organic matter at a faster rate (Cowman and Singer, 1996). As discussed in Section 3, Br-THMs were 643 generally more abundant in seawater filled swimming pools compared to those filled with freshwater, for 644 pools where treatment methods and location were comparable (Manasfi et al., 2016), consistent with the 645 646 higher concentrations of bromide entering in the seawater filled pools. Other Br-DBPs, e.g. HAAs (Parinet et al., 2012), have been found in higher concentrations in pools filled with seawater compared to 647 those filled with freshwater. Whilst this section has focused on the input of bromide originating from 648 filling waters, bromide may also be introduced by bromine based disinfectants, which is discussed further 649 650 in Section 4.2. Further discussion on the impact of halide ions on DBP formation is provided in Section 5.1. 651

#### 652 **4.2. Disinfectants**

Many studies have investigated the effect of different disinfectants on DBP formation, however 653 these studies are often performed at conditions more reflective of drinking water and may not be a true 654 representation of the chemistry that would occur in swimming pool waters. For example, although the 655 desired outcome is shared, protection against the microbial disease risk, disinfectants are generally added 656 to drinking waters in individual doses (e.g. at the end of the treatment process or the outlet of the 657 reservoir) whereas due to constant bather load, rapid loss of disinfectant and the inefficiency of manual 658 treatment (Nnaji et al., 2011), disinfectants in swimming pools are often continually added by means of 659 automatic dosing systems, with oxidant residuals often much higher than those found in drinking waters. 660 Whilst all studies have led to a better understanding of the chemistry of disinfectants, this review only 661 discusses studies carried out under conditions applicable to the swimming pool environment. 662

663 Swimming pool disinfectants are produced on a large industrial scale and hence may not be 100% 664 pure. Specific impurities, such as bromate, chlorite and chlorate, have been reported in feed stocks of 665 sodium hypochlorite in median concentrations of 1022, 2646 and 20 462 mg/L, respectively, as well as in 666 calcium hypochlorite pellets (median concentrations 240, 695 and 9516 mg/kg, respectively) (Garcia-667 Villanova et al., 2010). Similarly, chloride is commonly found as an impurity in sodium bromide 668 (Chlorine Chemistry Council, 2003; PWTAG, 1999). Fillers are often added to solid disinfectants (e.g. 669 BCDMH or hypochlorite pellets) and can potentially remain as a residue in waters and possibly lead to the formation of DBPs. Further studies on the impact of fillers on DBP formation are recommended. Naturally, disinfectants themselves can result in DBPs as they are reduced. For example, ClO<sub>2</sub> as a disinfectant introduces chlorite, chlorate and chloride due to the reaction and hydrolysis products of chlorine dioxide (Gordon et al., 1972). Bromide and chloride are introduced by bromine and chlorine based disinfectants, respectively, and can have an effect on DBP formation as discussed in **Section 5.2.** The occurrence of a range of inorganic anions in swimming pools and spas was discussed in **Section 3.10**.

As presented throughout Section 3, Br-DBPs are generally detected at higher concentrations in 677 pools treated with bromine based disinfectants compared to their chlorinated counterparts, whilst Cl-678 DBPs dominate in pools disinfected with chlorine. For example, Kelsall and Sim (2001) investigated 679 680 THMs in three pools treated with chlorine, chlorine in combination with ozone (Cl<sub>2</sub>/Ozone) and sodium bromide in combination with ozone (Br<sub>2</sub>/Ozone), in order to assess the disinfectant impact on THM 681 formation. Chloroform was the dominant THM in the chlorinated pools (up to 85 µg/L) but was not 682 detected in the Br<sub>2</sub>/ozone treated pool, due to the absence of chlorine, Similarly, bromoform was the 683 dominant THM in the Br<sub>2</sub>/ozone treated pool, but was below detection in the chlorinated pools 684 investigated (Kelsall and Sim, 2001). These observations may be explained by the minimal formation of 685 HOCl or HOBr, and therefore minimal formation of the chloro- or bromo-THMs, in the brominated and 686 chlorinated pools, respectively. Daiber et al (2016) compared the DBPs detected in a number of 687 swimming pools and spas employing either bromination or chlorination, reporting the dominance of Cl-688 DBPs and Br-DBPs in pools treated by chlorination and bromination, respectively. Additionally, on a 689 molar basis, the total DBP concentrations were higher in pools where chlorination (predominantly 690 691 hypochlorite) was employed, when compared to those where bromination (BCDMH) was employed, although in spas similar total DBP molar concentrations were observed regardless of disinfectant (Daiber 692 et al., 2016). These observations can be explained by the slower dissolution and formation (and hence 693 availability) of free chlorine equivalents from BCDMH compared to the readily available hypochlorite, 694 where the dissolution rate from BCDMH is increased in the spas due to the higher operating temperature. 695 Lourencetti et al. (2012) also reported the dominance of Br-THMs and Cl-THMs in the ambient air at 696 swimming pool sites treated with bromine and chlorine based disinfectants, respectively, with Richardson 697 et al. (2010) reporting a similar finding. Additionally, Richardson et al. (2010) reported a lower maximum 698 dichloramine concentration (<10 µg/L) in a pool treated with BCDMH compared to one where 699 chlorination was employed (650  $\mu$ /L). 700

Lee et al. (2009) reported both higher TTHM and Br-THM concentrations in pools treated with EGMO compared to pools where chlorination was employed, although this comparison was of mass concentrations. It is important to note that to accurately compare concentrations of groups of compounds, such as TTHMs, Br-THMs or HAA9, it is crucial to use molar concentrations. The use of mass or molar 705 concentrations for comparison has been noted along with each study throughout this review. In a 706 subsequent study, Lee et al. (2010) further investigated the effect of these treatment methods, by studying a wider range of DBPs: THMs, HAAs, HANs and CH. Considering average concentrations by mass, total 707 THMs and total HANs were higher in pools where EGMO was employed compared to chlorinated pools, 708 which is likely due to the higher abundance of brominated THMs and HANs detected in the EGMO 709 treated pools. Although higher concentrations of Br-HAAs were detected in the pools treated with 710 EGMO, Lee et al. (2010) reported a higher HAA9 concentration in pools treated with chlorination 711 compared to those treated by EGMO. Whilst concentrations varied greatly, compared to where 712 chlorination was employed, on average CH was detected at slightly lower concentrations in the EGMO 713 treated pools (Lee et al., 2010). Zhang et al. (2015) reported substantially lower DBP concentrations in 714 715 pools treated with chlorine dioxide and TCICA compared to pools treated by chlorination, when comparing molar totals of the sum of TTHMs, HAA9, CH, HAN-4, 1,1-DCP, 1,1,1-TCP and TCNM. 716 Pools treated by chlorination in combination with ozone were also investigated by Lee et al. (2009, 2010) 717 and Zhang et al. (2015), and these are discussed in Section 5.1. 718

In addition to comparing DBPs detected in real pools, several studies have been conducted on the 719 laboratory scale in order to better understand the impact of disinfectants on DBPs in the swimming pool 720 environment. Pu et al. (2013) investigated the effect of bromination versus chlorination on DBP 721 722 formation, by comparing TTHM and total HAN molar concentrations resulting from the oxidation of algae solutions under conditions comparable to pool waters. An increase in total molar HAN 723 concentrations was observed when bromination was employed over that observed during chlorination. 724 TTHM molar concentrations were comparable between chlorination and bromination (Pu et al., 2013). 725 Similarly, Judd and Jeffrey (1995) reported a 74% greater THM formation with the use of bromine 726 (HOBr) as a disinfectant, compared to when chlorine (HOCl) was used under the same conditions, in their 727 investigation carried out under conditions similar to that of real swimming pool waters. 728

More recently, Yang et al. (2016) investigated a range of disinfectants commonly used in 729 730 swimming pools (BCDMH, sodium hypochlorite and TCICA), analysing oxidant decay, reaction kinetics and DBP formation in laboratory scale studies of modelled swimming pool waters. Mainly brominated 731 DBPs were formed when BCDMH was employed, whilst mainly Cl-DBPs formed in experiments where 732 sodium hypochlorite and TCICA were used. Oxidant residuals were similar for BCDMH and sodium 733 734 hypochlorite, although a higher residual was observed in waters treated with TCICA. Although comparison of molar concentrations would be more accurate, on a mass basis, slightly lower total DBP 735 formation was reported for waters treated with TCICA compared to those treated with sodium 736 hypochlorite, whilst the use of BCDMH produced up to twice the concentration of DBPs compared to the 737 other disinfectants (Yang et al., 2016). Consistent findings were reported in real pools by Wang et al. 738 (2014), where, on a molar basis, lower HAA5 concentrations were observed in pools treated by TCICA 739

compared to those treated by chlorination. These observations were explained by (i) the slower release of
chlorine, and hence its availability to form DBPs, for TCICA and (ii) the slow dissolution and fast
consumption of HOBr for BCDMH (Yang et al., 2016).

#### 743 **4.3. Bather Load and Human Input**

Excluding disinfectants, bather load is the largest chemical input and oxidant consumer in swimming pool waters (Keuten et al., 2012) and can be divided into two main categories: human body excretions and personal care products. Although various studies exist in a more general sense, the following subsections will only present a review of literature discussing bather load and human input in relation to the swimming pool environment and will focus mainly on the impact on DBP formation.

## 749 4.3.1. Human Body Excretions

As the name suggests, human body excretions are comprised of any human derived input generally introduced via sweat, urine, saliva, hair or skin cells, and, although differing from person to person, can include urea, ammonia, uric acid, creatinine, creatine, lactic acid, citric acid, hippuric acid, uracil, ornithine, chloride, sulfate, cations such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup>, and amino acids, such as histidine, glycine, cysteine, asparagine, lysine, arginine and guanine (Hirokawa et al., 2007; Montain et al., 2007; Mosher, 1933).

756 Although not inclusive, bulk parameters such as TN (the total nitrogen content) or TON (the 757 organic nitrogen fraction), which are summarised in Table S14, can be used as an indication of contamination of human origin, as many human inputs contain nitrogenous compounds. In terms of TN, 758 chlorinated pools located indoors have higher reported concentrations than those located outdoors (0.8 to 759 12 and 0.6 to 8.4 mg/L, respectively), although the outdoor pools were treated additionally with ozone 760 (Yeh et al., 2014; Zhang et al., 2015). Additionally, TON concentrations followed the same trend, with 761 reported concentrations of 0.2 to 11 and 0.09 to 1.3 mg/L for indoor and outdoor pools, respectively (Yeh 762 et al., 2014; Zhang et al., 2015). The generally higher concentrations of TN and TON observed in indoor 763 pools (compared to outdoor pools) may be due to (i) indoor pools are often used by a larger number of 764 babies and children (Section 5.4), and (ii) indoor pools are generally operated at higher temperatures 765 (Section 5.5), both of which would see an increased release of nitrogen containing anthropogenic 766 767 chemicals and hence a higher nitrogen content. Parinet et al. (2012) presents the only known report of 768 TN in seawater filled swimming pools, where concentrations of 0.7 to 7.7 mg/L were reported, in their investigation of eight indoor pools treated by chlorination. It should be noted that human inputs differ 769 770 upon swimmer activity and water temperature, and these aspects are addressed in Sections 5.4 and 5.5, 771 respectively.

The quantity of contamination due to human input has been investigated in various studies. The release of chemicals from swimmers was investigated by Keuten et al. (2014), who found that on average 774 a person released 250, 77, 37 and 10 mg of non-purgeable organic carbon, TN, urea and ammonium, respectively, during a 30 minute swim time. Urea, a component of urine and sweat (Mosher, 1933), has 775 been detected in a range of pools in concentrations up to 3.7 mg/L (De Laat et al., 2011; Parrat et al., 776 2012; Schmalz et al., 2011a, 2011b; Tachikawa et al., 2005; Weng and Blatchley, 2011), with a full 777 summary provided in Table S14. Afifi and Blatchley (2016) also investigated urea in swimming pools, 778 reporting that it was correlated to the number of swimmers. Nitrate concentrations were found to vary, 779 with no trends observed for swimming pool type (ind88 mg/L found (Beech et al., 1980; Zhang et al., 780 2015). Concentrations varied greatly between pools located indoors, with nitrate levels reported between 781 2.2 to 129, 4.2 to 208, 1.2 to 26 and 11 to 49 mg/L for pools treated with sodium hypochlorite, chlorine 782 dioxide, chlorination in combination with ozone and EGMO, respectively (E et al., 2016; Lee et al., 2010; 783 Michalski and Mathews, 2007; Spiliotopoulou et al., 2015; Zhang et al., 2015). 784

The potential of DBP formation from human body derived precursors has been investigated at the laboratory scale, with studies investigating either individual precursors or body fluid analogue (BFA), a synthetic mixture containing the main components of bodily fluids, under conditions commonly reported in swimming pool waters.

The BFA (or precursor) to chlorine ratio has been shown to be the major factor affecting the 789 amount of DBPs formed (Hansen et al., 2012a, 2013a; Kanan, 2010; Schmalz et al., 2011a), with the 790 precursor source having some effect. Judd and Bullock (2003) compared the formation of THMs and 791 792 chloramines upon chlorination of BFA alone and BFA with a standard humic acid sample (as a soil analogue) in a model pool, reporting eight times higher concentration of THMs was produced when the 793 794 humic acid was present. Small increases in humic acid saw little change to chloramine concentrations, 795 however concentrations doubled upon doubling the humic acid concentration (Judd and Bullock, 2003). This study highlights the importance of humic substances on DBP formation in pools, which can be 796 minimised with correct swimmer hygiene. THMs were produced at a lower rate than HAAs upon 797 chlorination of BFA, with HNMs produced at the lowest rate (Kanan and Karanfil, 2011). In the same 798 799 study, individual BFA components at a concentration of 1 mg/L carbon were investigated for their potential DBP formation, with almost all components forming varying concentrations of chloroform, 800 DCAA and TCAA and TCNM, with citric acid leading to the highest formation (based on mass 801 concentration) in almost all cases (Kanan and Karanfil, 2011). Uric acid, citric acid and hippuric acid 802 803 have been shown to be the components of BFA most responsible for HAA formation upon chlorination 804 (Yang et al., 2016).

Additionally, a range of DBPs including halo(nitro)phenols were detected in pool waters, which were later confirmed to form from the chlorination of human derived precursors, particularly urine (Xiao et al., 2012). Although the formation of HAAs, THMs and HANs were observed upon chlorination of BFA (Hansen et al., 2012a), formation was dependent on pH. This is discussed in more detail in Section
5.5.

A mixture including hair, saliva, skin, urine and moisturising body lotion, as well as the individual 810 components, was investigated for potential formation of chloroform, bromodichloromethane, CH, DCAN 811 and 1,1,1-TCP upon chlorination in a study by Kim et al. (2002). Chloroform was the most abundant 812 DBP (on a mass concentration basis) in all cases, with DCAN formation higher upon chlorination of 813 components of human origin, which is likely due to the formation of nitrogen containing degradation 814 products which enhance DCAN formation (Kim et al., 2002). Additionally, the chlorination of skin 815 specimens by Xiao et al. (2012) led to the formation of HAAs and THMs, with Br-DBPs increasing with 816 increasing bromide concentrations. 817

In almost all samples analysed, saliva, urine, gastric juice, blood and faeces were found to contain 818 several secondary amine precursors, dimethylamine, pyrrolidine and piperidine (Tricker et al., 1992), 819 which may lead to N-nitrosamine formation. Additionally, Carter et al. (2015) demonstrated the formation 820 of NDMA from chloramination of synthetic urine, which was likely due to several mechanism pathways 821 involving dimethylamine and nitrate (Masuda et al., 2000; Mitch and Sedlak, 2001). In another study, 822 urea, ammonium ions, amino acids and creatinine were identified as the main precursors to trichloramine 823 formation, with urea responsible for 76% of the total trichloramine formation observed (Schmalz et al., 824 2011a). The degradation rate of urea was reported to be 1% per hour at chlorine concentrations equivalent 825 to those found in swimming pools, and its likely degradation products were suggested to be chlorinated 826 827 urea and trichloramine (De Laat et al., 2011). At a pH value similar to that expected in pools, formation of 828 trichloramine was reported to be favoured over the mono- or di-substituted analogues (Schmalz et al., 829 2011a).

UV treatment and chlorination of three amino acids, L-arginine, L-histidine, and L-glycine, led to 830 831 the formation of chloramines and cyanogen chloride (Weng and Blatchley, 2013). The formation of chloramines was suggested to be due to rapid N-chlorination, with UV irradiation and hydrolysis then 832 833 promoting cleavage and subsequent formation of ammonia, which formed chloramines upon further chlorination. The formation of CNCl was proposed to occur through a similar pathway of N-chlorination 834 followed by UV promoted hydrolysis, where reactions and by-products were found to be dependent on 835 both the chlorine to precursor ratio (Cl/P) and UV dose (Weng and Blatchley, 2013), Lian et al. (2014) 836 837 reported the formation of CNCl from the chlorination of uric acid, with reactions found to be not only dependant on the Cl/P ratio, but also on pH and temperature. Additionally, at Cl/P ratios greater than 1 838 (i.e. conditions reflective of real swimming pools), the formation of other intermediates and their 839 subsequent DBPs (due to ring cleavage and subsequent chlorination) were observed, which was likely due 840 to the lower stability of these products promoting decarboxylation or hydrolysis reactions (Lian et al., 841 842 2014). CNCl was also the major product observed upon chlorination of uric acid in a study by Li and 843 Blatchley (2007). For all these studies of CNCl formation (Li and Blatchley, 2007; Lian et al., 2014; 844 Weng and Blatchley, 2013), CNCl concentrations were found to decrease at higher chlorine doses. Li and Blatchley (2007) reported the formation of cyanogen chloride upon chlorination of L-histidine, also 845 observing the formation of other DBPs. Creatinine, urea, L-histidine and L-arginine all produced 846 trichloramine upon chlorination, with DCAN and dichloromethylamine observed in some cases (Weng 847 and Blatchley, 2013). Complex mechanisms were proposed for all compounds, and hypothesised to 848 involve several chlorine substitution, hydrolysis, and/or decarboxylation reactions, with several 849 intermediate species (Li and Blatchley, 2007). In a study of the reaction mechanism of the chlorination of 850 urea in a swimming pool context, molecular chlorine, Cl<sub>2</sub>, was found to be the chlorine species involved 851 in the rate-determining first step of N-chlorination of urea, with HOCl being the chlorine species involved 852 in the subsequent steps to ultimately form trichloramine and nitrate (Blatchley and Cheng, 2010). 853

Chlorination of six nitrogen containing precursors, glycine, asparagine, uracil, cytosine, guanine 854 and cysteine, all led to the formation of cyanogen chloride, with its concentration again found to be highly 855 dependent on the chlorine to precursor ratio (Shang et al., 2000). Although an overall mechanism was not 856 provided, the tentative identification of several other DBPs (DCAN, chloroform, acetone, N,N-857 dichloroaminoacetonitrile and N-chloroformamide) in this study suggested several mechanistic pathways 858 and therefore intermediate species are likely (Shang et al., 2000). Wlodyka-Bergier and Bergier (2016) 859 investigated urea, creatinine, glycine, histidine and arginine for their potential to form a series of DBPs 860 (chloroform, CAA, DCA, TCAA, TCAN, 1,1-DCP, 1,1-TCP, CH and TCNM) upon chlorination and 861 chlorination in combination with UV treatment. Although all investigated precursors showed a potential 862 to form all investigated DBPs, chloroform formation was highest from creatinine and glycine, HK 863 864 formation was highest for creatinine and histidine, CH, HAAs and HANs showed highest formation from histidine, whilst all precursors showed similar formation potentials for TCNM. The impact of UV 865 treatment had a significant effect on the DBP formation potential of the different precursors. For all 866 precursors, HAAs and TCNM concentrations increased when UV treatment was applied. Excluding 867 glycine, CH formation increased for all precursors, whilst only creatinine showed a decreased formation 868 potential for HANs, when UV was applied. For HKs, an increased formation was observed for urea and 869 870 arginine, with other precursors demonstrating a decreased formation potential when UV was applied. Although a large increase in chloroform formation was observed from urea and histidine, the effect of UV 871 treatment was somewhat ambiguous for other precursors investigated (Wlodyka-Bergier and Bergier, 872 2016). 873

# **4.3.2.** Pharmaceuticals and Personal Care Products

Although recent reviews by Bottoni et al. (2014), Sharifan et al. (2016) and Haman et al. (2015) discuss some potential issues of pharmaceuticals and personal care products (PPCPs) in aquatic environments, this review will present studies of PPCPs applicable to swimming pools (especially UV filters, antifungal agents and parabens that are commonly added to sunscreens and other cosmetic products), with a particular focus on the potential for DBP formation. Although known by various chemical and trade names, for the purpose of this review, some commonly reported PPCPs will be abbreviated as per **Table 3**, with full lists of names provided in **Table S15**.

