

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

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8 **Abstract**

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

28 Swimming pool chemical water quality is currently a topic of interest, with many studies occurring in
29 both the United States and Europe. Swimming pool chemical water quality is of possible public health
30 concern due to the formation of disinfection by-products (DBPs), where total DBP concentrations have
31 been shown to progressively increase in pools and spas (up to 610% and 900%, respectively) compared to
32 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
35 health effects of DBPs may be more pronounced. Uptake of DBPs are likely increased in children
36 compared to adults due to higher breathing rates of children (up to twice those of adults) and their lesser
37 developed gastrointestinal tracts and blood brain barriers possibly leading to higher absorption of DBPs
38 (Thompson, 2004). Additionally, children's organs are not fully developed, particularly the liver and
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
41 able to metabolise and remove DBPs sufficiently (Thompson, 2004). DBPs in swimming pools have been
42 potentially linked to several health issues, including asthma, bladder cancer, liver and kidney issues
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
45 water (Liviak et al., 2010b), which is likely due to more than one mutagen (Honer et al., 1980).
46 Respiratory issues, such as asthma, wheeze, cough and lower respiratory tract infections, have been
47 correlated with swimming pool attendance, which is likely due to chlorinated volatile DBPs, such as
48 chloramines (Bernard et al., 2006; Ferrari et al., 2011; Jacobs et al., 2007; Kaydos-Daniels et al., 2008;
49 Rosenman et al., 2015; Uyan et al., 2009). However, these studies are not conclusive and Goodman and
50 Hays (2008) suggested that "it is premature to draw conclusions about the causal link between swimming
51 and asthma", warranting further investigation of the health effects of the swimming pool environment.

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

58 Disinfection is essential to protect against the microbial disease risk in pools (Montgomery, 1985).
59 Studies of comparison of microbial disease and DBP risks in pools are limited, but, in drinking waters,
60 the risk of death or illness from pathogens is much higher than the risk of cancer from DBPs (Ashbolt,
61 2004; WHO, 2000). Although chlorine based disinfectants, calcium or sodium hypochlorite and chlorine
62 gas, are more commonly used (Montgomery, 1985), other disinfectants including chlorine dioxide (ClO₂),
63 chloroisocyanurates or their acid counterparts, bromine gas, sodium bromide (in combination with a
64 chlorine oxidiser), bromochlorodimethylhydantoin (BCDMH) or electrochemically generated mixed
65 oxidant (EGMO) can be employed for swimming pool disinfection.

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 (OCl^-) and hypobromite (OBr^-). All active
69 species (the acids (HOCl/HOBr) and the ions ($\text{OCl}^-/\text{OBr}^-$)) have the ability to inactivate microorganisms
70 and react with organic matter, leading to the formation of organic DBPs, chloride (Cl^-) and bromide (Br^-).
71 Hypochlorous acid is approximately 100 times more effective than the hypochlorite ion, whilst HOBr is
72 the stronger oxidising species (Chow et al., 2014). These reactions, and hence disinfectant speciation, are
73 both pH and chloride dependent (E et al., 2016; Hansen et al., 2012b), and care should be taken to
74 maximise the dominance of the more powerful oxidant species to ensure maximum disinfection power,
75 although DBP formation rates and the behaviour of DBP precursors will also be influenced by these more
76 reactive disinfectant species. Unlike other chlorine containing disinfectants, ClO_2 does not produce
77 HOCl : ClO_2 does not hydrolyse in water, rather it remains as a dissolved gas, with oxidation occurring
78 via electron exchange mechanisms (NRC, 1980). The other oxidants, BCDMH or EGMO (the production
79 of oxidants via the electrolysis of waters rich in sodium chloride), are also used as disinfectants in
80 swimming pool waters, however their chemistry is not as straightforward. BCDMH results in both HOCl
81 and HOBr (Elsmore, 1994), whilst EGMO leads to the presence of several oxidising species: HOCl ,
82 HOBr , ozone and hydrogen peroxide (Kraft et al., 1999; Patermarakis and Fountoukidis, 1990), with
83 HOBr and HOCl being the dominating species for BCDMH and EGMO, respectively. A detailed
84 discussion of the chemistry of swimming pool disinfectants is provided in **Section 2** below.