Thirty pharmaceuticals were investigated in seawater filled and freshwater pools by Teo et al. 882 (2016a), with only caffeine (16 to 1540 ng/L) and ibuprofen (16 to 83 ng/L) detected in twelve and eight 883 of the fifteen freshwater pools investigated, respectively. All thirty pharmaceuticals investigated were 884 below detection limits in the seawater filled pools (Teo et al., 2016a). Of thirty-two PPCPs, N,N-diethyl-885 *m*-toluamide, caffeine and tri(2-chloroethyl)phosphate were the only detectable PPCPs in swimming pool 886 waters investigated by Weng et al. (2014), who also showed the potential of PPCPs to form chlorinated 887 888 by-products. Similarly, the occurrence of thirty-two pharmaceuticals and fourteen UV filter compounds were investigated over a range of swimming pools, with over 88% of the pools containing 889 pharmaceuticals and over 94% containing UV filters (Ekowati et al., 2016). Only ten pharmaceuticals 890 (atenolol, carbamazepine, hydrochlorothiazide, metronidazole, ofloxacin, 891 sulfamethoxazole, acetaminophen, ibuprofen, ketoprofen and phenazone) and eleven UV filters (BP-1, BP-2, BP-3, BP-8, 892 THB, 4DHB, 4MBC, OD-PABA, 1HBT, MeBT and DMeBT) were detected, with maximum 893 concentrations of 904 and 69 ng/L, respectively. Generally, spas had higher concentrations than pools 894 and, whilst pharmaceuticals were lower in pools treated with sodium hypochlorite, UV filters were lower 895 in pools with EGMO/UV treatment (Ekowati et al., 2016). 896

A range of UV filters (BP-3, OMC, PBS, 4-MBC and OCR) were present in up to ten times higher 897 898 concentrations in a pool used exclusively by babies, compared to concentrations in a pool used by adults, 899 with maximum concentrations of 40 µg/L reported (Zwiener et al., 2006). Cuderman and Heath (2007) investigated a range of UV filters (4-MBC, OCR, OMC, BP-3, homosalate and avobenzone) and two 900 901 antifungal agents (2,4-DCPh and dichlorophen) in two individual swimming pools. 4-MBC (330 ng/L), OCR (17 ng/L) and OMC (15 ng/L) were detected in one pool and BP-3 (103 and 400 ng/L) was detected 902 903 in both pools. Homosalate, avobenzone, 2,4-DCPh and dichlorophen, were not detected in any of the investigated swimming pools (Cuderman and Heath, 2007). Similarly, avobenzone was not detected in a 904 905 swimming pool investigated by Giokas et al. (2004), however BP-3 (5.7 ng/L), 4-MBC (5.4 ng/L) and OMC (3.0 ng/L) were all detected. Higher concentrations (2400 to 3300 ng/L) of BP-3 were reported in a 906 907 swimming pool in an earlier study by Lambropoulou et al. (2002), who also reported finding OP-PABA in concentrations of below detection (<600) to 2100 ng/L. Vidal et al. (2010) compared the 908 concentrations of six UV filters (BP-3, amiloxate, 4-MBC, OCR, OD-PABA and OMC) in private and 909 public pools. Amiloxate was detected in the public pool (700 ng/L) and, although below the limit of 910 quantification (60 ng/L), 4-MBC was also detected. All other UV filters were below their respective 911

detection limits (60 to 3000 ng/L) in the public pools, with no UV filters detected in the private pool(Vidal et al., 2010).

Parabens are used as preservatives in some PPCPs (such as sunscreen) and have been investigated 914 in both pool waters and at the laboratory scale. Whilst none of the investigated parabens (BuP and BzP) 915 were detected in the actual pool water samples, the addition of sunscreen (200  $\mu$ L) to pool water resulted 916 in both parabens being detected: 29 µg/L of BuP and 43 µg/L of BzP (López-Darias et al., 2010). 917 Additionally, whilst the pool water was found to have no detectable levels of several endocrine disruptor 918 chemicals which are suspected to negatively affect reproductive function, increase risks of some cancers 919 and result in abnormal growth and neurodevelopment in children (UNEP and WHO, 2013), namely six 920 polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, phenanthrene, anthracene, 9-921 922 methylanthracene and fluoranthene) and six alkylphenols (4-tert-butyl-, 4-tert-octyl-, 4-octyl-, 4-cumyland 4-n-nonyl-phenol and bisphenol A), an increase in 4-n-nonylphenol (16 µg/L) was detected after the 923 addition of sunscreen to the swimming pool water (López-Darias et al., 2010). This study provides 924 evidence that sunscreens are a source of PPCPs in swimming pool waters. The occurrence of MeP, EtP, 925 PrP, BuP, 2,4,6-TCPh and 2,4-DCPh in swimming pool waters was investigated in two individual studies 926 by Regueiro et al. (2009a, 2009b). In one pool water sample, PrP (32 ng/L) and BuP (78 ng/L) were 927 quantified, MeP, EtP and 2,4,6-TCPh were detected, and 2,4-DCPh was below the limit of detection (<21 928 929 ng/L) (Regueiro et al., 2009a). In their later investigation of swimming pool waters, BuP (14 ng/L) was quantified, MeP, EtP, PrP and 2,4-DCPh were detected, and 2,4-DCPh was again below the detection 930 limit (Regueiro et al., 2009b). PrP (900 ng/L) was the only paraben detected in a swimming pool 931 investigated by Almeida and Nogueira (2014), where MeP, EtP and BuP were below the detection limits 932 (<100 ng/L). 933

A few studies have reported the formation of halogenated by-products from parabens in 934 swimming pool waters. Terasaki and Makino (2008) investigated seven parabens (MeP, EtP, PrP, iPrP, 935 BuP, iBuP and BzP) and their monochlorinated and dichlorinated by-products in two indoor and four 936 outdoor chlorinated swimming pools. Only one indoor and one outdoor pool showed detectable levels of 937 the investigated parabens or their chlorinated by-products. iPrP-Cl2 and BzP were quantified (25 and 28 938 ng/L, respectively), with MeP-Cl2 and BzP-Cl1 detected for the indoor pool, whilst iPrP-Cl2, BzP and 939 BzP-Cl1 were detected in the outdoor pool. All other compounds were below their respective limits of 940 detection (5-15 ng/L) (Terasaki and Makino, 2008). Li et al. (2015b) investigated a range of parabens 941 (MeP, EtP, PrP, BuP, PeP, HeP, OcP and BzP), some chlorinated by-products (MeP-Cl1, MeP-Cl2, EtP-942 Cl1 and EtP-Cl2) and their main hydrolysis product, *p*-hydroxybenzoic acid (PHBA) in a range of pools 943 treated by either chlorination or chlorination in combination with ozone. Of the detected parabens, MeP 944 and PrP dominated and accounted for over 91% of the total paraben concentrations on a molar basis. 945 Considering the summed concentrations of the investigated parabens and their chlorinated derivatives, 946

947 indoor pools had an approximately twenty times higher average concentration than pools located outdoors 948 (144 and 6.8 ng/L, respectively), which the authors suggest is likely due to (i) the lower paraben loading of outdoor pools as outdoor pools often have shorter opening times and (ii) the increased degradation of 949 parabens in outdoor pools via UV due to the prolonged exposure to sunlight. Additionally, paraben 950 concentrations were reported to be higher on weekends compared to weekdays, which is likely due to the 951 higher bather loads during weekends (Li et al., 2015b). Consistent with the authors' suggestions, parabens 952 have been shown to degrade in the presence of ozone and UV treatment (Cuerda-Correa et al., 2016), 953 which may explain the observations of Li et al. (2015b) as both ozone (via treatment) and UV (via 954 sunlight) were present in some pools. Further investigation into the degradation and transformation 955 products of parabens, particularly under conditions applicable to swimming pool waters, is therefore 956 warranted. 957

Although only limited studies exist, a range of other DBPs likely introduced via PPCPs have been 958 investigated in pools. Swimming pool water is suggested to increase the leaching of nanoparticles (TiO<sub>2</sub> 959 and ZnO) during swimming (Virkutyte et al., 2012), which have the potential to accumulate in swimming 960 pools (Jeon et al., 2016). A range of aliphatic and aromatic aldehydes (glyoxal, methylglyoxal, 2,5-961 butyraldehyde, propionaldehyde, dihydroxybenzaldehyde, 962 acetaldehyde, 3-hydroxybenzaldehyde, benzaldehyde, formaldehyde, valeraldehyde, 3-methylbenzaldehyde, 2-ethylbenzaldehyde and 2,5-963 dimethylbenzaldehyde) have been detected in both indoor and outdoor swimming pools in concentrations 964 up to 12 µg/L (Fernandez-Molina and Silva, 2013; Serrano et al., 2013). Halobenzoquinones (2,6-965 dichloro-, 2,3,6-trichloro-, 2,3-dibromo-5,6-dimethyl- and 2,6-dibromo-1,4-benzoquinone) have also 966 been detected in swimming pool waters, at concentrations up to 299, 11, 0.7 and 3.9 ng/L, respectively 967 (Wang et al., 2013). Only 3-chloro-, 4-chloro- and 2,4,5-trichloro-aniline were detected in swimming pool 968 waters (160, 200 and 40 ng/L, respectively) in an investigation of twenty seven amines, being aliphatic 969 970 amines, anilines and N-nitrosamines (Jurado-Sánchez et al., 2009). Daiber et al. (2016) detected several halogenated DBPs previously not reported in swimming pool waters, including 4,5-dibromo-1-methyl-971 972 1H-imidazole and 2,4,5-tribromo-1-methylimidazole, which likely result from the use of BCDMH as a disinfectant in these waters. Although found to be unlikely to pose a health risk, organophosphate flame 973 retardants (tributyl-, tris(2-chloroethyl)-, tris(1-chloro-2-propyl)-, tris(1.3-dichloro-2-propyl)-974 and triphenyl-phosphate) were detected in a range of indoor and outdoor pools (treated by chlorination or UV 975 in combination with chlorine) at concentrations between 5 and 1180 ng/L (Teo et al., 2016b). The 976 investigated organophosphate flame retardants were generally measured at higher concentrations in the 977 indoor swimming pools compared to the concentrations measured in the outdoor pools, and were found to 978 leach from swimsuits in laboratory studies (Teo et al., 2016b). 979

980 Some studies have investigated the possible DBP formation from the aforementioned PPCPs, by 981 carrying out laboratory studies under swimming pool conditions. Various PCPs, as well as pharmaceuticals, were subject to chlorination in a series of laboratory-scale studies, in which chloroform was produced in all cases (Rose and Herckes, 2014). Pharmaceuticals containing amine groups were the centre of a study by Shen and Andrews (2011) who reported all pharmaceuticals investigated produced NDMA upon chloramination. Based on molar concentrations, ranitidine led to the highest NDMA formation, with NDEA detected in some cases (Shen and Andrews, 2011). Two salicylates commonly found in several personal care products, benzyl salicylate and phenyl salicylate, were found to produce mono- and di-chloro substituted by-products upon their chlorination (de Oliveira e Sá et al., 2014).

Twenty-five possible by-products of the most commonly used UV filter, avobenzone, were 989 identified by Trebše et al. (2016), upon treatment with UV and chlorination under conditions similar to 990 that of swimming pools. Additionally, avobenzone was shown to only partially degrade upon 991 992 UV/chlorination treatment, and may persist in swimming pool waters, potentially leading to a high formation of by-products over time (Trebše et al., 2016). Similarly, a range of chlorinated by-product 993 intermediates were detected by Nakajima et al. (2009), who treated two UV filters commonly found in 994 sunscreens (OD-PABA and OMC) with sodium hypochlorite at a pH reflective of swimming pools. The 995 extent of the reactions was shown to be dependent on a range of parameters including pH and chlorine 996 dose. The toxicities of these by-products were evaluated and found to pose no significant health risk 997 (Nakajima et al., 2009). Manasfi et al. (2015) investigated the degradation of BP-3 under conditions 998 comparable to seawater filled swimming pools treated by chlorination. The proposed degradation 999 different by-products, mechanism included ten with final products of bromoform 1000 and tribromoacetaldehyde, which were found to increase with increasing chlorine dose and temperature 1001 (Manasfi et al., 2015). 1002

Although the aforementioned studies have provided some insight to the possible transformation by-products of both PPCPs and human body excretions, much is still unknown. Controlled laboratory and real pool investigations of human body excretions and PPCPs are required in order to fully understand their impact on DBP formation in the swimming pool environment. Human body excretions have been shown to be a major source of DBP formation in swimming pools, with TON reported to be the main precursor of N-DBPs (Shah and Mitch, 2011), and, as such, human body excretions in pools should be minimised.

# 1010 5. Disinfection By-Products: Other Factors to Consider

## 1011 5.1. Secondary Treatment

1012 Treatments such as ozone and UV are also employed to treat swimming pool waters, being used in 1013 addition to chlorination and bromination. Although many studies have evaluated the use of UV or ozone 1014 on DBP formation, this review will focus only on those studies carried out under conditions similar to 1015 those used to treat swimming pool waters. 1016 UV, like many other treatment methods, has advantages and disadvantages. The addition of chlorine prior to UV treatment is undesired, as although some contaminants are decreased by UV, so is 1017 the disinfectant residual (Rand and Gagnon, 2008). Due to this, a chlorination step post UV treatment is 1018 commonly adopted in the treatment of swimming pool waters. UV treatment is known to degrade 1019 chloramines (Cimetiere and De Laat, 2014; Soltermann et al., 2014), however many factors, particularly 1020 turn-over rate, affect the efficiency of this degradation. In addition, post-chlorination is reported to 1021 increase trichloramine stability (Soltermann et al., 2014). In a study of N-nitrosamine formation and 1022 degradation during UV treatment of pool water, UV treatment of monochloramine and chlorinated 1023 dimethylamine was found to lead to a substantial increase in NDMA formation, proposed to occur 1024 through reaction of nitric oxide or peroxynitrite with the dimethylaminyl radical, species produced by UV 1025 photolysis of monochloramine and chlorinated dimethylamine, respectively (Soltermann et al., 2013). 1026 Despite the problematic NDMA being generally efficiently degraded by UV treatment, in the swimming 1027 pool environment where high levels of nitrogen containing NDMA precursors exist, the rate of formation 1028 of NDMA outweighed that of its degradation, resulting in a net increase in NDMA concentration 1029 (Soltermann et al., 2013). Removal of N-nitrosamines from swimming pool waters requires UV doses 1030 over thirty times those currently employed at swimming pool sites (Soltermann et al., 2013). Soltermann 1031 et al. (2013) concluded that UV treatment would only be useful for reduction in N-nitrosamine 1032 1033 concentrations if the pool water contained high N-nitrosamine concentrations compared to the concentrations of chloramines and chlorinated secondary amines. 1034

The effect of UV treatment on DBPs has been reported, where many studies focused on volatile 1035 DBPs. In a laboratory based study by Hansen et al. (2013b), solutions containing the following DBPs, 1036 trichloro-, bromodichloro-, dibromochloro- and tribromo-methane, TCAN, DBAN, BCAN, DCAN, CH, 1037 1,1,1-TCP, 1,1-DCP and TCNM, were exposed to medium pressure UV treatment with DBP 1038 concentrations measured over time. Generally, Br-DBPs were degraded faster than their chlorinated 1039 counterparts, although the order of degradation (listed from fastest to slowest) was found to be TCNM, 1040 1041 tribromomethane, dibromochloromethane, DBAN, TCAN, BCAN, CH, bromodichloromethane, DCAN, 1,1,1-TCP, trichloromethane and 1,1-DCP (Hansen et al., 2013b). In experiments where chlorine was 1042 added prior to UV treatment, no increase in DBP degradation was observed, indicating that DBPs are not 1043 degraded by chlorine radicals (Hansen et al., 2013b). Whist this study showed the degradation rates of the 1044 investigated DBPs due to UV, it does not truly represent conditions of real swimming pools where 1045 chlorination generally occurs post-UV treatment. 1046

1047 A later study by Spiliotopoulou et al. (2015) expanded the work by Hansen et al. (2013b) by 1048 evaluating changes in DBP concentrations in samples of swimming pool waters treated by UV and UV-1049 post chlorination, although TCNM, BCAN, DBAN and TCAN were excluded in this study. DCAN, 1050 1,1,1-TCP and 1,1-DCP were all found to increase in waters treated with UV-post chlorination, although 1051 with extended UV exposure, concentrations decreased, as observed by Hansen et al. (2013b). Similar 1052 results were reported for THMs, although with longer UV exposure, more Br- and less Cl-THMs were 1053 detected. These observations suggest that (i) DBPs are not formed in the UV reactor but in the subsequent 1054 chlorination stage and (ii) that bromide released from the photodecay of Br-DBPs within the UV reactor 1055 leads to the formation of HOBr upon addition of chlorine, which subsequently induces Br-DBP formation 1056 (Spiliotopoulou et al., 2015).

1057 Cimetiere and De Laat (2014) also investigated the effect of UV-post chlorination on a range of 1058 DBPs (HAAs, THMs, DCAN, 1,1,1-TCP, TCNM and TOX) by exposing swimming pool water samples 1059 to medium pressure UV, followed by chlorination. Results suggest that UV-post chlorination had little 1060 effect on HAAs, slightly increased the concentrations of TOX and CH, but significantly increased the 1061 concentrations of THMs (particularly bromodichloro- and dibromochloro-methane), DCAN, 1,1,1-TCP 1062 and TCNM (Cimetiere and De Laat, 2014). Whilst tribromomethane was found to decrease in this study, 1063 the increase of other Br-THMs is consistent with the model proposed by Spiliotopoulou et al. (2015).

Perhaps the best representation of UV treatment in pools is that by Afifi and Blatchley (2016), 1064 of DBPs (cyanogen chloride, who compared concentrations cyanogen bromide, DCAN, 1065 dichloromethylamine, mono-, di- and tri-chloramine, and trichloro-, tribromo- and dibromochloro-1066 methane) in a single chlorinated swimming pool at times where (i) no UV was employed, (ii) medium 1067 pressure UV-post chlorination was employed and (iii) low pressure UV-post chlorination was employed. 1068 Whilst some differences were observed between the two UV treatments, regardless of the UV type and in 1069 comparison to where only chlorination was present, trichloromethane, tribromomethane, cyanogen 1070 1071 bromide, dichloromethylamine and the inorganic chloramines were all detected at lower concentrations, whilst increases in DCAN and dibromochloromethane were observed. No change was observed for 1072 cyanogen chloride. Although some finding are supported by the aforementioned studies (Cimetiere and 1073 De Laat, 2014; Hansen et al., 2013b; Spiliotopoulou et al., 2015), this is the first in-depth investigation of 1074 the impact of UV-post chlorination treatment in a real swimming pool. These differing outcomes 1075 1076 highlight the uncertainty of the effects of UV treatment on DBPs in the swimming pool environment, warranting further investigation into DBP chemistry after UV-post chlorination treatment. Future work 1077 should follow the work by Afifi and Blatchley (2016) and assess this chemistry on a larger scale, i.e. 1078 continual precursor input and treatment, which is more reflective of swimming pool waters. Whilst the 1079 1080 studies presented here focused generally on swimming pools, the effect of UV treatment on suspected DBP precursors introduced via bather load was discussed in Section 4.3. 1081

Like UV treatment, ozonation is often employed prior to chlorination, as a secondary treatment in swimming pools. As discussed in **Section 3**, swimming pools treated with ozone generally contained lower concentrations of the investigated DBPs than pools where ozone was not employed. For example, TTHM concentrations were lowest in swimming pools where ozone/chlorination was used, compared to those treated exclusively by chlorination, which the authors attribute to the oxidation of long chained organic molecules by hydroxide ions (introduced by use of sodium hypochlorite) at the relatively high pH (up to 8.5) found in these pools, leading to a higher formation of THMs compared to that observed in the ozone/chlorine pools where ozone is the more dominant oxidant and hence oxidation by hydroxide ions would be less prevalent (Lee et al., 2009). Similar results were reported by Kelsall and Sim (2001), where lower TTHMs (13 to 24  $\mu$ g/L) were detected in swimming pools treated by chlorination in combination with ozone than pools treated only by chlorination (21 to 87  $\mu$ g/L).

In a laboratory scale study, Hansen et al. (2016) investigated the effect of ozone treatment on the 1093 formation of a range of DBPs (trichloro-, bromodichloro-, dibromochloro- and tribromo-methane, 1094 DCAN, BCAN, DBAN, TCAN, 1,1,1-TCP, 1,1-DCP and TCNM) in tap water, swimming pool water and 1095 1096 swimming pool water where BFA was added. Initial ozone dose was found to react directly with the added BFA pollutants, reducing their reactivity with chlorine and hence a lower THM formation was 1097 observed. However, upon subsequent ozone treatments, an increase in THMs was observed, which the 1098 authors explained by the increased half-life of ozone (as no functional groups remained for reaction), in 1099 which ozone decomposed to radicals which reacted with organic precursors and made them more 1100 susceptible to reaction with chlorine. Other DBPs, DCAN, 1,1,1-TCP, TCNM, were also found to 1101 increase with subsequent treatments (Hansen et al., 2016). This study suggested that, although ozone 1102 treatment has the potential to reduce DBPs in swimming pools, it must be carefully employed, as DBP 1103 formation can also be enhanced under periods of low precursor input (e.g. overnight). 1104

The use of an ozone-bromine treatment, the formation of HOBr by oxidation of bromide by ozone, for pools has been suggested by Hoffmann et al. (2015), who successfully applied this treatment method to a hydrotherapy pool for three years, in which microbiological parameters were found to meet guideline values. In waters rich in bromide, ozone has the potential to form bromate, but bromate formation was controlled by pH in the pool (Hoffmann, 2015). Although this study demonstrated the potential use of an ozone-bromine treatment in pools, DBP formation was not closely examined and future work should assess the impact of ozone-bromine treatment on the formation of DBPs, particularly Br-DBPs.

Cheema et al. (2017) investigated the effect of a combined treatment method of UV followed by 1112 ozonation and chlorination on a range of DBPs (trichloro-, bromodichloro- and dibromochloro-methane, 1113 DCAN, BCAN 1,1-DCP, 1,1,1-TCP and TCNM) by exposing real swimming pool waters to one-off and 1114 repeated treatments. With the exception of TCNM, all DBPs were found in lower concentrations after an 1115 initial treatment than in the pre-treated water. Although an increase in TCNM was observed upon the 1116 initial combined treatment, an overall decrease was observed after subsequent repeated treatments 1117 (Cheema et al., 2017). As swimming pools are continually treated, this study demonstrated that a 1118 combined UV, ozonation and chlorination treatment method may help reduce DBPs in swimming pool 1119

waters, however further studies should assess the impact of continual precursor input on this combinedtreatment method, which would be more reflective of real swimming pools.

In addition, pools where UV treatment was combined with chlorination are reported to be less toxic, with up to 3x less cytotoxicity observed (Liviac et al., 2010b; Plewa et al., 2011). Whilst secondary treatments have been shown to increase the overall quality of swimming pool water, further studies are required to fully understand the chemistry underpinning secondary treatment methods under conditions more reflective of swimming pools, e.g. continual chlorine residual and continual precursor input. Further studies should investigate a wider range of DBPs under these conditions, in both laboratory and swimming pool studies.

## 1129 5.2. Halide Anions: Bromide and Chloride

One major impact of the disinfectant is the introduction of halide ions, which in turn can affect the formation of DBPs. As previously discussed in **Sections 2.1** and **4.2**, after oxidation reactions in the pool, chlorine based disinfectants introduce chloride (Cl<sup>-</sup>), whilst bromine based disinfectants introduce bromide (Br<sup>-</sup>), and these ions can often accumulate due to the continual recirculation in pools. Highlighting the impact of the disinfectant on the ionic composition of pool waters, chloride has been reported at concentrations up to 3233 mg/L for freshwater chlorinated swimming pools (E et al., 2016).

E et al. (2016) presented a linear correlation of the concentrations of three volatile DBPs, trichloramine, trichloromethane and DCAN, with chloride concentrations, in both bench scale experiments and real swimming pool waters. The authors attributed this relationship to chloride promoting speciation shifts of free chlorine from HOCl to the more reactive  $Cl_2$  (Voudrias and Reinhard, 1988), hence a higher formation of these chlorinated DBPs (E et al., 2016). Additionally, oxidant consumption was shown to increase with increasing chloride levels (E et al., 2016).

## 1142 **5.3. Swimming Pool Location**

The location of a swimming pool, whether indoor or outdoor, may also affect the formation and 1143 occurrence of DBPs. Although bound by similar constraints, the contaminants found in indoor swimming 1144 pools can differ greatly to those found in pools located outdoors. Intuitively, the occurrence of sunscreens 1145 and their components is likely to be greater in outdoor swimming pools compared to those located 1146 indoors. Similarly, contaminants, such as plant material, insects, pesticides, fertilizers, bird droppings and 1147 possibly even animals, are more likely to be found in outdoor swimming pools (Simard et al., 2013). This 1148 difference in contaminants and their subsequent reactions will result in the occurrence of different DBPs 1149 in outdoor pools compared to indoor pools. 1150

1151 One distinct difference between pools located indoors and outdoors is that outdoor pools are 1152 subject to natural UV irradiation and, although this is a less energetic radiation source than that typically

used as secondary treatment, DBPs have been shown to decrease in sunlight exposure (Chen et al., 2010). 1153 DBP formation from sunscreen agents has been demonstrated (in laboratory based studies) to occur upon 1154 exposure to irradiation similar to that of sunlight (Sakkas et al., 2003), which is discussed in Section 1155 **4.3.2**. Disinfectant residual is also known to degrade by solar photolysis, which may affect the formation 1156 of DBPs where more disinfectant is added to maintain the desired oxidant residual. Solar irradiation is 1157 likely to have a lesser impact on DBP occurrence and formation in swimming pools compared to UV 1158 based secondary treatments (Section 5.1) due to the less energetic nature of the irradiation. Additional 1159 work is required to assess the impact of solar irradiation on DBPs in the swimming pool environment. 1160

Indoor swimming pools are often operated at higher temperatures than those located outdoors and, as discussed in **Section5.5**, the increased temperature can have several effects on DBP formation. Factors such as higher reaction rates and increased volatilisation of some DBPs will impact their occurrence in indoor swimming pools. On the one hand, higher volatilisation would lead to lower concentrations of DBPs in the water but would increase their concentration in the ambient air, but on the other hand, DBPs in the ambient air of indoor pools may become trapped and hence be observed at higher concentrations, compared to outdoor pools where volatile DBPs can easily disperse.

As suggested above, the volatile THMs and chloramines were detected at lower concentrations in 1168 indoor pools compared to those located outdoors in a study by Zwiener et al. (2006). However, other 1169 studies have reported the opposite, such as the study by Simard et al. (2013) where higher THM 1170 concentrations were observed in outdoor swimming pools compared to those indoor. Higher total 1171 inorganic chloramine concentrations (up to 1723 µg/L) were reported for the indoor swimming pools, 1172 with lower concentrations (up to 845 µg/L) reported in the outdoor pools (Simard et al., 2013). In 1173 contrast, Li and Blatchley (2007) found maximum trichloramine concentrations were higher in an outdoor 1174 swimming pool (up to 160 µg/L) compared to an indoor swimming pool (100 µg/L). Natural UV 1175 treatment may help to explain the lower concentrations of N-nitrosamines detected in outdoor pools 1176 compared to indoor pools (Walse and Mitch, 2008). 1177

1178 Although swimming pool location cannot be directly correlated to DBP formation, for the reasons 1179 stated above, pool location may assist in the explanation of differences in DBP occurrence, where other 1180 parameters are comparable.

# 1181 5.4. Swimmers: Activity and Usage

1182 The water quality, and hence DBP formation, of swimming pools is dependent on both the 1183 number of swimmers and type of activity undertaken. Based on studies by Keuten et al. (2012), athletic 1184 swimmers (those who swim for exercise) are more likely to introduce more DBP precursors from sweat, 1185 whilst recreational swimmers (those who swim for leisure) are more likely to introduce more DBP 1186 precursors via urine. Hence, in terms of DBPs and water quality, swimming pools used mainly by athletic swimmers, such as lap pools, competition pools and pools designated for exercise (e.g. water aerobics/aquafitness), would differ from those used mainly by recreational swimmers, e.g. leisure pools, paddling pools. Additionally, although more reflective of bather load input (**Section 4.3**), pools used by specific people (e.g. babies, toddlers or children) may have different water chemistry and hence DBP formation.

In a very early study, Goshorn (1922) used the concentrations of nitrites, nitrates, urea and free 1192 ammonia as a measure of contamination in five swimming pools located in Philadelphia, USA, in order to 1193 investigate anthropogenic input based on gender. Swimming pools used exclusively by women were 1194 found to have the highest contamination, with pools used exclusively by men exhibiting the lowest 1195 (Goshorn, 1922). Similarly, Yeh et al. (2014) reported higher chlorinated HAA concentrations in a 1196 1197 swimming pool used mainly by babies and mothers compared to concentrations found in other investigated pools, and, although only indicative, proposed that baby swimming pools contain higher 1198 concentrations of other DBPs due to the likely higher anthropogenic input. 1199

The effect of heavy use was investigated by Weng and Blatchley (2011), who studied an indoor 1200 chlorinated swimming pool during a swimming competition. Trichloramine was found to double in 1201 concentration over the first day and increase over the time of the competition. Similarly, DCAN and 1202 dichloromethylamine were both found to increase over the time of the swim competition. Urea 1203 concentrations significantly increased during the day, however concentrations decreased overnight. Weng 1204 and Blatchley (2011) suggested that the observed urea decrease overnight is likely a result of surface 1205 water mixing with deeper parts of the swimming pool (resulting in a lower urea concentration at the 1206 1207 surface where samples were collected), rather than reactions with chlorine, as the urea-chlorine reactions have shown to be quite slow (De Laat et al., 2011). 1208

Swimmers and water activity can have a twofold effect on DBPs in the swimming pool 1209 environment. Whilst bather load increases the DBP precursors in swimming pool waters, swimming 1210 activity is known to increase volatilisation of some volatile DBPs, mainly THMs and chloramines, and 1211 1212 hence decrease their concentrations in the swimming pool water and increase their concentrations in the ambient air. Although no correlation was observed for other DBPs (HAAs, HANs, HKs or TCNM), this 1213 may explain why THMs showed no correlation with the number of swimmers in a study by Hang et al. 1214 (2016). Supportive results were reported by Aggazzotti et al. (1995), where an increase in 1215 1216 trichloromethane concentrations in the ambient air of a swimming pool was linked to the number of swimmers at the time of sampling, with similar results reported by Chen et al. (2016). Daiber et al. (2016) 1217 also reported an increase of non-volatile DBPs (HAA9) and decrease of volatile DBPs (TTHMs) with an 1218 increasing number of swimmers and water activity. In addition, Aggazzotti et al. (1998) reported an 1219 increase in THM concentrations in swimming pool air during water activity, when compared to those 1220 measured in the air above still waters. Similarly, a strong correlation between water jets, swimmer 1221

1222 activity and THM removal from water has been found (Kristensen et al., 2010; Marco et al., 2015). The trichloramine concentrations in the ambient air was found to increase  $(0.11 \text{ to } 0.36 \text{ mg/m}^3)$  when school 1223 children entered a pool compared to when no swimmers were present, which was suggested to be a result 1224 of the increased mass transfer coefficient due to increased water agitation (Zwiener and Schmalz, 2015). 1225 An earlier study showed increase in mass transfer coefficients of trichloramine by swimming activity, 1226  $(1.8 \times 10^{-3} \text{ to } 7 \times 10^{-3} \text{ g/(h m^2)})$ , and by splashing or water jets (up to  $12.6 \times 10^{-3} \text{ g/(h m^2)})$  (Schmalz et al., 1227 2011a). This trend is likely to extend to other volatile DBP classes, with agitation leading to decreased 1228 concentrations in swimming pool waters, and increased concentrations in swimming pool air. This 1229 transfer of volatile DBPs to the gas phase is of high importance due to the inhalation uptake mechanism 1230 and further studies are required to fully understand the water-to-air relationship in terms of volatile DBPs 1231 and water activity. 1232

Keuten et al. (2012) investigated the anthropogenic chemical release from a 60 second shower by 1233 following three parameters: TOC, TN and intracellular adenosine triphosphate, where an average release 1234 of 211, 46 and 1.6 mg per person was found for the three parameters, respectively. These studies show 1235 that a pre-swim shower will help to minimise the anthropogenic input from bathers into pool waters. 1236 Although showering before swimming is mandatory in some countries, studies have shown that many 1237 swimmers are still unaware of the impact their swimming habits can have. Surveys of swimmers in 1238 countries where pre-swim showering is encouraged found as much as 50% of swimmers were unware of 1239 the correct reasoning behind pre-swim showering (Pasquarella et al., 2013, 2014). Whilst most swimmers 1240 (50.5%) gave the correct reasoning, "to wash oneself", many (44.3%) believed pre-swim showers are 1241 encouraged to "get you used to the temperature of the water", with a few (5.2%) indicating both reasons 1242 (Pasquarella et al., 2013, 2014). A key study highlighting the importance of swimmer education is that 1243 by Galle et al. (2016), who conducted a self-administering survey of 184 adults and 184 children in 1244 regards to five unhealthy behaviours common to swimming pools: (i) lack of pre-bathing shower, (ii) lack 1245 of pre-bathing footbath, (iii) no use of proper footwear, (iv) no use of proper swimming cap and (v) 1246 consumption of food in swimming pool environment. Although approximately 83% of children and 80% 1247 of adults stated they were aware of the rules, only 2% of people could correctly identify why the rules 1248 were in place. Additionally, results suggest that there is no correlation between viewing regulations and 1249 adopting the healthy behaviour, although an adoption of healthy behaviour (or decrease in unhealthy 1250 behaviour) was observed to increase with awareness and education level (Gallè et al., 2016). These 1251 studies show that more attention to swimmer education is required in order to decrease swimmer input to 1252 pools, which would minimise DBP formation and generally increase the quality of the swimming pool 1253 environment. 1254

## 1255 5.5. Temperature and pH

As mentioned in throughout this review, swimming pool water temperature has been shown to affect (i) the release of human derived input, (ii) volatilisation rates of volatile DBPs and (iii) reaction rates of DBP formation, all of which are interrelated. In addition, pools operated at elevated temperatures are required to maintain a higher disinfectant residual, which may also affect the formation of DBPs.

Heated waters were shown to promote the release of bather load derived DBP precursors, 1260 particularly those that contain nitrogen, as perspiration rate increased with increasing water temperature 1261 (Keuten et al., 2014). The increased concentrations of DBP precursors, combined with the higher 1262 disinfectant residual required in waters at elevated temperatures, likely result in an increase in DBP 1263 formation in heated swimming pools and spas. In a study of two outdoor swimming pools, Simard et al. 1264 (2013) reported higher concentrations of THMs and HAAs in the heated swimming pool. Formation of 1265 1266 HAAs were shown to significantly increase with temperature in a laboratory scale study by Kanan (2010) where DBP formation in waters at 26 °C and 40°C was compared. The same study also reported that 1267 HNM formation in waters at 40°C was twice as high as in waters at 26°C (Kanan, 2010). NDMA 1268 concentrations were reported to be up to 10 times higher in heated spas compared to swimming pools at 1269 lower temperatures (Walse and Mitch, 2008). 1270

Many studies have investigated the effect of pH on DBP formation in drinking waters, however 1271 few studies have investigated its effect in the swimming pool environment. The effect of pH (6 - 8) on 1272 the formation of THMs, HAAs, HANs and trichloramine was investigated by Hansen et al. (2012a) via a 1273 series of experiments involving chlorination of BFA at different pH values. Although no significant 1274 change in HAA concentrations was observed at any pH within the range investigated, THM 1275 concentrations were found to increase with increasing pH, whilst concentrations of HANs were found to 1276 decrease. In particular, one order of magnitude difference was observed in trichloramine concentrations at 1277 pH 6 compared to 7.5, with higher concentrations being evident at the lower pH values, confirming 1278 results previously reported by Schmalz et al. (2011a). A second laboratory study by Hansen et al. (2013a) 1279 reported a negligible genotoxicity effect at pH values between 6.8 and 7.5, however a significant increase 1280 in genotoxicity was observed below pH 6. Trichloromethane concentrations were observed to increase 1281 when the pH was above 7.2, similarly HANs increased at pH values below 6, and for these reasons, 1282 Hansen et al (2013a) suggest swimming pools operate at a pH range of 7 to 7.2 in order to minimise DBP 1283 formation. Swimming pool filter particles collected from a hot tub filter bed in Denmark were 1284 investigated by Hansen et al. (2012b), where chlorination of these filter particles under swimming pool 1285 conditions (pH 6 to 8, 25°C and in the presence of constant free chlorine residual) produced similar trends 1286 to the previous studies where chlorination of BFA was performed (Hansen et al., 2012a, 2013a), i.e. the 1287 THMs increased, whilst HANs decreased, with increasing pH. However, where no change in HAA 1288 concentration was observed in the previous studies of BFA, in this study of swimming pool filter 1289 particles, concentrations of HAAs were found to increase with increasing pH (Hansen et al., 2012b). Both 1290

1291 genotoxicity and cytotoxicity were also found to increase significantly with decreasing pH, which was 1292 reported to be likely due to the increased formation of HANs

Although knowledge has been gained from these studies, the difference in laboratory to real pool studies highlights the need for further investigation at both the laboratory scale and real pool scale. Future laboratory studies should encompass a wider range of DBPs and be conducted at conditions more suited to swimming pool waters. Additionally, the impact of temperature should be assessed for all DBP classes, in both laboratory and full scale studies, to provide a better understanding of the role of temperature on (i) reaction and formation rates of DBPs and (ii) the partitioning of DBPs from water to the air phase.

# 1299 6. Disinfection By-Products: The Health Impacts

Swimming pool waters have shown increased genomic DNA damage effects on Chinese hamster 1300 ovary cells compared to the corresponding filling water (Liviac et al., 2010b), an increase which is likely 1301 due to more than one mutagen (Honer et al., 1980). Swimming pools treated exclusively with chlorine 1302 were found to be more toxic than those treated in combination with ozone (Fernandez-Luna et al., 2009) 1303 or UV (Liviac et al., 2010b; Plewa et al., 2011), which was attributed to the lower DBP formation when 1304 these secondary treatments were employed, compared to that when chlorination was used alone. Reported 1305 cases of contact dermatitis were much higher in swimming pools where chlorine gas was employed as the 1306 disinfectant compared to those that employed TCICA, BCDMH, calcium hypochlorite or sodium 1307 hypochlorite, which was proposed to be due to the more aggressive environment produced by (i) an 1308 increased demand (and use) of gaseous disinfectant due to the higher ability of chlorine gas to oxidise 1309 organic nitrogen, and (ii) the reduction in pH when gaseous chlorine is employed (Pardo et al., 2007). 1310 Treatment type was investigated for perceived health effects (eye or skin irritation, respiratory problems 1311 or skin dryness) in a self-reported survey of 1001 users across twenty indoor pools (Fernandez-Luna et 1312 al., 2015). Pools treated by chlorine based disinfectants had the highest reports of health problems, with 1313 slightly lower reports for pools treated by bromine based disinfectants. Pools where secondary treatment, 1314 ozone or UV, was employed in addition to chlorine or bromine generally had lower reported health 1315 problems than pools treated by the corresponding disinfectant alone. EGMO treated pools had the lowest 1316 reported health problems of all pools investigated (Fernandez-Luna et al., 2015). The authors proposed 1317 that the higher perceived health problems in chlorinated pools can be explained by higher DBP formation 1318 (particularly chloramines and THMs) in these pools compared to pools employing additional secondary 1319 treatment or EGMO, although did not provide evidence to support this claim. The authors also 1320 acknowledged that factors other than DBPs, particularly the number of swimmers and the oxidising 1321 power of the different disinfectants and hence their ability to destroy DBPs, may also be involved 1322 (Fernandez-Luna et al., 2015). 1323

1324 A study from 'source to pool' by Daiber et al., (2016) showed swimming pools disinfected by bromine based disinfectants were 1.8x more mutagenic than comparable pools treated by chlorine. In 1325 comparison to their respective filling waters, pools were found to be 2.4x more mutagenic, whilst spas 1326 were found to be 4.1x more mutagenic, with spas being 1.7x more mutagenic than pools. Mutagenicity 1327 was correlated to Br-HAAs ( $r^2=0.98$ ) and N-DBPs ( $r^2=0.97$ ) for the chlorine treated waters, with an 1328 increase in correlation with Br-DBPs (r<sup>2</sup>=0.82) observed in bromine treated waters. Bromine 1329 incorporation into DBPs was proposed to increase mutagenicity, although the DBP class must also be 1330 considered (Daiber et al., 2016). 1331

A recent study by Li et al. (2015a) investigated the behaviour and appearance of rats over a 12 1332 week swimming program, where participants were exposed to waters with similar conditions to real 1333 swimming pools (free chlorine: 1.4 to 1.6 mg/L, pH 6.5 to 7.0 and water temperature 25 to 30°C) once a 1334 day for five days, with two days rest, for a total of 12 weeks. Some disease symptoms were induced: 1335 bloody eyes, bloody noses, loss of hair; decreased training effects (rats in chlorinated water reached 1336 exhaustion significantly faster than the control group), and deterioration of key organs (liver and lungs); 1337 all of which were proposed to be likely due to the chlorinated DBPs, trichloromethane (0.7 µg/L) and 1338 trichloramine (1.1 mg/L), also measured in the study. The intensity and frequency of training, as well as 1339 water choking, may be the primary cause of the lung damage observed in the rats (Li et al., 2015a). 1340

Rosenman et al. (2015) found a positive correlation with swimming pool attendance and several 1341 health issues, particularly asthma. Similarly, Fitch et al. (2008) reported that exposure to chlorinated 1342 pools may irritate the airways, with extended exposure likely to increase the risk of developing asthma. 1343 Several studies have suggested asthma is likely due to chlorinated volatile DBPs such as chloramines 1344 (Bernard et al., 2006; Ferrari et al., 2011; Jacobs et al., 2007; Kaydos-Daniels et al., 2008; Rosenman et 1345 al., 2015; Uyan et al., 2009), with one study reporting a direct link between trichloramine in the air of 1346 indoor swimming pool complexes and asthma in young children (Bernard et al., 2006) and another 1347 laboratory based study reporting a causal effect of trichloramine on lung cells (Schmalz et al., 2011a). A 1348 swimming pool located indoors at a hotel in the USA was found to induce negative health effects on 1349 hundreds of occupants, the most severe case resulting in the hospitalisation of a child, which was likely 1350 due to exposure to toxic levels of chloramines in the air of the swimming pool complex (CDC, 2007). 1351 Competitive and regular swimmers have been reported to have higher cases of asthma and other 1352 respiratory issues than any other type of professional sports person (Nemery et al., 2002). Considering 1353 showering, bathing, water ingestion and swimming, Font-Ribera et al. (2010a) estimated the daily THM 1354 uptake, based on THM blood levels and using published uptake algorithm factors, for children, and 1355 estimated that children who swam in indoor pools treated with chlorine or bromine would have up to four 1356 times higher THM uptake than those who did not swim in pools, with swimming pools estimated to be 1357 the main pathway of THM exposure. This is likely due to the inhalation of THMs during swimming, as 1358

the breathing zone for swimmers is the water-air interface, where high concentrations of volatilisedTHMs have been reported (Catto et al., 2012a).