85 There is currently no international standard for the treatment of swimming pools, with regulations
86 often provided by state or local governing bodies. For example, the USA’s Centre for Disease Control
87 (CDC) have released the ‘Model Aquatic Health Code’ (MAHC) which other governing bodies are
88 encouraged to adopt (CDC, 2016). Similarly, the Australian National Health and Medical Research
89 Centre (NHMRC) encourages Australian pool operators to adopt their ‘Guidelines for managing Risks in
90 Recreational Waters’ (NHMRC, 2008), whilst the DIN 19643 is regulation in Germany (German Institute
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
96 understanding of treatment methods is required. Development of international swimming pool guideline
97 recommendations, similar to the World Health Organisation’s “Guidelines for Drinking Water Quality”,
98 would be beneficial in assisting governing bodies worldwide to develop local guidelines based on their
99 local requirements. Since the required free chlorine equivalent residual in swimming pools is higher than
100 that reported in drinking water distribution systems (e.g. minimum 0.2 mg/L, Chow et al., 2014) and there
101 is a build-up of organic compounds in swimming pool waters such that the total organic carbon content is
102 usually much higher (e.g. <33 mg/L, Plewa et al., 2011) than that detected in drinking waters (e.g. 1.8 to

103 3.6 mg/L, McDonald et al., 2013), DBP formation is a magnified issue in swimming pool waters
104 compared to drinking waters.

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

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

133 There are three DBP uptake mechanisms applicable to the swimming pool environment: ingestion,
134 absorption and inhalation. Ingestion and absorption both occur during swimming activities as some water
135 is often accidentally swallowed and DBPs may be absorbed through the skin. For example, Dufour et al.
136 (2006) found the average volume of water ingested by adults during a 45 minute swim was 16 mL (21
137 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)
140 investigated trihalomethanes (THMs), halo ketones (HKs) and haloacetic acids (HAAs), reporting that
141 THMs had the highest skin permeability, with brominated THMs being more permeable than chlorinated
142 THMs. HKs were reported to be less permeable to human skin than THMs, but more permeable than
143 HAAs, which showed almost no permeability (Xu et al., 2002). Haloacetonitriles (HANs) were
144 investigated by Trabaris et al. (2012), with dibromoacetonitrile being found to have the highest
145 permeability to human skin, whilst chloroacetonitrile had the least. HANs were shown to be less
146 permeable to human skin than chloral hydrate (Trabaris et al., 2012). Both studies correlated an increase
147 in temperature to increased human skin permeability of selected DBPs (Trabaris et al., 2012; Xu et al.,
148 2002). Inhalation is particularly important for volatile DBPs and has been reported to be the major route
149 of human exposure of DBPs in the swimming pool environment (Aggazzotti et al., 1998; Aprea et al.,
150 2010; Chen et al., 2011; Erdinger et al., 2004). In the swimming pool environment, THM uptake via
151 inhalation has been estimated to have a higher associated cancer risk than uptake via ingestion or dermal
152 routes (Lee et al. 2009), where estimations were calculated using the US EPA guidelines for carcinogen
153 risk assessment and the Swimmer Exposure Assessment Model using standard values from the US EPA
154 Exposure Factors Handbook. Similar results were reported by Chen et al. (2011), who found that 99% of
155 the risk arising from THM exposure was due to inhalation of chloroform. . An increase in water
156 temperature, swimming activity and blowers/jets causes an increased volatilization rate of volatile DBPs
157 and hence this inhalation uptake mechanism can become of high importance, particularly for indoor
158 heated swimming pools (Aggazzotti et al., 1998; Kristensen et al., 2010; Marco et al., 2015).

159 Currently, few guidelines appear to exist worldwide for the concentrations of DBPs specifically in
160 the swimming pool environment. DBPs are regulated in drinking waters; however, due to the uptake
161 mechanism ratio shift from ingestion (drinking waters) to inhalation (swimming pool waters), the
162 drinking water DBP guidelines may not be directly applicable to assess the health risk associated with
163 DBPs in swimming pool waters. Drinking water guidelines may, however, act as an indicative health
164 guideline value where no swimming pool specific guideline value exists. Current swimming pool specific
165 regulations mainly provide health guidelines for chloramines (measured as combined chlorine), which are
166 encouraged to be no greater than half that of the free chlorine equivalent concentrations in pool water,
167 although lower ideal concentrations (less than 0.2 to 0.4 mg/L) have been suggested (CDC, 2016; WHO,
168 2006). Trichloramine in the swimming pool air has also been regulated, with WHO (2006) recommending
169 maximum concentrations of 0.5 mg/m³, although some European countries propose a lower guideline for
170 trichloramine in the air of indoor swimming pool complexes, 0.2 to 0.3 mg/m³ (Cassan et al., 2011;
171 Umweltbundesamtes, 2011). THMs are the only organic DBP class known to be regulated in swimming
172 pool waters. For the total THM concentrations (sum of trichloro-, bromodichloro-, dibromochloro- and
173 tribromo-methane), the German standard DIN 19643 suggests a guideline value of 20 µg/L in swimming

174 pool waters (German Institute for Standardization, 2012), whilst Denmark's Statutory Order no 623
175 recommends total THM concentrations do not exceed 25 µg/L in pool waters (Lovtidende, 2012).