Higher respiratory problems were reported in those who attended swimming pools compared to 1361 the general population (Jacobs et al., 2007), with asthma found to be higher in swimmers compared to 1362 those who did not swim (Ferrari et al., 2011). Similar results were reported by Kaydos-Daniels et al. 1363 (2008), where, in a survey of 32 swimmers, the most reported illnesses were found to be cough (84%), 1364 eye irritation (78%) and rash (34%). A survey of lifeguards who regularly work at indoor swimming 1365 pools found 55% suffered from respiratory and other health issues (Boskabady et al., 2014). THM 1366 concentrations in alveolar air were greatest in those who worked poolside compared to those who worked 1367 in reception or café areas of an indoor swimming pool complex (Fantuzzi et al., 2010). Uyan et al. (2009) 1368 suggested that lifeguards are at risk of developing eye, nose and throat issues, where the risk increases 1369 upon longer term exposure. Although in agreement that asthma is more commonly found in those who 1370 swim regularly, Goodman and Hays (2008) suggested that "it is premature to draw conclusions about the 1371 causal link between swimming and asthma". 1372

No significant change in lung function was observed in a study by Font-Ribera et al. (2010b), who 1373 investigated the effect of swimming at an indoor swimming pool complex on respiratory health. Lung 1374 damage, as measured by changes in serum surfactant-associated protein A, was found to be negligible in a 1375 study of twenty swimmers who completed a single 40 minute session of aerobic swimming at indoor 1376 swimming pools, two treated by chlorination and one treated by chlorination in combination with UV 1377 (Llana-Belloch et al., 2016). Despite the increase of total chloramines in the air with swimmers activity 1378 (hence exposure via inhalation), no lung epithelial damage or oxidative stress was observed. Although the 1379 authors acknowledge the limitations of the study (a single swim session and relatively low free chlorine in 1380 some pools (below detection to 0.3 mg/L f1.3 mg/L for chlorine/UV pools)), they concluded that short 1381 term exercise in a pool was not correlated to lung damage (Llana-Belloch et al., 2016). 1382

Agopain et al. (2013) reportedly showed no link exists between attendance at indoor chlorinated 1383 swimming pools and birth defects, in their study of maternal swimming pool use during early pregnancy. 1384 Similarly, no adverse health effects were observed in a study investigating swimming pool attendance and 1385 asthma (Fitch et al., 1976). Font-Ribera et al. (2009) reported lower health issues (asthma, current rhinitis 1386 and allergic rhinitis symptoms) in children who attended swimming pool complexes before the age of 2, 1387 compared to those who attended after the age of 4; however, an increase in eczema was found in children 1388 of all ages (Font-Ribera et al., 2009). Respiratory issues (lower respiratory tract infections, wheeze and 1389 otitis) were found to be higher in children who attended baby swim classes in their first 6 months and 1390 may be related to later respiratory issues up to 18 months of age (Nystad et al., 2008). Inflammation of 1391 the airways and immunoglobulin E (IgE) sensitization to house dust mites were also found to be higher in 1392

children who attended swimming pool complexes at an early age (Voisin et al., 2014). Additionally,children who did not swim until a later age had lower cases of ear infections (Schoefer et al., 2008).

Villanueva et al. (2007) investigated the bladder cancer risk associated with exposure to THMs, 1395 by examining several exposure routes: ingesting of chlorinated drinking water, as well as inhalation and 1396 dermal absorption during bathing, showering and swimming in chlorinated pools. Several factors (e.g. 1397 age, type of activity, frequency and duration of swim) were evaluated for swimmers and odds ratios were 1398 determined. The study reported that exposure to THMs via swimming may be associated with the 1399 formation of bladder cancer and was the first study to demonstrate that inhalation and dermal absorption 1400 are additional exposure routes to THMs, where previous reports considered only ingestion (Villanueva et 1401 al., 2007). A later study by Lee et al. (2009) used their measured THM concentrations in 183 indoor 1402 1403 swimming pools (treated by either chlorine, chlorine in combination with ozone or EGMO) to estimate the associated lifetime cancer risk posed to swimmers. Results showed that the cancer risk via inhalation 1404 was up to three times higher than the negligible risk factor (defined by the US EPA), whilst the risk factor 1405 from ingestion or dermal absorption was negligible in almost all cases. Dermal absorption was associated 1406 with an increased risk factor in pools treated with EGMO, which was suggested to be due to the higher 1407 concentrations of brominated THMs (bromodichloro- and dibromochloro-methane) measured in these 1408 pools compared to those treated by chlorine or chlorine in combination with ozone (Lee et al., 2009). 1409 1410 Additionally, brominated THMs have been shown to increase the genotoxicity effect (Kogevinas et al., 2010), demonstrating the high importance of minimisation of the formation of brominated THMs. 1411

Similarly, brominated HAAs have been shown to be more toxic than their chlorinated counterparts (Liviac et al., 2010a; Plewa et al., 2008). DeAngelo and McMillan (1990) found both DCAA and TCAA produced liver cancer in mice, with DCAA more potent than TCAA. Yeh et al. (2014) suggests that HAAs may be the decomposition products of other compounds, but has shown that HAAs degrade to the equally toxic THMs. Despite HAAs having low skin permeability (Xu et al., 2002), they are still of high importance due to the transformations suggested by Yeh et al. (2014) giving rise to a wider variety of uptake mechanisms and therefore a wider range of health issues.

CH is a genotoxic and carcinogenic DBP that can be formed from a wide range of precursors 1419 evident in swimming pool waters, and has been found to decompose to chloroform and TCAA, two other 1420 potentially toxic DBPs (Barrott, 2004). HANs are another genotoxic and cytotoxic class of DBP (Plewa 1421 1422 et al., 2008) and are often reported to be responsible for the majority of the cytotoxicity in swimming pool waters (Hansen et al., 2012a; Pu et al., 2013). Limited data exists on the health effects of HKs, however 1423 their skin permeability has been found to triple with increasing temperature (Xu et al., 2002), therefore 1424 HKs should be of high importance in the absorption uptake mechanism, particularly in heated swimming 1425 pools and spas. Chronic cytotoxicity and genomic DNA damage have been shown in hamsters that were 1426 exposed to HNMs, with brominated NMs showing higher toxicity than their chlorinated analogues (Plewa 1427

et al., 2004). Even at low concentrations, HAAms are of high importance as they have reportedly shownmuch higher toxicity than many other classes of DBPs (Plewa et al., 2007).

1430 Nitrosamines, particularly NDMA, have been found to have several negative health effects, as 1431 summarised by the California Department of Public Health (2007). Not only are nitrosamines 1432 carcinogenic in animals, they are probable carcinogens in humans, rendering them important in the 1433 swimming pool environment, even at the nanogram per litre level.

Despite the many studies of the health impacts of swimming pools, as summarised by Lubick (2007) and Richardson et al. (2010), no definitive answers can yet be drawn in regards to the potential health effects. Many studies are only suggestive, reporting health issues that may be correlated with attending swimming pools, particularly those that are indoors and disinfected with chlorine. The lack of certainty and conflicting reports suggest that further investigation into the health impacts of swimming pools is warranted.

## 1440 **7.** <u>Conclusions</u>

Disinfection is required to minimise the significant microbial disease risk in pools, however, leads 1441 to the unwanted formation of DBPs. Studies of DBPs in swimming pool waters have increased in recent 1442 years, focusing not only on the well documented THM and HAA DBP classes, but preliminary studies 1443 have expanded to other DBP classes, such as N-nitrosamines, HANs, HKs, haloacetaldehydes, 1444 halonitromethanes and haloacetamides. HAAs are generally more prevalent than THMs in swimming 1445 pool waters, which is likely due to the volatile nature of THMs, decreasing their concentration in 1446 1447 swimming pool water but increasing their concentration in swimming pool air, as well as their rates of formation. THMs, along with other volatile DBPs, such as chloramines, are suggested to be responsible 1448 for many of the respiratory health issues potentially associated with indoor swimming pools. Other 1449 volatile or semi-volatile DBPs, such as cyanogen halides, may also have a negative impact on respiratory 1450 health, however further investigation is required to fully understand their effects. 1451

Various factors affect DBP formation in pools, including the filling water, type of disinfectant and 1452 treatment method, numbers of swimmers and particularly input from swimmers (bather load). High use 1453 has been correlated with increasing concentrations of some DBPs, such as THMs, and TOC and 1454 mutagenicity. Volatilisation of THMs increases during swimmer activity, resulting in an initial decrease 1455 in THM concentration in the pool, with increasing concentrations observed during periods of low use 1456 (swimming pool closed). Similar effects are seen in waters with elevated temperatures, such as heated 1457 spas. These types of pools are still of high importance due to the dominant inhalation uptake mechanism 1458 demonstrated in the swimming pool environment. 1459

Limited knowledge exists on the transformation of PPCPs in the swimming pool environment. Due to the high occurrence of nitrogen containing components, PPCPs likely result in the formation of N-DBPs, which may be more detrimental to human health than those that are entirely carbonaceous. Further studies on N-DBPs are required to fully understand their formation in the swimming pool environment. Cyanogen chloride and cyanogen bromide should be of high interest, since not only are they highly toxic DBPs, they are also intermediate products in a series of DBP formation reactions. Further knowledge of the role of these cyanogen halides may help in understanding the chemistry of swimming pool waters.

Initial studies show the presence of bromide is correlated with an increase in brominated DBPs, which are more detrimental to human health than the chlorinated analogues. Further studies are required to fully understand the role of bromide in the swimming pool environment, particularly in seawater filled swimming pools and those that use bromine based disinfectants, where bromide/bromine concentrations are higher.

Whilst swimming pools have been correlated to respiratory health effects, such as asthma, the 1472 health effects of many DBPs at the concentrations reported in swimming pool waters and under 1473 swimming pool exposure conditions are yet to be defined. Apart from Germany and Denmark, no known 1474 1475 swimming pool specific guidelines exist for DBPs worldwide. While of the same order of magnitude as their drinking water THM guideline value (10 µg/L) (TrinkwV, 2001), the German (German Institute for 1476 Standardization, 2012) and Danish (Lovtidende, 2012) swimming pool guideline values for THMs are 1477 approximately five times lower than that recommended by the World Health Organisation for THMs in 1478 drinking waters (WHO, 2011), demonstrating the need for swimming pool specific guidelines. Further 1479 investigation into DBPs and anthropogenic chemicals within the swimming pool environment should aim 1480 to support development of swimming pool specific guidelines in the future. 1481

#### 1482 8. <u>Acknowledgements</u>

1483 R. Carter would like to acknowledge Curtin University for an Australian Postgraduate Award, and
1484 Water Research Australia and ChemCentre (Western Australia) for a PhD Top Up Scholarship.

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**Table 1**: Recommended minimum free chlorine equivalent concentrations (mg/L) and pH values for

swimming pools and spas by selected organisations.

Disinfectant	pH Range	Swimming Unstabilised	g Pools Stabilised*	Spas	Reference
Chlorine Bromine	7.2-7.8	1 2	2	3 6	(NHMRC, 2008)
Chlorine	6.5-7.6	0.3-0.6	0.3-0.6	0.7-1	(German Institute for Standardization, 2012)
Chlorine	7.2-7.4	0.5-1	2.5-5	-	(PWTAG, 2003)
Chlorine Bromine	7.2-7.8	1 3	2	3 4	(CDC, 2016)
Chlorine Bromine	7.2-7.8	0.5-1.2 4-6	0.5-1.2	2-3 4-6	(WHO, 2006)

\*Stabilised refers to the use of cyanuric acid. Stabilisation not possible with bromine based disinfectants.

Table 2: Summary of the occurrence of disinfection by-products in swimming pool and spa waters. Unless otherwise stated, concentrations are presented in  $\mu$ g/L and represent a range of the average concentrations reported. Where only one value is present, either only one known report exists or, of the existing reports, only one presented data regarding average concentrations. Where no data is included, either the concentration(s) were below the limit of detection or there is no known report of the given disinfection by-product(s). More complete summaries can be found in **Tables S1** to **S12**.

		S	wimming Pe	ools		S	pas	
Disinfection By-Product	Chlorine Based	Bromine Based	EGMO	Chlorine & Ozone	Seawater Filled	Chlorine Based	Bromine Based	Reference(s)
Trihalomethanes (THMs)								
Bromodichloromethane	0.13-167	0.5-0.7	9.8-10	1.1-106	0.29-5	0.1	2.9	(Aprea et al., 2010; Beech et al., 1980; Benoit and Jackson, 1987; Carter et al., 2015; Chowdhury et al., 2016; Daiber et al., 2016; Font-Ribera et al.,
Dibromochloromethane	0.49-120	2.4-2.5	8.9-9.1	0.2-2	3.57-27	0.14	4.67	2010a; Glauner et al., 2005; Golfinopoulos, 2000; Hang et al., 2016; Kelsall and Sim, 2001; Lee et al.,
Tribromomethane	0.04-44	57-152	4.1-19	47	50-651	0.11	182-1253	2009; Lee et al., 2010; Lourencetti et al., 2012; Manasfi et al., 2016; Parinet et al., 2012;
Trichloromethane	8.65-243	0.2-0.21	14-27	7.4-141	0.1-6	19-264 <sup>b</sup>	1.6	Richardson et al., 2010; Weaver et al., 2009; Zhang et al., 2015)
Haloacetic Acids (HAAs)								
Bromoacetic Acid	2-12	4.7		16	3.75-55		46-62	
Bromochloroacetic Acid	1.8-510	2.2		425	4.27-65	<b>2</b> .6 <sup>b</sup>	13-294	(Catte et al. 2012h; Chandhum et al. 2016; Deihan
Bromodichloroacetic Acid	2.71-61	8.9			2.03-12	12 <sup>b</sup>	10-117	(Catto et al., 2012b; Chowdhury et al., 2016; Daiber et al., 2016; Font-Ribera et al., 2016; Hang et al.,
Chloroacetic Acid	4.22-109			41	1.25-96	31 <sup>b</sup>	-3.9	2016; Kanan, 2010; Lee et al., 2010; Manasfi et al.,
Dibromoacetic Acid	1-28	123			16-307		337-1795	2016; Parinet et al., 2012; Sarrion et al., 2000; Tang
Dibromochloroacetic Acid	2.7-33	4.05		1.2	3.1-103		4.4-14	and Xie, 2016; Wang, 2011; Yeh et al., 2014;
Dichloroacetic Acid	23-982	2.2	34	12-200	1.67-4.79	343 <sup>b</sup>	27-89	Zhang et al., 2015)
Tribromoacetic Acid	5.6-19	72		8.1	43-186		73-97	
Trichloroacetic Acid	19-978	64	97	17-20	2.56-27	1865 <sup>b</sup>	13-37	
Halamines and Cyanogen Hal	ides							
Dichloramine	11-430	51			220		40-142	(Afifi and Blatchley, 2016; Catto et al., 2012b;
Monochloramine	10-323	67-270			220		48-205	Chowdhury et al., 2016; Daiber et al., 2016; Font-
Trichloramine	7-1500	12			70		91-183	Ribera et al., 2010b; Font-Ribera et al., 2016; Lian
Cyanogen Chloride	4.4-24	3.7					3.2	et al., 2014; Richardson et al., 2010; Simard et al.,
Cyanogen Bromide	3.3-25	19-52					4.9-125	2013; Weaver et al., 2009)
Haloacetonitriles (HANs)	1							
Bromoacetonitrile	1							(Carter et al., 2015; Daiber et al., 2016; Hang et al.,

Bromochloroacetonitrile	0.63-9.2	1.8	3.5	0.4	0.93		1.8-5.6	2016; Kanan, 2010; Lee et al., 2010; Li and
Chloroacetonitrile	1.14-2.4							Blatchley, 2007; Manasfi et al., 2016; Tardif et al.,
Dibromoacetonitrile	0.2-5.8	37	2.6	0.4	19		80-219	2016; Yeh et al., 2014; Zhang et al., 2015)
Dichloroacetonitrile	0.1-75		3.8	1.3-5.3	8.99	14 <sup>b</sup>		
Trichloroacetonitrile	0.03-1.2							
N-Nitrosamines								
N-Nitrosodiethylamine	1.2-35 <sup>d</sup>							
N-Nitrosodimethylamine	5.3-52					5.5-313		
N-Nitrosodi-n-butylamine	15-141							(Carter et al., 2015; Jurado-Sánchez et al., 2010;
N-Nitrosoethylmethylamine	7.1-16							Kim and Han, 2011; Walse and Mitch, 2008; Wang,
N-Nitrosomorpholine	3.1-26							2011)
<i>N</i> -Nitrosopiperidine	4.4							
<i>N</i> -Nitrosopyrrolidine	4.5-77 <sup>d</sup>							
Haloacetaldehydes (HALs)	•							
Dibromoacetaldehyde	2.4							
Dibromochloroacetaldehyde	0.3							
Dichloroacetaldehyde	1.8-23 <sup>c</sup>							(Carter et al., 2015; Daiber et al., 2016; Lee et al.,
Tribromoactetaldehyde					0.4-2.2 <sup>c</sup>			2010; Manasfi et al., 2016; Serrano et al., 2011)
Trichloroacetaldehyde	17-301		10	3.6	190	405	2.9	
Haloketones (HKs)								
Chloroacetone	1.9							
1,2-Dichloroacetone	0.8							(Carter et al., 2015; Hang et al., 2016; Manasfi et
1,1,1-Dichloropropanone	0.4-21							al., 2016; Spiliotopoulou et al., 2015; Yeh et al.,
1,1,1-Trichloropropanone	1.3-46			11				2014)
Halonitromethanes (HNMs)	•							
Bromochloronitromethane	4							
Bromonitromethane	1.5							(Kanan, 2010; Montesinos and Gallego, 2012; Yeh
Tribromonitromethane	1.2							et al., 2014; Zhang et al., 2015)
Trichloronitromethane	0.1-1.2			0.4				
Haloacetamides (HAAms)								
Dibromoacetamide	0.6-1.9							
Dichloroacetamide	1.5							(Carter et al., 2015; Yeh et al., 2014)
Trichloroacetamide	2-2.7							
Inorganic Anions								
Bromate	3	10-900 <sup>b,c</sup>						(Chowdhury et al., 2016; E et al., 2016; Lee et al.,
Bromide	0.2-79 <sup>a</sup>				0.6-86ª			2010; Manasfi et al., 2016; Parinet et al., 2012;
Chlorate	0.04-37 <sup>a</sup>							Righi et al., 2014; Spiliotopoulou et al., 2015)

Chlorite	20-22 <sup>c</sup>					
Nitrate	0.004-63ª		23ª	13 <sup>a</sup>		
Total Organic Halogen (TOX)						
Total Organic Halogen (TOX)	140-480		47-1215	880-1080 <sup>c</sup>		
Total Organic						(Dellamental 2016, Faut Dilamental 2016)
Bromine (TOBr)	0.75-200	4897	0.3-16	53-84 <sup>c</sup>	4197-18239	(Daiber et al., 2016; Font-Ribera et al., 2016; Kalaall and Sim 2001; Vab et al. 2014)
Chlorine (TOCl)	139-3682	1337	47-1198	1081-9512 <sup>c</sup>	1213-13860	Kelsall and Sim, 2001; Yeh et al., 2014)
lodine (TOI)	0.63		0.04-1.9			

2131 (a) Reported in mg/L. (b) Ozone also employed. (c) Range presented. (d) Treatment method not provided. EGMO: Electrochemically-Generated Mixed-Oxidant.

- **Table 3**: Commonly used names and abbreviations (Abbr.) for selected components commonly used in
- 2134 personal care products.

<u>Antifungal Agents</u>			<u>Parab</u>	ens					
Common Name	Abbr.	Common Name	Abbr.	Common Na	me	Abbr.			
dichlorophene	dichlorophen	methylparaben	MeP	isobutylparab	en	iBuP			
5-chloro-(2,4-dichlorophenoxy)phenol	2,4-DCPh	ethylparaben	EtP	pentylparabe	en	PeP			
2,4,6-trichlorophenol	2,4,6-TCPh	propylparaben	PrP	heptaparabe	en	HeP			
		isopropylparaben	iPrP	octylparabe	n	OcP			
		butylparaben	BuP	benzylparabe	en	BzP			
UV Filters									
Common Name	Abbr.	Com	non Nam	e	A	bbr.			
isoamyl 4-methoxycinnamate	Amiloxate	4-hydrox	ybenzopher	none	4	-HB			
avobenzone	Avobenzone	1H-be	enzotriazole	2	1	HBT			
2,4-dihydroxybenzophenone	BP-1	3,3,5-trimethylcyclo	hexyl-2-hy	droxybenzoate	Hon	nosalate			
2,2',4,4'-tetrahydroxybenzophenone	BP-2	4-methylben	zylidene ca	umphor	4-	MBC			
benzophenone-3	BP-3	oct	ocrylene		(	DCR			
2,2'-dihydroxy-4-methoxybenzophenone	BP-8	octyldimethyl-pa	ara-aminob	enzoic acid	OD	-PABA			
benzyl salicylate	BzS	octylmethoxycinnamate			0	OMC			
4, 4'-dihydroxybenzophenone	4-DHB	2-phenyl-3H-benzi	midazole-5	-sulfonic acid	]	PBS			
5,6-dimethyl-1H-benzotriazole monohydrat	phenyl salicylate				PS				
ethyl 4-aminobenzoate	Et-PABA	2 ,3 ,4 -trihyd	lroxybenzo	phenone	]	ГНВ			

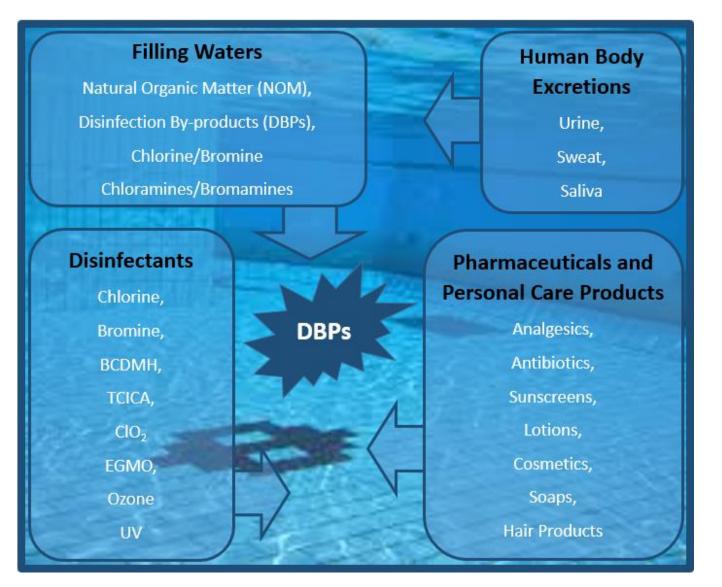
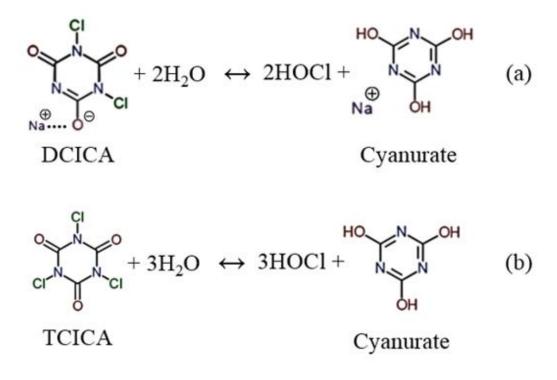
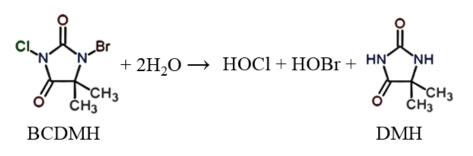


Figure 1: Disinfection By-product precursors and disinfectants in swimming pool and spa waters. Adapted from Carter et al., (2015).



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Figure 2: Formation of HOCl by the use of (a) DCICA and (b) TCICA, where DCICA is added as its sodium salt.



**Figure 3**: Formation of HOBr and HOCl via the hydrolysis of BCDMH.

# Occurrence and Formation of Disinfection By-Products in the Swimming Pool Environment: A Critical Review

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Tables on the following pages illustrate data that support the statements of the manuscript, but are not essential to presentation of the central points of the paper.

		Disinfostis-		Trihalomethane Conc					
Country	Pool(s) Type	Disinfection Method	Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane	Tribromomethane (Bromoform)	Analytical Method	Reference
	Outdoor*	Cl		6 (NR-21)	5 (NR-19)	27 (NR-102)	651 (NR-1166)		
USA	Outdoor	Cl		106 (NR-271)	34 (NR-117)	15 (NR-83)	2 (NR-8)	LLE GC-ECD	(Beech et al., 1980)
	Outdoor	Cl		103 (NR-386)	13 (NR-98)	3 (NR-38)	<1 (NR-6)		
Sweden	NR	Cl		(50-100)				LLE GC-ECD	(Norin and Renberg, 1980)
	NR	Br					(NR-400)		
Germany	Covered	Cl	174 (59-1224)	198 (43-980)	23 (0.1-150)	11 (0.1-140)	4 (nd-88)	LLE GC-ECD	(Lahl et al., 1981)
France	NR NR	Cl Br		256 (43-665) 32 (18-45)			5.4 (1-14) 289 (177-600)	PT GC-ECD	(Chambon et al., 1983)
Italy	NR	Cl		115 (62-179)	8 (6-10)	1.4 (0.8-2)	nd	HS GC-ECD	(Aggazzotti and Predieri, 1980
Canada	Spa Spa	Cl Br		154 (5-750)		1253 (37-3600)		PT GC-MS	(Benoit and Jackson, 1987)
Germany	Indoor Indoor	NR NR		95 (41-118) 81 (44-170)	0.5 (0.2-1.5) 9 (6-20)	0.1 (0.05-0.3) 1.5 (1.2-2.2)		GC	(Puchert et al., 1989)
Italy	Indoor	NR		274 (142-349)	~ (~ =~)			HS GC-ECD	(Aggazzotti et al., 1990)
Canada	Indoor	NR		365 (159-568)				HS GC-ECD	(Lévesque et al., 1994)
Italy	Indoor	NR		62 (3-179)				HS GC-ECD	(Aggazzotti et al., 1995)
Germany	Indoor	Cl		(3-28)	(0.7-5.6)	(0.03-6.5)	(nd-2.3)	HS GC-ECD	(Cammann and Hübner, 1995
Italy	Indoor	Cl		34 (25-43)	2.3 (1.8-2.8)	0.8 (0.5-10)	0.1 (0.1-0.1)	HS GC-ECD	(Aggazzotti et al., 1998)
Greece	Indoor	Cl		8.7 (4-26)	2.7 (0.3-7)	1.2 (0.5-3)	0.3 (0.07-0.9)	PT GC-ECD	(Golfinopoulos, 2000)
Canada	Indoor	Cl		(18-80)				HS GC-ECD	(Lévesque et al., 2000)
	Indoor	Cl/Oz	(13-24)	(13-24)	(0.1-0.9)	nd	nd		
Australia	Indoor	Cl	(21-87)	(20-85)	(0.2-2)	nd	nd	NR	(Kelsall and Sim, 2001)
	Indoor	Br/Oz	(107-158)	nd	(0.3-0.5)	(0.8-1.2)	(106-157)		
Italy	Indoor	Cl	40	33	4.3	1.9	0.4	HS GC-ECD	(Fantuzzi et al., 2001)
UK	Indoor	Cl	132 (57-223)	121 (45-212)	8.3 (2.5-23)	2.7 (0.7-7)	0.9 (0.7-2)	HS GC-ECD	(Chu and Nieuwenhuijsen, 200
Germany	Indoor	Cl		7.1-25				PT GC-ECD	(Erdinger et al., 2004)
Germany	Indoor Outdoor	Cl Cl	21 (35-47)					PT GC-ECD	(Glauner et al., 2005)
Poland	Indoor	Cl		(10-41)	(0.7-5.7)	(0.4-1.6)		TL-HS-DAI GC–ECD	(Kozlowska et al., 2006)
USA	Indoor Outdoor	NR NR		0.1 (nd-0.14) (0.08-0.13)				MIMS	(Li and Blatchley, 2007)
Spain	Indoor	Cl		110 (95-120)	2.2 (2-2.3)			HS GC-MS	(Caro and Gallego, 2007)
Spain	Indoor	Cl	80 (63-98)	67 (47-82)	9.3 (5.1-12)	3.2 (1.4-4.6)	1.4 (1-1.9)	HS GC-MS	(Villanueva et al., 2007)
Italy	Indoor	Cl	(27-98)					HS GC-MS	(Aggazzotti et al., 2007)
Spain	Indoor	Cl		127 (85-155)	2 (1.8-2.2)			HS GC-MS	(Caro and Gallego, 2008)
Thailand	Outdoor	Cl	47 (26-65)	20 (9.5-37)	13 (8.9-18)	10 (5.2-23)	3 (nd-6.6)	HS GC-ECD	(Panyakapo et al., 2008)
Taiwan	Indoor	NR		56 (44-74)				PT GC-MS	(Hsu et al., 2009)
	Indoor	Cl		41 (0.2-102)	3 (nd-11)	0.5 (nd-5.6)	nd		
Korea	Indoor	Cl/Oz		29 (0.2-65)	2.4 (nd-5.7)	0.2 (nd-3.4)	nd	PT GC-MS	(Lee et al., 2009)
	Indoor	EGMO		27 (6.8-56)	9.8 (1.6-27)	9.1 (nd-30)	19 (nd-36)		
USA	Indoor	Cl	88 (3.3-311)	73 (nd-298)	45 (nd-150)	6.7 (nd-55)	7.3 (nd-68)	MIMS	(Weaver et al., 2009)
USA	Indoor	Cl	63 (26-213)	62 (25-207)	2 (1-28)	2 (<1-4)	1 (nd-1)	LLE GC-ECD	(Kanan, 2010)
Italy	Indoor	CIC	41 (7-134)	, ,	. /	· · ·	. /	SHS GC-ECD	(Fantuzzi et al., 2010)
Spain	Indoor	Cl	45 (35-75)	16 (8.5-21)	12 (9.3-23)	11 (6.5-23)	6.1 (3-16)	PT GC-MS	(Font-Ribera et al., 2010c)
Spain	Indoor	Cl	45				×· · · /	PT GC-MS	(Kogevinas, 2010)
-r	Indoor	Cl		21 (nd-46)	2.1 (nd-7)	nd	nd		(
Korea		Cl/Oz						PT GC-MS	(Lee et al., 2010)
	Indoor Cl/Oz	CI/OZ		7.4 (nd-21)	1.1 (nd-2.5)	nd	nd		

**Table S1**: Reported Occurrence of Trihalomethanes in Swimming Pool and Spa Waters.

_	Pool(s)	Disinfection		Trihalomethane Conc	centration in Swimming Poo	l Water (µg/L); mean (min-m	,	<b>.</b>		
Country	Туре	Method	Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane	Tribromomethane (Bromoform)	Analytical Method	Reference	
	Indoor	EGMO		15 (nd-40)	10 (nd-34)	8.9 (nd-32)	4.1 (nd-18)	-		
	Indoor	SDCIC		86 (36-127)	1.9 (1.6-2)	nd	nd			
Italy	Indoor	Cl		12 (10-14)	18 (16-19)	18 (15-20)	4.6 (3.9-5.9)	PT GC-MS	(Aprea et al., 2010)	
	Indoor	SDCIC		23 (11-41)	2.3 (nd-3.3)	1 (0.5-1.5)	0.1 (0.1-0.5)			
Sacia	Indoor	NR	43					PT GC-MS	(East Dibase at al. 2010a)	
Spain	Outdoor	NR	151					PT OC-MS	(Font-Ribera et al., 2010a)	
Secie	Indoor	Cl	92 (29-247)	77 (22-217)	11 (3.6-25)	2.4 (0.4-5.3)	1.5 (0.2-2.8)	PT GC-MS	(Fourt Dihara at al. 2010h)	
Spain	Indoor	Br	110 (82-150)	1.1 (0.5-2.2)	1 (0.3-2.5)	2.6 (1.2-5.1)	105 (79-147)	PT OC-MS	(Font-Ribera et al., 2010b)	
Spain	Indoor	Cl		15 (8.4-21)	14 (9.3-27)	13 (6.5-23)	7.2 (3-16.5)	PT GC-MS	(Richardson et al., 2010)	
Span	Indoor	BCDMH		0.2 (0.1-0.3)	0.4 (0.2-0.7)	2.4 (2.1-2.7)	57 (52-64)	PT OC-MS	(Richardson et al., 2010)	
USA	Indoor	Cl		(20-30)		(0.5-2.5)		MIMS	(Weng and Blatchley, 2011)	
France	Indoor	Cl	26 (4.8-81)	22 (3.5-73)	2.6 (0.6-15)	0.8 (0.3-3.8)	0.4 (0.3-2.2)	LLE GC-MS	(Bessonneau et al., 2011)	
Canada	Indoor	Cl		83 (30-160)	112 (39-187)	17 (4.6-38)	4.0 (nd-7.3)	LLE GC-ECD	(Wang, 2011)	
Callada	Outdoor	Cl		556 (170-882)	125 (34-315)	10 (6.3-13)	nd	LLE UC-ECD	(wang, 2011)	
Taiwan	Indoor	NR		9.8 (8-12)				PT GC-MS	(Chen et al., 2011)	
Germany	Indoor	Cl		(6-7.6)				HS GC-ECD	(Schmalz et al., 2011b)	
Portugal	Indoor	Cl	(22-577)	(2-520)				HS-SPME GC-ECD	(Sa et al., 2011)	
Itoly	Indoor	Cl		15 (8.5-20)	14 (9.4-25)	13 (6.7-23)	7.2 (3.1-16)	PT GC-MS	(Lourencetti et al., 2012)	
Italy	Indoor	Br		0.2 (0.1-0.3)	0.4 (0.2-0.6)	2.4 (2.1-2.6)	60 (52-61)	FT UC-MIS	(Lourencetti et al., 2012)	
France	Indoor*	Cl	408 (233-996)	0.1 (0.01-0.2)	0.3 (0.05-1.1)	25 (14-64)	383 (220-931)	HS GC-MS	(Parinet et al., 2012)	
France	Indoor*	DCICA	(32-78)	(0.2-0.3)	(0.3-0.7)	(3-3.2)	(29-74)	115 0C-1415	(1 at met et al., 2012)	
Canada	Indoor	Cl	26 (10-46)					HS-SPME GC-ITMS	(Catto et al., 2012)	
Switzerland	Indoor	Various Cl	30 (15-110)					HS GC-MS	(Parrat et al., 2012)	
Portugal	Indoor	Cl	61 (nd-155)	(6.3-123)	(1-22)	(1-9.8)	(1-5.9)	HS-SPME GC-ECD	(Silva et al., 2012)	
Canada	Indoor	Cl	44 (18-114)					LLE GC-MS	(Simard et al., 2013)	
Canada	Outdoor	Cl	98 (12-311)					LEE OC-M5	(Simard et al., 2015)	
USA	Indoor	Cl		81 (12-282)	2 (nd-10)		1.4 (nd-32)	MIMS	(Afifi and Blatchley, 2015)	
Australia	Outdoor	Cl		76 (65-84)	2.3 (2-2.6)	0.3 (0.3-0.4)	<0.1	LLE GC-ECD	(Yeh et al., 2014)	
Portugal	Indoor	Cl		(17-407)				HS-SPME GC-ECD	(Maia et al., 2014)	
	Indoor	Various Cl	37 (6.8-134)	29 (2.5-122)	5.5 (1.4-18)	2.3 (0.2-12)	0.4 (<0.1-3.6)			
Italy	Indoor	Cl	32 (6.8-98)					HS GC-ECD	(Righi et al., 2014)	
	Indoor	DCICA	54 (14-134)					115 00 202	(11giii 01 uii, 2011)	
	Indoor	TCICA	32 (12-53)					_		
China	Outdoor	Cl	55 (27-74)					LLE GC-ECD	(Zhang et al., 2015)	
<u> </u>	Indoor	Cl/Oz	31 (7.6-57)	20 (15 50)	4.4.(1.4.10)	0.0 (0.0.1.()	0.04 (0.02.0.07)		(0.11)	
Denmark	NR	Cl	25 (12, 17)	30 (15-59)	4.4 (1.4-10)	0.8 (0.3-1.6)	0.04 (0.03-0.07)	PT GC-MS	(Spiliotopoulou et al., 2015)	
Taiwan	Indoor	Cl	25 (13-47)	47 (20, 50)	21(27.2.0)	05(0007)	0.2 (0.02.0.5)	PT-HS GC-ECD	(Peng et al., 2015)	
Australia	Indoor	Cl		47 (39-50)	3.1 (2.7-3.9)	0.5 (0.2-0.7)	0.3 (0.02-0.5)	HS-SPME GC-MS	(Carter et al., 2015)	
Canada	Spa Indoor	Cl Cl	84 (29-140)	19 63 (22-100)	0.1 9.9 (1.2-38)	0.2 21 (nd-56)	0.1 13 (nd-25)	HS-SPME GC-ITMS	(Tardif et al., 2015)	
	Indoor*			63 (22-100) <5ª	9.9 (1.2-38) <5ª	21 (nd-56) <5 <sup>a</sup>				
Saudi Arabia	Indoor*	Cl	61 (29-96)				50 (43-58)	LLE GC-MS	(Chowdhury et al., 2016)	
USA	Spa Indoor	Br/TCICA BCDMH		nd nd	nd nd	14 2.5 (2.4-2.6)	253 152 (118-186)	MIMS	(Daiber et al., 2016)	

	Pool(s)	Disinfection		Trihalomethane Conc	entration in Swimming Poo	l Water (µg/L); mean (min-m	ax).			
Country	Туре	Method	Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane	Tribromomethane (Bromoform)	Analytical Method	Reference	
	Spa	Cl/Oz		(nd-31)	nd	nd	nd	-		
	Spa	BCDMH		1.6 (nd-2.0)	2.9 (nd-2.9)	4.7 (3.0-7.1)	182 (168-198)			
	Indoor	Cl		19 (13-25)	6.2 (1.3-11)	17 (nd-28)	21 (nd-22)			
Spain	Indoor	Cl	49 (30-75)	37 (24-62)	7.1 (3.8-13)	2.0 (0.9-4.7)	0.9 (0.2-1.9)	HS GC-MS	(Font-Ribera et al., 2016)	
China	Indoor	Cl		243 (46-467)	167 (9.9-318)	13 (nd-226)	44 (1.9-133)	LLE GC-MS	(Hand at al 2016)	
China	Indoor	Cl/Oz		141 (96-213)	106 (85-141)	2.0 (1.5-4.9)	47 (38-59)	LLE GC-M5	(Hang et al., 2016)	
Energy	Outdoor	Cl	80	70	7.9	1.9	0.6		(Mana 6 at al. 2016)	
France	Indoor*	Cl	70 (50-92)	nd	nd	3.6 (1.6-5.2)	66 (49-87)	LLE GC-ECD	(Manasfi et al., 2016)	
China	Outdoor	Cl	56					LLE GC-ECD	(Tang and Xie, 2016)	
Canada	Indoor	Cl	65 (21-132)	38 (6.7-127)	9.7 (nd-30)	11 (nd-51)	6.6 (nd-46)	HS-SPME GC-ITMS	(Tardif et al., 2016)	
China	Outdoor	Cl	90 (32-170)					HS GC-MS	(Yang et al., 2016)	

\*Seawater filled. **a:** Specific values not reported. **nd:** Not Detected. **NR:** Not Reported. **BCDMH:** 1-Bromo-3-chloro-5,5-dimethylhydantoin. **Br:** Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). **CIC:** Chloroisocyanurate. **CI:** Chloroisocyanurate. **CI:** Chloroisocyanurate acid. **EGMO:** Electrochemically-Generated Mixed-Oxidant. **Oz:** Ozone. **SDCIC:** Sodium dichloroisocyanurate. **TCICA:** Trichloroisocyanuric acid. **Various CI:** Refers to any of the following individually or in combination: Cl Based, SDCIC, CIC, DCICA and/or TCICA. **DAI:** Direct Aqueous Injection. **ECD:** Electron Capture Detector. **GC:** Gas Chromatography. **HS:** Headspace. **ITMS:** Ion Trap Mass Spectrometry. **LLE:** Liquid-Liquid Extraction. **MIMS:** Membrane-Inlet Mass Spectrometry. **MS:** Mass Spectrometry. **PT:** Purge and Trap. **SHS:** Static Headspace. **SPME:** Solid-Phase Microextraction. **TL:** Thin Layer.

Country	Pool(s)	Disinfection			Haloacetic .	Acid Concentr	ation in Swim	ming Pool Wate	r (µg/L); mear	n (min-max).			Analytical	Reference
Country	Туре	Method	THAA	TCAA	DCAA	CAA	BAA	DBAA	TBAA	BDCAA	DBCAA	BCAA	Method	Kelerence
Spain	NR	Cl		42	69	25	7.1	15					SPE CZE	(Martínez et al., 1999)
Switzerland	NR	Cl		45 (17-95)	76 (0.9-240)	47 (11-117)							LLE GC-MS	(Berg et al., 2000)
Spain	NR	Cl	330	155	45	4.2	nd	2.8	19	61	33	11	HS–SPME GC–ITMS	(Sarrión et al., 2000)
Portugal	NR	NR	2333 (1300- 3200)	1400 (1000- 1700)		378 (15-1000)			15	533 (208-912)	62		SPE-LC ESI-MS	(Loos and Barceló, 2001)
Italy	Indoor	Cl	(109-387) <sup>a</sup>										IC-MS	(Aggazzotti et al., 2007)
USA	Indoor	Cl	960 (172-9005)	241 (76-1925)	504 (52-6787)	nd	2 (<1-5)	4.5 (<1-25)	nd	22 (8-110)	3 (<1-32)	5 (1-176)	LLE GC-ECD	(Kanan, 2010)
	Indoor	Cl		156 (20-636)	68 (14-246)									
Korea	Indoor	Cl/Oz		17 (1-86)	12 (nd-32)								LLE GC-ECD	(Lee et al., 2010)
	Indoor	EGMO		97 (1-413)	34 (1.5-96)									
Spain	NR	NR	(201-363)	(55-195)	(94-130)	(34-42)		(1.4-1.6)		(<1-5)			SBME GC-MS	(Cardador and Gallego, 2010)
Canada	Indoor	Cl	427 (201-700)	116 (17-234)	173 (49-384)	24 (9.8-46)	12 (3.8-27)	28 (5.4-88)	5.6 (0.2-10)	18 (0.4-33)	9.1 (0.3-21)	46 (7.1-106)	LLE GC-ECD	(Wang, 2011)
	Outdoor	Cl	1039 (144-2777)	382 (43-961)	540 (71-1517)	110 (18-300)	nd	nd	nd	2.7 (2.3-3.3)	nd	8.3 (2-12)		
Spain	Indoor	Cl		110 (85-166) 120	77 (60-109) 151	23 (8.5-36) 26							HS GC-MS	(Cardador and Gallego, 2011)
•	Outdoor	Cl		(99-146)	(130-170)	(19-34)								2011)
France	Indoor*	Cl	757 (323-2233)	27 (2.9-87)	4.8 (2.2-8.7)	120 (99- 146)	55 (8.2-155)	307 (132-1089)	164 (49-428)	13 (5-20)	103 (36-243)	65 (27-216)	LLE GC-ECD	(Parinet et al., 2012)
	Indoor*	DCICA	(84-123)	(4.6-15)	(1.4-2.1)	(1.3-1.5)	(4.3-6.5)	(11-17)	(4-5)	(1.2-2.3)	(50-67)	(5.1-5.3)		
Canada	Indoor	Cl	238 (111-391)	118 (54-201)	103 (48-192)					15 (nd-24)		1.8 (0.4-3)	LLE GC-ECD	(Catto et al., 2012)
Portugal	Indoor	Cl	(10-183)	(0.5-73)	(0.4-54)	(0.6-13)		(0.1-12) <sup>b</sup>	(0.4-0.9)	(0.1-12) <sup>b</sup>	(0.2-0.9)	(0.4-25)	HS-SPME GC-ECD	(Sa et al., 2012)
Portugal	NR	NR	106 (76-154) <sup>e</sup>	54 (29-76)	51 (29-84)	2.4 (nd-2.7)	nd	0.6 (0.3-0.7)					HPLC ESI-TQMS	(Prieto-Blanco et al., 2012)
Canada	Indoor	Cl	364 (104-1195)											(Simond et al. 2012)
Canada	Outdoor	Cl	808 (155-2224)										- PT GC-ECD	(Simard et al., 2013)
Saudi Arabia	NR	NR		(nd-13)	(11-35)	(46-49)	(8.6-25)	(16-17)				(6.8-7.1)	SPME UPLC–UV	(Nsubuga and Basheer, 2013)
China	Indoor	NR	95 (13-133)°	53 (6-90)	34 (5-60)									·
Ciillia	Outdoor	NR	156 (89-332) <sup>e</sup>	53 (33-98)	81 (44-195)									
	Indoor	NR	1613 (70-3980)°	890 (20-2970)	727 (50-750)								LLE GC-ECD	(Wang et al., 2014)
USA	Outdoor	NR	1442 (800-2430) <sup>e</sup>	680 (370-1140)	700 (310-1330)									
	Spa	NR	1067 (690-1360) <sup>e</sup>	330 (40-530)	450 (50-750)									

**Table S2**: Reported Occurrence of Haloacetic Acids in Swimming Pool and Spa Waters.

<b>G</b> (	Pool(s)	Disinfection			Haloacetic	Acid Concentra	ation in Swimm	ning Pool Wate	r (μg/L); mean	(min-max).			Analytical	D C
Country	Туре	Method	THAA	TCAA	DCAA	CAA	BAA	DBAA	TBAA	BDCAA	DBCAA	BCAA	Method	Reference
	Indoor	Various Cl		893 (110-1700)	983 (230-2100)	43 (32-64)	<0.5	<0.5		17 (<0.5-22)	<0.5	<0.5		
Australia	Outdoor	Various Cl		978 (650-1300)	856 (480-1400)	73 (<0.5-120)	<0.5	<0.5		8.8 (7-12)	<0.5	<0.5	LLE GC-ECD	(Yeh et al., 2014)
	Baby	Various Cl		(1600- 2600)	(400-2400)	(<0.5-110)	<0.5	<0.5		(14-16)	<0.5	<0.5		
Italy	Indoor	Various Cl	164 (11-403)	53 (<1-291)	11 (<1-65)								IC-MS	(Righi et al., 2014)
Australia	Indoor	Cl		NQ	409 (113-656)	80	nd	3.0	nd	NQ	NQ	32	LLE GC-MS	(Carter et al., 2015)
	Spa	Cl		NQ	668	NQ	nd	nd	nd	NQ	NQ	nd		
Canada	Indoor	Cl	303 (123-606) <sup>d</sup>	139 (23-289)	127 (32-281)	15 (4.4-33)	4 (nd-4.7)	11 (nd-25)				16 (1.8-35)	LLE GC-ECD	(Tardif et al., 2015)
China	Outdoor	Cl	168 (95-351)										LLE GC-ECD	(Zhang et al., 2015)
China	Indoor	Cl/Oz	102 (14-161)											(Zhang et al., 2013)
Saudi Arabia	Indoor*	Cl		2.6 (0.5-4.7)	1.7 (0.8-2.6)	1.25 (0.04-2.2)	3.8 (1.4-6.9)	16 (5.9-28)	186 (5.8-73)	2.1 (0.3-4.4)	25 (7.3-48)	5.2 (1.5-8.7)	LLE GC-MS	(Chowdhury et al., 201
Indoor	Indoor	BCDMH		64 (52-77)	2.2 (1.1-3.3)	nd	4.7 (4.2-5.2)	123 (115-131)	72 (50-93)	8.9 (6.3-12)	4.1 (2.5-5.6)	2.2 (nd-2.2)		
	Indoor	Cl		158 (65-249)	163 (89-201)	13 (8.3-19)	6.6 (1.2-12)	14 (nd-19)	nd	15 (8.6-21)	5.0 (nd-6.1)	25 (11-39)		
USA	Spa	BCDMH		37 (28-49)	27 (23-32)	3.9 (3.8-4.0)	62 (26-90)	337 (91-506)	97 (26-175)	10 (6.7-14)	4.4 (2.9-6.3)	13 (7.7-17)	LLE GC-MS	(Daiber et al., 2016)
	Spa	Br/TCICA		13	89	nd	47	1795	74	117	14	294		
	Spa	Cl/Oz		(nd-1865)	(nd-343)	(nd-31)	nd	nd	nd	(nd-12)	nd	(nd-2.6)		
Spain	Indoor	Cl	111 (73-144)	63 (39-84)	30 (15-52)			1.0 (0.5-3.1)		12 (4.8-24)		4.9 (2.4-8.8)	LLE GC-MS	(Font-Ribera et al., 2016)
China	Indoor	Cl		19 (nd-43)	365 (nd-2435)	10 (nd-94)	2.1 (nd-27)	nd	nd	nd	nd	510 (nd-1353)	LLE GC-MS	(Hang et al., 2016)
Cinna	Indoor	Cl/Oz		21 (nd-49)	200 (36-536)	41 (nd-475)	16 (nd-103)	nd	8.1 (nd-122)	nd	1.2 (nd-18)	425 (190-657)	ELE CC MD	(Hang et al., 2010)
France	Indoor	Cl	116 (107-132)	nd	nd	nd	nd	66 (63-72)	43 (36-53)	nd	3.1 (2.7-3.5)	4.3 (3.5-4.8)	LLE GC-ECD	(Manasfi et al., 2016)
	Outdoor	Cl	498	461	23	nd	nd	1.7	nd	7.3	2.7	2.4		
China	Outdoor	Cl	1364										LLE GC-ECD	(Tang and Xie, 2016)
Canada	Indoor	Cl	295 (109-886) <sup>c</sup>	107 (24-250)	134 (27-500)	17 (2.1-78)	3.8 (nd-15)	17 (nd-70)				31 (1.2-118)	LLE GC-ECD	(Tardif et al., 2016)
China	Outdoor	Cl	798 (191-1906)	492	462								LLE GC-MS	(Yang et al., 2016)

\*Seawater filled. **a**: HAA3; Sum of CAA, DCAA and TCAA. **b**: The range values refer to the sum (DBAA+BDCAA). **c**: HAA6; Sum of CAA, DCAA, TCAA, BAA, and BCAA. **d**: HAA5; Sum of CAA, DCAA, TCAA, BAA and DBAA. **nd**: Not Detected. **NR**: Not Reported. **NQ**: Detected but not quantifiable. **BAA**: Bromoacetic Acid. **BCAA**: Bromochloroacetic Acid. **BDCAA**: Bromochloroacetic Acid. **CAA**: Chloroacetic Acid. **DBAA**: Dibromochloroacetic Acid. **DCAA**: Dibromochloroacetic Acid. **DBAA**: Dibromocacetic Acid. **TBAA**: Tribromoacetic Acid. **TCAA**: Trichloroacetic Acid. **THAA**: Total Haloacetic Acids: Sum of CAA, DCAA, TCAA, BAA, BBAA, BBAA, BBCAA, CDBAA and BDCAA. **BCCAA**: Dibromochloroacetic Acid. **TBAA**: Tribromoacetic Acid. **TCAA**: Trichloroacetic Acid. **THAA**: Total Haloacetic Acids: Sum of CAA, DCAA, TCAA, BAA, BBAA, BBAA, BBCAA, CDBAA and BDCAA. **BCDMH**: 1-Bromo-3-chloro-5,5-dimethylhydantoin. **Br**: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). **Cl**: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). **Oz**: Ozone. **TCICA**: Trichloroisocyanuric acid. **Various Cl**: Refers to any of the following individually or in combination: Cl Based, Sodium dichloroisocyanurate (SDCIC), chloroisocyanurate (CIC), dichloroisocyanuric acid (DCICA) and/or TCICA. **CZE**: Capillary Zone Electrophoresis. **ECD**: Electron Capture Detector. **ESI**: Electrospray Ionisation. **GC**: Gas Chromatography. **HPLC**: High Performance Liquid Chromatography. **HS**: Headspace. **IC**: Ion Chromatography. **ITMS**: Ion Trap Mass Spectrometry. **LLE**: Liquid-Liquid Extraction. **MS**: Mass Spectrometry. **SBME**: Solvent Bar Microextraction. **SPHE**: Solid-Phase Extraction. **SPME**: Solid-Phase Microextraction. **TQMS**: Triple Quadrupole Mass Spectrometry. **UPLC**: Ultra Performance Liquid Chromatography. **UVD**: Ultraviolet Detection.

		Disinfection	Chloramine C	oncentration in Swimmir	ng Pool Water (μg/L); m	ean (min-max).		
Country	Pool(s) Type	Method	Total Inorganic Chloramines	Trichloramine (NCl <sub>3</sub> )	Dichloramine (NHCl <sub>2</sub> )	Monochloramine (NH2Cl)	Analytical Method	Reference
Japan	Outdoor	NR			(40-120)	(110-190)	DPD/KI Colorimetric	(Tachikawa et al., 2005)
USA	Indoor	NR		90 (70-100)			MIMS	(Li and Blatchley, 2007)
USA	Outdoor	NR		(70-160)			MIMS	(Li and Blatchiey, 2007)
USA	Indoor	Cl	513 (nd-2070)	94 (nd-3412)	121 (nd-417)	311 (nd-1880)	MIMS	(Weaver et al., 2009)
Spain	Indoor	Cl			430 (160-650)		DPD/KI Colorimetric	(Font-Ribera et al., 2010c)
Sure in	Indoor	Cl		<100	380 (<10-650)	290 (100-640)	DPD/KI Colorimetric	(Dishandaan et al. 2010)
Spain	Indoor	BCDMH		<100	<10	270 (240-300)	DPD/KI Colorimetric	(Richardson et al., 2010)
USA	Indoor	Cl		(100-780)	(180-750)	(180-300)	MIMS	(Weng and Blatchley, 2011)
Canada	Indoor	Cl				40 (10-60)	DPD/KI Colorimetric	(Warg 2011)
Canada	Outdoor	Cl				10 (9-11)	DPD/KI Colorimetric	(Wang, 2011)
Canada	Indoor	Cl	689 (376-981)	341 (nd-650)	25 (nd-593)	323 (188-434)	DPD/KI Colorimetric	(Catto et al., 2012)
Canada	Indoor	Cl	527 (268-802)	232 (nd-557)	11 (nd-70)	284 (nd-450)	DPD/KI Colorimetric	(Catto et al., 2012)
Canada	Indoor	Cl	736 (311-1723)				DPD/KI Colorimetric	(Simard et al., 2013)
Canada	Outdoor	Cl	142 (8-845)				DPD/KI Colorimetric	(Simard et al., 2013)
USA	Indoor	Cl		420 (nd-2190)	65 (nd-250)	89 (nd-620)	MIMS	(Afifi and Blatchley, 2015)
Switzerland	Indoor/Outdoor	Various <sup>a</sup>		29 (2.4-58)			MIMS	(Soltermann et al., 2014)
China	Indoor	Cl		7 (5-11)			MIMS	(Lian et al., 2014)
Canada	Indoor	Cl		600 (400-800)			DPD/KI Colorimetric	(Lévesque et al., 2015)
Saudi Arabia	Indoor*	Cl		70 (nd-110)	220 (10-490)	220 (70-450)	DPD/KI Colorimetric	(Chowdhury et al., 2016)
	Indoor	Cl		319 (66-527)	41 (nd-55)	58 (43-71)		
	Indoor	BCDMH		12 (5.6-18)	51 (45-56)	67 (nd-67)		
USA	Spa	BCDMH		183 (3.7-363)	40 (39-41)	48 (43-52)	MIMS	(Daiber et al., 2016)
	Spa	Br/TCICA		91	142	205		
Spain	Indoor	Cl		1500 (nd-1600)	300 (nd-700)	200 (nd-700)	DPD/KI Colorimetric	(Font-Ribera et al., 2016)
	Indoor	Cl		50 (nd-300)	300 (180-400)	180 (100-200)		
Spain	Indoor	Cl		50 (nd-300)	350 (300-400)	320 (300-400)	DPD/KI Colorimetric	(Llana-Belloch et al., 2016)
	Indoor	UV only		nd	nd	nd		

Table S3: Reported	Occurrence of Inorganic	Chloramines in	Swimming Poo	ol and Spa Waters.

\*Seawater filled. nd: Not Detected. NR: Not Reported. a: Cl in conjunction with UV or Oz. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). Oz: Ozone. UV: Ultraviolet. DPD: diethyl-p-phenylenediamine. KI: Potassium Iodide. MIMS: Membrane-Inlet Mass Spectrometry.

Country	Pool(s) Type	Disinfection Method		Haloacetoni	Analytical						
			BAN	CAN	BCAN	DBAN	DCAN	TCAN	THAN	Method	Reference
USA	Indoor	NR					100 (100-100)			MIMC	(Li and Blatchley, 2007)
	Outdoor	NR					(20-30)			MIMS	
USA	Indoor	Cl					15 (0.6-87)			MIMS	(Weaver et al., 2009)
USA	Indoor	Cl	1.0 (nd-1.0)	1.2 (nd-3.0)	2.7 (nd-13)	1.8 (nd-5.0)	15 (4-47)	(nd-1.0)	16 (5.0-53)	LLE GC-ECD	(Kanan, 2010)
Korea	Indoor	Cl/Oz			0.4 (nd-0.6)	0.4 (nd-0.8)	1.3 (0.2-3.2)	nd		LLE GC-ECD	(Lee et al., 2010)
	Indoor	EGMO			3.5 (nd-8.0)	2.6 (nd-6.8)	3.8 (nd-9.0)	nd			
	Indoor	Cl			0.8 (nd-1.9)	0.5 (nd-0.9)	3.9 (0.5-12)	nd			
USA	Indoor	Cl					(100-200)			MIMS	(Weng and Blatchley, 2011)
USA	Indoor	Cl					8.6 (0.7-31)			MIMS	(Afifi and Blatchley, 2015)
Australia	Outdoor	Cl			0.6 (0.5-0.8)	0.3 (nd-0.3)	7.1 (4.9-8.9)	0.3 (nd-0.3)		LLE GC-ECD	(Yeh et al., 2014)
Australia	Indoor	Cl	nd	2.4	nd	0.2	8.9 (3.9-12)	0.4		LLE-GC-MS	(Carter et al., 2015)
	Spa	Cl					9.0			LLE-OC-M5	
Denmark	NR	Cl					4.2 (1.9-7.2)			PT GC-MS	(Spiliotopoulou et al., 2015)
Canada	Indoor	Cl			3.2 (0.5-11)	2.9 (nd-15)	12 (424)	0.2 (nd-1.1)		LLE GC-ECD	(Tardif et al., 2015)
China	Indoor	TCICA							5.0 (1.3-13) <sup>a</sup>	LLE GC-ECD	(Zhang et al., 2015)
	Outdoor	Cl							3.6 (0.8-8.3) <sup>a</sup>	LEE GC-LEED	
USA	Spa	Br/TCICA			5.6	219	nd	nd		MIMS	(Daiber et al., 2016)
	Indoor	BCDMH			1.8 (nd-1.8)	37 (35-39)	nd	nd			
	Spa	Cl/Oz			nd	nd	(nd-14)	nd			
	Spa	BCDMH			1.8 (nd-1.8)	80 (47-98)	nd	nd			
	Indoor	Cl			5.6 (nd-7.4)	nd	4.9 (1.8-9.4)	nd			
Spain	Indoor	Cl			3.0 (1.8-4.7)	1.3 (1.1-3.6)	7.3 (3.8-12)			HS GC-MS	(Font-Ribera et al., 2016)
China	Indoor	Cl/Oz			nd	nd	5.3 (4.2-8.5)	nd		LLE GC-MS	(Hang et al., 2016)
	Indoor	Cl			5.6 (nd-89)	3.1 (nd-34)	17 (nd-206)	0.1 (nd-0.5)			(114115 et 41., 2010)
France	Indoor*	Cl			0.9 (0.9-1.0)	19 (13-28)	nd	nd		LLE GC-ECD	(Manasfi et al., 2016)
	Outdoor	Cl			9.2	2.5	75	1.2			
Canada	Indoor	Cl			5.8 (0.3-30)	5.8 (nd-31)	9.8 (2.3-23)	0.03 (nd-0.1)		LLE GC-ECD	(Tardif et al., 2016)

**Table S4**: Reported Occurrence of Haloacetonitriles in Swimming Pool and Spa Waters

\*Sea water filled. a: Refers to HAN-4; Sum of TCAN, BCAN, DBAN and DCAN. BAN: Bromoacetonitrile. CAN: Chloroacetonitrile. BCAN: Bromochloroacetonitrile. DBAN: Dibromoacetonitrile. DCAN: Dichloroacetonitrile. TCAN: Trichloroacetonitrile. THAN: Total haloacetonitrile: Sum of BAN, CAN, BCAN, DBAN, DCAN and TCAN. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Br: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). EGMO: Electrochemically-Generated Mixed-Oxidant. Oz: Ozone. TCICA: Trichloroisocyanuric acid. ECD: Electron Capture Detector. GC: Gas Chromatography. HS: Headspace. LLE: Liquid-Liquid Extraction. MIMS: Membrane-Inlet Mass Spectrometry. MS: Mass Spectrometry. PT: Purge and Trap.

Country	Pool(s) Type	Disinfection Method		N-Nitros	amine Concen		D.C.					
			NDMA	NDEA	NEMA	NDBA	NMOR	NPIP	NDPA	NPYR	- Analytical Method	Reference
USA	Indoor	Cl	32 (nr-42)			NQ		NQ			SPE GC-MS	(Walse and Mitch, 2008)
	Outdoor	Cl	5.3 (nr-6.9)			NQ		NQ				
	Spa	Cl	313 (nr-429)			NQ		NQ				
Spain	NR	NR	5.5 (5.0-5.9)	1.2 (1.1-1.4)						4.5	SPE GC-MS	(Jurado-Sánchez et al., 2010)
USA	Indoor	Cl	17 (2-83)								SPE GC-MS	(Kanan, 2010)
Korea	Indoor	Cl	52 (0.7-208)	31 (1.4-53)			3.1 (0.3-34)				SPE HPLC-FLD	(Kim and Han, 2011)
Italy	NR	NR								77 (53-127)	SPE GC-MS	(Pozzi et al., 2011)
Canada	Indoor	Cl	5.2 (1.0-9.8)	14.8 (5.9-53)	7.1 (2.6-26)	15 (6.8-22)	15 (12-18)	4.4 (3.2-5.5)	nd	nd	SPE GC-MS	(Wang, 2011)
Canada	Outdoor	Cl	6.6 (3.1-15)	35 (3.5-72)	16 (15-17)	141 (1.6-403)	5.9 (5.8-6.0)	nd	nd	nd		
Taiwan	Indoor	NR	(7.2-100)	(1.4-3.7)	(nd-1.7)						SPE GC-MS	(Fu et al., 2012)
	Outdoor	NR	(nd-4.7)	(nd-9.0)	nd							
Australia	Indoor	Cl	34 (31-38)	3.3 (3.2-3.4)	nd	24 (15-33)	26 (26-27)	nd	nd	nd	SPE GC-MS	(Carter et al., 2015)
Australia	Spa	Cl	5.5	nd	nd	nd	nd	nd	nd	nd		
Canada	Indoor	Cl	43 (2.4-105)								LLE GC-MS-MS	(Tardif et al., 2015)
Spain	Indoor	Cl	11 (8.0-14)								SPE GC-MS-MS	(Font-Ribera et al., 2016)
Canada	Indoor	Cl	43 (2.8-105)								LLE GC-MS-MS	(Tardif et al., 2016)

**Table S5**: Reported Occurrence of *N*-Nitrosamines in Swimming Pool and Spa Waters.

nd: Not Detected. NQ: Detected but not quantifiable. NR: Not Reported. NDBA: N-Nitrosodi-n-butylamine. NDEA: N-Nitrosodiethylamine. NDMA: N-Nitrosodimethylamine. NDPA: N-Nitrosodipropylamine. NEMA: N-Nitrosoethylmethylamine. NMOR: N-Nitrosomorpholine. NPIP: N-Nitrosopiperidine. NPYR: N-Nitrosopyrrolidine. Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). FLD: Fluorescence Detection. GC: Gas Chromatography. HPLC: High Performance Liquid Chromatography. LLE: Liquid-Liquid Extraction. MS: Mass Spectrometry. SPE: Solid-Phase Extraction.

~	Pool(s)	Disinfection		Haloketone Concentr	ation in Swimming Pool W	ater (μg/L); mean (min-max).				
Country	Туре	Method	Trichloroacetaldehyde (CH)	Dichloroacetaldehyde (DCAL)	Dibromoacetaldehyde (DBAL)	Dibromochloroacetaldehyde (DBCAL)	Tribromoacetaldehyde (TBAL)	Analytical Method	Reference	
	Indoor	EGMO	10 (nd-23)							
Korea	Indoor	Cl/Oz	3.6 (nd-10)					LLE GC-ECD	(Lee et al., 2010)	
	Indoor	Cl	17 (5.1-35)							
Spain	NR	NR	(53-340)	(1.8-23)				MLLE LVI-PTV-GC-MS	(Serrano et al., 2011)	
Australia	Outdoor	Cl	21 (19-24)					LLE GC-ECD	(Yeh et al., 2014)	
China	Outdoor	Cl	58 (16-156)						(71	
China	Indoor	Cl	47 (6.0-132)					LLE GC-ECD	(Zhang et al., 2015)	
Australia	Indoor	Cl	301 (177-400)		2.4	0.3		LLE GC-MS	(Conton at al. 2015)	
Australia	Spa	Cl	405					LLE GC-MS	(Carter et al., 2015)	
E	Outdoor*	Cl	190						(Manager et al. 2016)	
France	Indoor*	Cl	nd				(0.4-2.2)	LLE GC-ECD	(Manasfi et al., 2016)	
	Indoor	Cl	120 (68-165)							
USA	Indoor	BCDMH	nd					MIME	(Deiher et al. 2016)	
USA	Spa	Cl/Oz	(nd-101)					MIMS	(Daiber et al., 2016)	
	Spa	Br	2.9 (1.3-3.9)							

### **Table S6**: Reported Occurrence of Haloacetaldehydes in Swimming Pool and Spa Waters

\*Seawater filled. nd: Not Detected. NR: Not Reported. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Br: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). Oz: Ozone. ECD: Electron Capture Detector. GC: Gas Chromatography. LLE: Liquid-Liquid Extraction. LVI: Large Volume Injection. MIMS: Membrane-Inlet Mass Spectrometry. MLLE: Micro-Liquid-Liquid Extraction. MS: Mass Spectrometry. PTV: Program Temperature Vaporiser.

	Pool(s)	Disinfection	Haloketone	Concentration in Swimming Poo	ol Water (µg/L); mean (min-	max).		
Country	Туре	Method	1,1-Dichloropropanone (1,1-DCP)	1,1,1-Trichloropropanone (1,1,1-TCP)	1, 2-Dichloroacetone (1,2-DCA)	Chloroacetone	Analytical Method	Reference
Australia	Outdoor	Cl	0.4 (0.3-0.5)	6.9 (3.6-9.6)			LLE GC-ECD	(Yeh et al., 2014)
Australia	Indoor	Cl	0.7	5.8	0.8	1.9	LLE GC-MS	(Carter et al., 2015)
Denmark	NR	Cl		1.3 (0.4-3.1)			PT GC-MS	(Spiliotopoulou et al., 2015)
Canada	Indoor	Cl		3.1 (0.4-11)			LLE GC-ECD	(Tardif et al., 2015)
China	Indoor	Cl	1.8	$(0.2-7.4)^{a}$			LLE GC-ECD	(Zhang et al., 2015)
Ciiiia	Outdoor	Cl	2.4	(0.9-6.3) <sup>a</sup>			ELE GC-ECD	(Zhang et al., 2015)
	Spa	Br/TCICA	nd	nd				
	Indoor	BCDMH	nd	nd				
USA	Spa	Cl/Oz	nd	(nd-9.7)			MIMS	(Daiber et al., 2016)
	Spa	BCDMH	nd	nd				
	Indoor	Cl	1.4 (nd-1.4)	1.8 (nd-2.4)				
Spain	Indoor	Cl	2.1 (1.4-5.8)				LLE GC-MS	(Font-Ribera et al., 2016)
China	Indoor	Cl/Oz	nd	11 (7.1-15)				(Hanna at al. 2016)
China	Indoor	Cl	0.7 (nd-7.7)	46 (1.9-180)			LLE GC-MS	(Hang et al., 2016)
France	Indoor*	Cl	nd	nd				(Manastratal 2016)
France	Outdoor	Cl	21	72			LLE GC-ECD	(Manasfi et al., 2016)
Canada	Indoor	Cl		1.9 (0.3-7.3)			LLE GC-MS-MS	(Tardif et al., 2016)

## Table S7: Reported Occurrence of Haloketones in Swimming Pool and Spa Waters.

\*Seawater filled. a: Refers to the sum of 1,1-di- and 1,1,1-tri-chloropropanone. nd: Not Detected. NR: Not Reported. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Br: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). CI: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). Oz: Ozone. TCICA: Trichloroisocyanuric acid. ECD: Electron Capture Detector. GC: Gas Chromatography. LLE: Liquid-Liquid Extraction. MIMS: Membrane-Inlet Mass Spectrometry. MS: Mass Spectrometry. PT: Purge and Trap.

	Pool(s)	Disinfection	Н	alonitromethane Concentra	ation in Swimming Pool Wa	ater (µg/L); mean (min-max).			
Country	Туре	Method	Total halonitromethanes (THNMs)	Trichloronitromethane (TCNM)	Tribromonitromethane (TBNM)	Bromochloronitromethane (BCNM)	Bromonitromethane (BNM)	Analytical Method	Reference
Germany	NR	NR		0.2 (nd-0.8)				NR	(Puchert et al., 1989)
USA	Indoor	Cl	4.8 (1.4-13)	1.1 (nd-2.3)		4.0 (0.8-11)	1.5 (nd-2.2)	LLE GC-ECD	(Kanan, 2010)
Spain	NR	NR		1.2 (0.4-1.9)				HS SPME GC-MS	(Montesinos and Gallego, 2012)
Australia	Outdoor	Cl		1.2 (1.2-1.3)	1.2 (nd-1.2)			LLE GC-ECD	(Yeh et al., 2014)
Canada	Indoor	Cl		0.9 (nd-5.0)				LLE GC-ECD	(Tardif et al., 2015)
China	Indoor	Cl		0.1 (nd-0.1)				LLE GC-ECD	(7hong at al. 2015)
Cililia	Outdoor	Cl		nd				LLE UC-ECD	(Zhang et al., 2015)
-	Indoor	BCDMH		nd					
	Indoor	Cl		nd					
USA	Spa	NR		nd				MIMS	(Daiber et al., 2016)
	Spa	BCDMH		nd					
	Spa	Cl/Oz		nd					
China	Indoor	Cl		1.0 (nd-4.5)				LLE GC-ECD	(Hang at al 2016)
China	Indoor	Cl/Oz		0.4 (nd-2.1)				LLE GC-ECD	(Hang et al., 2016)
France	Indoor	Cl		nd				LLE GC-ECD	(Manasfi et al. 2016)
гтапсе	Outdoor	Cl		4.5	nd			LLE GU-EUD	(Manasfi et al., 2016)
Canada	Indoor	Cl		0.3 (0.02-3.7)				LLE GC-ECD	(Tardif et al., 2016)

**Table S8**: Reported Occurrence of Halonitromethanes in Swimming Pool and Spa Waters.

\*Seawater filled. nd: Not Detected. NR: Not Reported. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). Oz: Ozone. ECD: Electron Capture Detector. GC: Gas Chromatography. HS: Headspace. LLE: Liquid-Liquid Extraction. MIMS: Membrane-Inlet Mass Spectrometry. MS: Mass Spectrometry. SPME: Solid-Phase Microextraction.

#### Table S9: Reported Occurrence of Haloacetamides in Swimming Pool and Spa Waters

Country	Pool(s)	Disinfection			Haloacetic	Acid Concentra	tion in Swimı	ning Pool Wate	r (µg/L); mean	(min-max).			Analytical	Defenence
Country	Туре	Method	TCAAm	DCAAm	TBAAm	DBAAm	BCAAm	BDCAAm	DBCAAm	BIAAm	CIAAm	DIAAm	Method	Reference
Australia	Outdoor	Cl	2.7 (2.4-3.1)	nd	nd	1.9 (nd-2.0)	nd	nd	nd	nd	nd	nd	LLE GC-ECD	(Yeh et al., 2014)
Australia	Indoor	Cl	2.0	1.5		0.6							LLE GC-MS	(Carter et al., 2015)

nd: Not Detected. TCAAm: Trichloroacetamide. DCAAm: Dichloroacetamide. TBAAm: Tribromoacetamide. DBAAm: Dibromoacetamide. BCAAm: Bromochloroacetamide. BDCAAm: Bromodichloroacetamide. DBCAAm: Dibromochloroacetamide. BIAAm: Bromoiodoacetamide. ClaAm: Chloroiodoacetamide. DIAAm: Diiodoacetamide. Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). ECD: Electron Capture Detector. GC: Gas Chromatography. LLE: Liquid-Liquid Extraction. MS: Mass Spectrometry.

<b>a</b> .	Pool(s)	Disinfection		Inorganic Anions in	Swimming Pool Water (µg/	L); mean (min-max).		<b>D</b> 4
Country	Туре	Method	Bromide (Br <sup>-</sup> )	Bromate (BrO <sub>3</sub> <sup>-</sup> )	Chlorite (ClO <sub>2</sub> <sup>-</sup> )	Chlorate (ClO <sub>3</sub> <sup>-</sup> )	Nitrate (NO <sub>3</sub> <sup>-</sup> )	Reference
USA	Outdoor	NR				16000 (NR-124000)	8600 (NR-54000)	(Beech et al., 1980)
	Indoor	Cl		<10		(<20-15000)		
Australia	Indoor	Cl/Oz		(<10 -80)		(<20-110000)		(Kelsall and Sim, 2001)
	Indoor	Br/Oz		(<10-900)		<20		
Italy	Indoor	Cl				(190-12500)		(Aggazzotti et al., 2007)
Thailand	NR	NR	2200 (nd-3900)					(Panyakapo et al., 2008)
	Indoor	Cl					11000 (6600-24000)	
Korea	Indoor	Cl/Oz					13000 (1200-22000)	(Lee et al., 2010)
	Indoor	EGMO					23000 (11000-49000)	
a .	Indoor	Cl	<100					
Spain	Outdoor	Cl	<200					(Cardador and Gallego, 2011)
Portugal	Indoor	Various <sup>a</sup>			nd	(25-270)		(Riberio et al., 2011)
<b>F</b>	Indoor*	Cl	86000 (73000-107000)					(Denim et et el. 2012)
France	Indoor*	DCICA	(68000-70000)					(Parinet et al., 2012)
CI ·	Indoor	Cl	<2					
China	Outdoor	Cl	<2					(Xiao et al., 2012)
Australia	Outdoor	Cl	<5					(Yeh et al., 2014)
	Indoor	Various Cl		3 (<2-48)	(<20-22)	3700 (<5-20000)		
T. 1	Indoor	Cl				2000 (100-20000)		
Italy	Indoor	SDCIC				40 (5-60)		(Righi et al., 2014)
	Indoor	TCICA				1700 (200-4500)		
Denmark	NR	Cl					4.0 (2.2-6.1)	(Spiliotopoulou et al., 2015)
al :	Indoor	ClO <sub>2</sub>					51950 (13550-207610)	
China	Outdoor	Cl					37680 (12930-88350)	(Zhang et al., 2015)
Saudi Arabia	Indoor*	Cl	560 (160-1090)					(Chowdhury et al., 2016)
China	Indoor	Cl	nd				63000 (18000-129000)	(E et al., 2016)
	Indoor	Cl	78870 (72000-90500)					
France	Outdoor	Cl	200					(Manasfi et al., 2016)

### Table S10: Reported Occurrence of Inorganic Anions in Swimming Pool and Spa Waters

\*Seawater filled. a: Eight of the 54 pools investigated were sea water filled. nd: Not Detected. NR: Not Reported. Br: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). ClO<sub>2</sub>: Chlorine dioxide. DCICA: Dichloroisocyanuric acid. EGMO: Electrochemically-Generated Mixed-Oxidant. Oz: Ozone. SDCIC: Sodium dichloroisocyanurica. TCICA: Trichloroisocyanuric acid. Various: Refers to any of the following individually or in combination: Cl Based, SDCIC, chloroisocyanurate (CIC), DCICA, TCICA, Br based (NaBr or Br<sub>2</sub>) and/or ultraviolet (UV). Various Cl: Refers to any of the following individually or in combination: Cl Based, SDCIC, chloroisocyanurate (CIC), DCICA, TCICA, Br based (NaBr or Br<sub>2</sub>) and/or ultraviolet (UV).

<b>C (</b>			Total Organ	nic Halogen in Swimming Pool	Water (µg/L); mean (min-ma	x).	
Country	Pool(s) Type	Disinfection Method	тох	TOCI	TOBr	ΤΟΙ	Reference
	Indoor	Cl/Oz	(880-1080)				
Australia	Indoor	Cl	(930-1380)				(Kelsall and Sim, 2001)
	Indoor	Br/Oz	(810-970)				
Germany	Indoor	Cl	235				(Glauner et al., 2005)
	Outdoor	Cl	(161-177)				
Germany	Indoor	Cl		(124-136)			(Schmalz et al., 2011b)
	Indoor	Cl		246	4		
China	Outdoor	Cl		213	4		(Xiao et al., 2012)
	Indoor	Cl	1508	1490	15	3.2	
	Outdoor	Cl	699 (194-1150)	680 (193-1117)	18 (1.6-32)	0.6 (nd-1.3)	
Australia	Indoor	EGMO	1538	1524	12	1.3	(Yeh et al., 2014)
	Outdoor	EGMO	1049	1039	8	2.5	
	Baby	EGMO	(2894-3015)	(2825-2907)	(69-107)	(nd-1.3)	
	Indoor	Cl		3682 (1428-4828)	200 (137-280)		
	Indoor	BCDMH		1337 (1162-1511)	4897 (4106-5688)		
USA	Spa	BCDMH		1213 (950-1394)	4197 (2198-5444)		(Daiber et al., 2016)
	Spa	Br/TCICA		13860	18239		
	Spa	Cl/Oz		(1081-9512)	(53-84)		
Spain	Indoor	Cl	480 (420-570)	450 (390-550)	600 (500-800)		(Font-Ribera et al., 2016)

## **Table S11**: Reported Occurrence of Total Organic Halogen in Swimming Pool and Spa Waters.

nd: Not Detected. **TOBr**: Total organic bromine. **TOCI**: Total organic chlorine. **TOI**: Total organic iodine. **TOX**: Total organically bound halogen. **BCDMH**: 1-Bromo-3-chloro-5,5-dimethylhydantoin. **Br**: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). **Cl**: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). **EGMO**: Electrochemically-Generated Mixed-Oxidant. **Oz**: Ozone. **TCICA**: Trichloroisocyanuric acid.

	Disinfection		Trihalomethane Con	centration in Swimming Poo	ol Air (μg/m³); mean (min-ma	ax).	Collection height above	Collection		
Country	Method	Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane	Tribromomethane (Bromoform)	water's surface (cm)	Method	Analytical Method	Reference
Germany	Cl		117 (10-384)	9.5 (0.1-39)			Directly	XAD <sub>2</sub> -Resin	LD GC-MS/ECD	(Lahl et al., 1981)
Canada	Cl <sup>a</sup> Br <sup>a</sup>		154 (4-750)			747 (nd-1910)	10-20	Tenax	PT GC-MS	(Benoit and Jackson, 1987)
Italy	NR		214 (66-650)			/ I/ (Id 1)10)	150	Glass Vial	DI GC-MS	(Aggazzotti et al., 1990)
Canada	NR		1252 (507-1630)				150	Glass Vial	DI GC-MS	(Lévesque et al., 1994)
Germany	Cl		(7.8-191)	(nd-22.4)	(nd-2.9)		NR	NR	HS GC-ECD	(Cammann and Hübner, 1995)
Italy	NR		222 (16-853)				150	Glass Vial	DI GC-MS	(Aggazzotti et al., 1995)
Italy	NR		92 (69-103) <sup>a</sup> 170 (135-195) <sup>b</sup>	11 (7-14) <sup>b</sup> 20 (16-24) <sup>c</sup>	5.2 (4-7) <sup>b</sup> 11 (9-14) <sup>c</sup>	0.2 <sup>b</sup> 0.2 <sup>c</sup>	150	Glass Vial	DI CG-MS	(Aggazzotti et al., 1998)
Canada	Cl		(78-239)				Directly	Aluminized Bags	HS GC-EDC	(Lévesque et al., 2000)
Italy	NR	58	46	8.7	3.1	0.8	Directly	Tedlar Bags	DI GC-MS	(Fantuzzi et al., 2001)
Germany	NR		(85-235)				150	Activated Carbon	HS GC-ECD	(Erdinger et al., 2004)
Italy	Cl	(39-119)					NR	NR	HS GC-MS	(Aggazzotti et al., 2007)
Spain	Cl		242 (92-340)	9.1 (4.3-12)			50	Chromosorb 102	ATD GC-MS	(Caro et al., 2007)
Taiwan	NR		3510 (46-13000)				20-250	Summa Canisters	GC-MS	(Hsu et al., 2009)
France	Cl		39 (17-81)				100	Tenax	ATD GC-MS	(Thiriat et al., 2009)
Italy	Cl		85 (21-182) <sup>d</sup> 52 (12-127) <sup>e</sup>				150	Activated Carbon	LLE GC-MS	(Aprea et al., 2010)
Italy	Cl	81 (36-127)					NR	Tedlar Bags	DI GC-MS	(Fantuzzi et al., 2010)
Spain	Cl	74					NR	Tenax	PT GC-MS	(Kogevinas, 2010)
Spain	Cl	74 (44-125)	35 (19-62)	15 (7.5-24)	13 (6-26)	11 (4-23)	60	Tenax	PT GC-MS	(Font-Ribera et al., 2010c)
Spain	Cl BCDMH		32 (12-62) 4.4 (1.7-9.4)	15 (7.5-23) 2.9 (1.7-4.8)	14 (6.1-26) 7.3 (6.1-9.7)	11 (4.4-23) 75 (53-101)	60	Tenax	ATD GC-MS	(Richardson et al., 2010)
France	Cl		75 (1.5-793)		× ,	, , ,	NR	Tenax	ATD GC-MS	(Bessonneau et al., 2011)
Portugal	Cl	(98-1225) (51-519)					5 150	Glass Vial	HS-SPME GC-ECD	(Sa et al., 2011)
Spain	Cl Br		32 (18-61) 4.5 (1.8-6.9	15 (8.2-23) 3 (1.9-4.2)	14 (6.4-22) 7.3 (6.4-8.7)	6.4 (5.9-22) 75 (55-92)	60	Tenax	ATD GC-ECD	(Lourencetti et al., 2012)
Canada	Cl	130 (47-311)	129 (46-307)	1.6 (nd-4.3)	· · · · ·	× ,	30 and 150	Activated Carbon	LD-USH GC-ECD	(Catto et al., 2012)
	Cl	90 (34-180)	89 (34-178)	1.1 (nd-2.6)						
Portugal	Cl		(45-373)				30	Activated Carbon	HS-SPME GC-ECD	(Silva et al., 2012)
Taiwan	Cl		36 (13-182)				150	-	OP-FTIR	(Chen et al., 2016)
Canada	Cl	195 (117-320) 60 (2.9-140) <sup>f</sup>	148 (54-241) 53 (2.7-134) <sup>f</sup>	25 (3.8-86) 4.9 (0.1-16) <sup>f</sup>	16 (0.2-95) 1.9 (nd-4.8) <sup>f</sup>	9.6 (nd-36) 1.2 (nd-1.8) <sup>f</sup>	- 150	Activated Carbon	LD GC-ECD	(Tardif et al., 2015)
Saudi Arabia	Cl*	83 (36-134)					60	Tenax	ATD GC-ECD	(Chowdhury et al., 2016)
Canada	Cl	191 (58-552)	119 (20-320)	31 (1.3-155)	27 (nd-205)	14 (nd-103)	150	Activated Carbon	LD GC-ECD	(Tardif et al., 2016)
		· · · · /	× · · · · /	· · · · · /	· · · · · /	· · · · · · · · · · · · · · · · · · ·				(

## Table S12: Reported Occurrence of Trihalomethanes in the Ambient Air of Indoor Swimming Pool Complexes.

a: Spa. b: No water activity. c: During water activities – swimmers. d: Sampling over 9 hours. e: Sampling over 24 hours. f: Offices. nd: Not Detected. NR: Not Reported. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin. Br: Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). ATD: Automatic Thermal Desorption. DI: Direct Injection. ECD: Electron Capture Detector. FTIR: Fourier Tranform Infrared Spectroscopy. GC: Gas Chromatography. HS: Headspace. LD: Liquid-Desorption. LLE: Liquid-Liquid Extraction. MS: Mass Spectrometry. OP: Open Path. PT: Purge and Trap. SPME: Solid-Phase Microextraction. USH: Ultrasound Heating.

Country	Disinfection Method	Trichloramine (NCl <sub>3</sub> ) Concentration in Swimming Pool Air (µg/m <sup>3</sup> )	Collection height above water's surface (cm)	Collection Method	Analytical Method	Reference
Belgium	Cl	(250-450)	NR	NR	NR	(Bernard et al., 2006)
Netherlands	Cl/Oz <sup>a</sup>	560 (130-1340)	30	Quartz Fibre <sup>c</sup>	LD-IC-MS	(Jacobs et al., 2007)
Netherlands	CI/OZ "	660 (380-1100) <sup>b</sup>	150	Quartz Fible	LD-IC-MS	(Jacobs et al., 2007)
с. :	Cl	290 (170-430)	60			
Spain	BCDMH	80 (70 -100)	60	Quartz Fibre <sup>c</sup>	LD-IC-MS	(Richardson et al., 2010)
France	Cl	190 (20- 1260)	NR	Quartz Fibrec	LD-IC-MS	(Bessonneau et al., 2011)
Germany	Cl	(160-190)	NR	NR	NR	(Schmalz et al., 2011a)
Canada	Cl	180 (80-350)	150	Activated Carbon	LD-USH-GC-ECD	(Catto et al., 2012)
Switzerland	Various Cl	110 (1-890)	NR	Quartz Fibre <sup>c</sup>	LD-IC-MS	(Parrat et al., 2012)
Italy	NR	637 (204-1020)	150	Glass Vial	DPD/KI Colorimetric	(Predieri and Giacobazzi, 2012)
Taiwan	NR	(20-150)	100	Quartz Fibrec	LD-IC-MS	(Chu et al., 2013)
Sweden	NR	200 (40-360)	130	Quartz Fibrec	LD-IC-MS	(Fornander et al., 2013)
USA	Cl	150 (nd-620)	NR	Glass Vial	DPD/KI Colorimetric	(Afifi and Blatchley, 2015)
Canada	Cl	380 (110-700)	30	Pallflex Tissuquartz <sup>d</sup>	IC	(Lévesque et al., 2015)
Canada	Cl	270 (60-450) <sup>b</sup>	150	Teflon <sup>e</sup>	LD-IC-MS	(Tardif et al., 2015)
Sweeden	Cl	130 (20-290)	130	NR <sup>e</sup>	IC	(Johannesson et al., 2016)
		230 (nd-560) <sup>b</sup>	150	T (1 e		
Canada	Cl	150 (70-320) <sup>f</sup>	150	Teflon <sup>e</sup>	LD-IC-MS	(Tardif et al., 2016)
Spain	Cl	473 (249-858)	150	Quartz Fibre <sup>c</sup>	LD-IC-MS	(Font-Ribera et al., 2016)

## **Table S13**: Reported Occurrence of Trichloramine in the Ambient Air of Indoor Swimming Pool Complexes.

a: Number of pools treated with chlorine (76%), salt electrolysis (11%) chlorine/salt electrolysis (5%) and ozone/chlorine (8%). b: Refers to total chloramines (sum of mono-, di- and tri-chloramine). c: Injected with diarsenic-trioxide, sodium carbonate and glycerol. d: Cellulose filter impregnated with sodium carbonate. e: Filter media impregnated with sodium carbonate and arsenic trioxide. f: Refers to monochloramine. NR: Not Reported. BCDMH: 1-Bromo-3-chloro-5,5-dimethylhydantoin.. Cl: Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). Oz: Ozone. Various Cl: Refers to any of the following individually or in combination: Cl Based, Sodium dichloroisocyanurate (SDCIC), chloroisocyanurate (CIC), dichloroisocyanuric acid (DCICA) and/or trichloroisocyanuric acid (TCICA). DPD: diethyl-*p*-phenylenediamine. ECD: Electron Capture Detector. GC: Gas Chromatography. IC: Ion Chromatography. KI: Potassium Iodide. LD: Liquid-Desorption. MS: Mass Spectrometry. USH: Ultrasound Heating.

Country Pool(s) Type		Disinfanti M-41-	Total Carbon, Total Nitrogen an	nd Urea in Swimming Pool Wate	r (mg/L); mean (min-max).	Daf
Country	Pool(s) Type	Disinfection Method	Total Organic Carbon (TOC)	Total Nitrogen (TN)	Urea	Reference
Canada	Spa	Br	111 (5-345)			(Benoit and Jackson 1987)
	Spa	Cl	36 (1-155)			· · · · · · · · · · · · · · · · · · ·
England	Indoor	NR	6.3 (3.3-13)			(Chu and Nieuwenhuijsen 2002)
Japan	Outdoor	NR			(0.2-0.7)	(Tachikawa et al., 2005)
Germany	Indoor	Cl	1.7			(Glauner et al. 2005)
Germany	Outdoor	Cl	(1.6-2)			(Glatifier et al. 2003)
Thailand	NR	NR	1.1 (0.6-1.5)			(Panyakapo et al. 2008)
Thanana			0.9 (0.6-1.5) <sup>a</sup>			(Tanyakapo et al. 2000)
	Indoor	Cl	4.4 (0.2-71)			
Korea	Indoor	Cl/Oz	3.7 (0.2-82)			(Lee et al. 2009)
	Indoor	EGMO	3.5 (0.4-12)			
USA	Indoor	Cl	7.1 (3-24)	3.6 (0.8-12)		(Kanan 2010)
	Indoor	Cl	2.3 (0.5-7)			
Korea	Indoor	Cl/Oz	1.7 (0.7-3)			(Lee et al. 2010)
	Indoor	EGMO	3.2 (1.9-5.8)			
France	Indoor	Cl	3.5 (1.6-7.3)		1.1 (0.1-3.7)	(De Laat et al. 2011)
France	Indoor	Cl	3.1 (1.8-7.3)			(Bessonneau et al. 2011)
Germany	Indoor	Cl	1.3ª		0.8	(Schmalz et al., 2011b)
Germany	Various	NR			1.3 (0.5-2.1)	(Schmalz et al., 2011a)
	Indoor	Cl/UV	(5.2-18)			
	Indoor	BCDMH	125			
USA	Indoor	Cl	23 (13-33)			(Plewa et al., 2011)
	Outdoor	Cl	33			
	Spa	Cl	12			
Portugal	Indoor	Cl	4 (1.13-6.7)			(Sa et al., 2011)
e	Indoor	Cl	2.1 (0.02-4.4)			
Canada	Outdoor	Cl	6.2 (0.02-16			(Wang, 2011)
USA	Indoor	Cl	× · · · · · · · · · · · · · · · · · · ·		(<0.1-0.3)	(Weng and Blatchley, 2011)
-	Indoor	Cl	4.8 (3.6-8.6)	3 (0.7-7.7)		
France	Indoor	DCICA	(2.8-3.3)	(1.3-2.7)		(Parinet et al., 2012)
	Indoor	Cl	3.2			
China	Outdoor	Cl	2.8			(Xiao et al., 2012)
Portugal	NR	NR	5.4 (2.4-7.4)			(Prieto-Blanco et al., 2012)
Switzerland	Indoor	NR			0.3 (nd-2)	(Parrat et al., 2012)
			12 (10-15)			
<i>a</i> 1	Indoor	Cl/UV	7.3 (4.9-9.5 ª			
Canada	<b>.</b> .		13 (11-16)			(Wang et al., 2013)
	Indoor	Cl	7.9 (5.9-11) <sup>a</sup>			
	0 í			2.9 (0.6-4.6)		····
Australia	Outdoor	Cl	3.4 (3.1-3.9)	0.4 (0.1-0.7) <sup>b</sup>		(Yeh et al., 2014)
Switzerland	Various	Various		()	0.3 (<0.1-0.6)	(Soltermann et al., 2014)
USA	Indoor	Cl			0.1	(Afifi and Blatchley, 2015)
Portugal	Indoor	NR	7.2 (7.1-7.3)			(Maia et al., 2014)
- ortugui	Indoor	NR	4.7 (1.3-8.4)			(1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.
USA	Outdoor	NR	2.5 (0.9-8.5)			
0011	Spa	NR	8.1 (3.7-11)			(Wang et al., 2014)
	Indoor	NR	11 (2.7-27)			(wang ti al., 2014)
China	Outdoor	NR	9.5 (nd-13)			
		Cl				
Australia	Indoor	Cl	5.7 (3.6-7.2) 12			(Carter et al., 2015)
<b>D</b> ·	Spa					
Denmark	NR	Cl	1.9 (1.6-2.2)			(Spiliotopoulou et al., 2015)

# **Table S14**: Reported Occurrence of Total Organic Carbon, Total Nitrogen and Urea in Swimming Pool and Spa Waters.

China	Indoor Outdoor	Cl/Oz Cl	8.9 (2.5-27) 9.5 (3.2-13)	2.2 (0.2-11) <sup>b</sup> 0.9 (0.2-1.3) <sup>b</sup>	(Zhang et al., 2015)
Saudi Arabia	Indoor*	Cl	2.1 (1.3-3.9) 1.9 (1.0-3.6) <sup>a</sup>		(Chowdhury et al., 2016)
Spain	Indoor	Cl	2.4 (1.8-10)		(Font-Ribera et al., 2016)
China	Indoor	Cl/Oz	13 (8.0-25) <sup>a</sup>		(Hong et al. 2016)
China	Indoor	Cl	22 (4.2-39) <sup>a</sup>		(Hang et al., 2016)
France	Indoor	Cl	11 (10-12)		(Manasfi et al., 2016)
Trance	Outdoor	Cl	11		(Malash et al., 2010)
China	Outdoor	Cl	1.1 (NR)		(Tang and Xie, 2016)
Canada	Indoor	Cl	1.0 (1.4-10) <sup>a</sup>		(Tardif et al., 2016)
China	Outdoor	Cl	4.5 (1.06.5)	5.8 (4.1-8.4)	(Yang et al., 2016)

\*Sea water filled. **a:** Reported as dissolved organic carbon (DOC). **b:** Reported as Total Organic Nitrogen (TON). **nd:** Not Detected. **NR:** Not Reported. **Br:** Bromine Based (NaBr in combination with an oxidiser or Br<sub>2</sub>). **CI:** Chlorine Based (NaOCl, Ca(OCl)<sub>2</sub> or Cl<sub>2</sub>). **BCDMH:** 1-Bromo-3-chloro-5,5-dimethylhydantoin. **DCICA:** Dichloroisocyanuric Acid. **EGMO:** Electrochemically-Generated Mixed-Oxidant. **Various:** Refers to any of the following individually or in combination: CI Based, Br Based.

 Table S15: Common and other names of selected personal care products.

Antifungal Age	nts
Dichlorophen	Dichlorophene; 4-chloro-2-[(5-chloro-2-hydroxyphenyl)methyl]phenol; eptiphene; <i>o</i> -benzyl- <i>p</i> -chlorophenol; <i>ortho</i> -benzyl- <i>p</i> -chlorophenol; benzylchlorophenol; 5-chloro-2-hydroxydiphenylmethane; 4-chloro-alpha-phenyl- <i>o</i> -cresol; chlorofene; 4-chloro-2-(phenylmethyl)phenol; benzyl- <i>p</i> -chlorophenol; 4-chloro-alpha-phenylcresol; 2-benzyl-4-chlorophenol; 4-chloro-2-(phenylmethyl)phenol; 5-chloro-2-hydroxydiphenylmethane; <i>o</i> -benzyl <i>para</i> chlorophenol; <i>p</i> -chloro- <i>o</i> -benzylphenol; ketolin-h; santophen 1; neosobenil; sentiphene clorofenum
2,4-DCPh	<b>5-chloro-(2,4-dichlorophenoxy)phenol</b> ; 2,4,4'-trichloro-2'-hydroxydiphenyl ether; trichloro-2'-hydroxydiphenyl ether; triclosan; CH-3565, Lexol 300, Irgasan DP 300, Ster-Zac
2,4,6-TCPh	2,4,6-trichlorophenol; phenaclor; Dowicide 2S; Dowcide 2S; omal
Parabens	
MeP	methylparaben; methyl-4-hydroxybenzoate; methyl p-hydroxybenzoate; methyl parahydroxybenzoate; Nipagin M; E218; Tegosept; Mycocten
EtP	<b>ethylparaben</b> ; ethyl-4-hydroxybenzoate; ethyl <i>para</i> hydroxybenzoate; ethyl <i>para</i> -hydroxybenzoate; ethyl- <i>p</i> -hydroxybenzoate; 4-hydroxybenzoic acid ethyl ester; E214
PrP	propylparaben, propyl-4-hydroxybenzoate; 4-hydroxybenzoesäurepropylester; propyl-p-hydroxybenzoate; propyl parahydroxybenzoate; nipasol; E216
iPrP	isopropylparaben
BuP	butylparaben; butyl-4-hydroxybenzoate; butyl-parahydroxybenzoate; butyl-p-hydroxybenzoate
iBuP	isobutylparaben
PeP	pentylparaben; pentyl-4-hydroxybenzoate; amyl-4-hydroxybenzoate; pentyl-p-hydroxybenzoate; n-pentyl-4-hydroxybenzoate
HeP	<b>heptaparaben</b> ; heptyl- <i>p</i> -hydroxybenzoate; heptyl-4-hydroxybenzoate; n-heptyl-4-hydroxybenzoate; n-heptyl- <i>p</i> -hydroxybenzoate; heptyl- <i>para</i> -hydroxybenzoate; nipaheptyl; E209
OcP	octylparaben; octyl-4-hydroxybenzoate; n-octyl-4-hydroxybenzoate; octyl-p-hydroxybenzoate
BzP	<b>benzylparaben</b> ; benzyl-4-hydroxybenzoate; benzyl <i>p</i> -hydroxybenzoate; benzyl <i>para</i> hydroxybenzoate; phenylmethyl 4-hydroxybenzoate; nipabenzyl; parosept; benzyl parasept
UV-Filters	
Amiloxate	<b>isoamyl 4-methoxycinnamate</b> ; 3-methylbutyl-(2 <i>E</i> )-3-(4-methoxyphenyl)acrylate; isopentyl 4-methoxycinnamate; isoamyl- <i>p</i> -methoxycinnamate
Avobenzone	<b>avobenzone</b> ; 1-(4-methoxyphenyl)-3-(4- <i>tert</i> -butylphenyl)propane-1,3-dione; butylmethoxydibenzoylmethane; 4- <i>tert</i> -butyl-4'-methoxydibenzoylmethane; Eusolex 9020; Parsol 1789; Milestab 1789; Escalol 517; Neo Heliopan 357
BP-1	2,4-dihydroxybenzophenone
BP-2	2,2',4,4'-tetrahydroxybenzophenone
BP-3	<b>benzophenone-3</b> ; oxybenzone; (2-hydroxy-4-methoxyphenyl)-phenylmethanone; 2-hydroxy-4-methoxybenzophenone; Eusolex 4360; Milestab 9; Escalol 567; KAHSCREEN BZ-3
BP-8	2,2'-dihydroxy-4-methoxybenzophenone
BzS	benzyl salicylate; benzyl 2-hydroxybenzoate
4-DHB	4, 4'-dihydroxybenzophenone
DMeBT	5,6-dimethyl-1 <i>H</i> -benzotriazole monohydrate
Et-PABA	ethyl 4-aminobenzoate
4-HB	4-hydroxybenzophenone
1HBT	1H-benzotriazole
Homosalate	3,3,5-trimethylcyclohexyl-2-hydroxybenzoate; Eusolex HMS
4-MBC	4-methylbenzylidene camphor; enzacamene; (3E)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]-2-norbornanone; 3-(4-methylbenzylidene)bornan-2-one;

	3-(4-methylbenzylidene)-dl-camphore; Eusolex 6300
OCR	octocrylene; 2-ethylhexyl-2-cyano-3,3-diphenyl-2-propenoate; 2-ethylhexyl-2-cyano-3,3-diphenylacrylate; Eusolex OCR
OD-PABA	octyldimethyl-para-aminobenzoic acid; 2-ethylhexyl-4-(dimethylamino)benzoate; Padimate O; Escalol 507; Sundown
OMC	octylmethoxycinnamate; (RS)-2-ethylhexyl-(2E)-3-(4-methoxyphenyl)prop-2-enoate; ethylhexyl-methoxycinnamate; (E)-3-(4-methoxyphenyl)-prop-2-enoic
OMC	acid 2-ethylhexyl ester; octinoxate; Eusolex 2292; Uvinul MC80
PBS	2-phenyl-3H-benzimidazole-5-sulfonic acid; Ensulizole
PS	phenyl salicylate; phenyl 2-hydroxybenzoate
THB	2,3,4-trihydroxybenzophenone

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