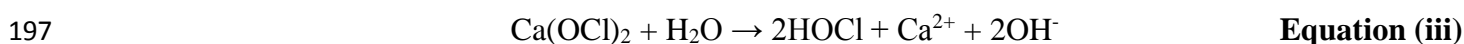
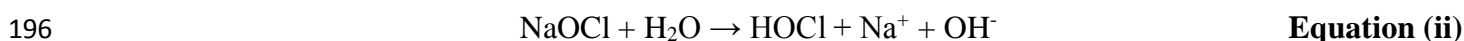
176 This critical review summarises chemical contaminants and DBPs reported in swimming pool waters,
177 as well as in air above swimming pools. Factors that have been found to affect DBP formation in pools
178 are also discussed. The impact of the swimming pool environment on human health is reviewed.

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

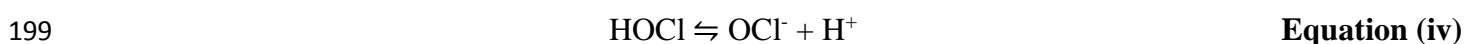
180 Although many oxidants can form by the addition of one disinfectant to water, the type of the
181 disinfectant (chlorine or bromine based) refers to the most dominant species. Although specific
182 disinfectants will be provided in some examples, for the purpose of this review, chlorination (treated by
183 chlorine) refers to the use of disinfectants where HOCl is the primary oxidant (sodium hypochlorite
184 (NaOCl), calcium hypochlorite (Ca(OCl)₂), chlorine gas (Cl₂), sodium dichloroisocyanurate (SDCIC),
185 chloroisocyanurate (CIC), dichloroisocyanuric acid (DCICA) or trichloroisocyanuric acid (TCICA)),
186 whilst bromination (treated by bromine) refers to the use of disinfectants where HOBr is the primary
187 oxidant, the main examples being bromochlorodimethylhydantoin (BCDMH) and sodium bromide
188 (NaBr) in the presence of an oxidant. EGMO and ClO₂ will be discussed separately to other disinfectants,
189 where possible. Waters which are treated in combination with a secondary treatment (e.g. UV or ozone)
190 will be distinguished from those treated solely by disinfectants.

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.



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



200 Both HOCl and OCl⁻ have the ability to inactivate microorganisms (disinfect), as well as react
201 with organic matter leading to the formation of Cl-DBPs and oxidised organic matter/ chloride. Although
202 the predominant chlorine species is HOCl, the highly reactive, but less abundant, electrophiles, Cl₂O and
203 Cl₂, may also be present in swimming pool waters and, due to their higher reactivity compared to HOCl
204 (De La Mare et al., 1975), may be responsible for the formation of some Cl-DBPs. In a study of aromatic

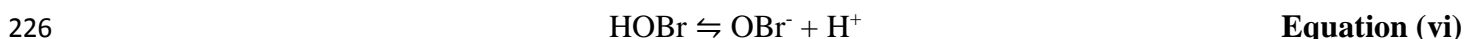
205 ethers, (Sivey and Roberts, 2012),. Although unexplored specifically in swimming pools, Cl₂O and Cl₂
206 were shown to be important species in generation of DBPs from aromatic ether DBP precursors of
207 moderate reactivity (Sivey and Roberts, 2012).

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

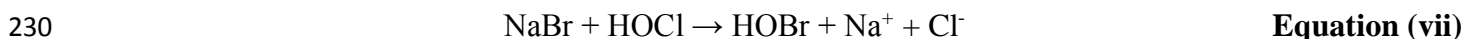
214 In pools, the majority of chlorine (97%) is bound to the cyanurates which are poor oxidants
215 compared to HOCl, but despite this and due to the equilibrium, as HOCl is depleted, chlorinated
216 cyanurates ‘release’ chlorine to reform HOCl, and hence maintain the desired free chlorine residual.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

221 **2.2. Bromine Based Disinfectants**

222 Similar to the formation of HOCl and OCl⁻ via chlorine based disinfectants, bromine based
223 disinfectants result in the formation of HOBr, which further dissociates to OBr⁻ as per **Equations (v)** and
224 **(vi)**.



227 Unlike Cl₂, bromine gas is rarely used as a disinfectant, instead HOBr may be formed by
228 combining sodium bromide (NaBr) with an oxidant (usually chlorine based, although ozone is often
229 used), as per **Equation (vii)**.



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

234 The most common bromine based disinfectant is BCDMH, which forms both HOBr and HOCl in
235 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).

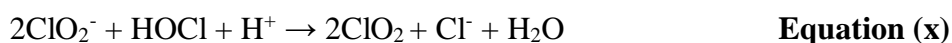


2.3. Chlorine Dioxide

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, ClO₂ does not produce HOCl as it does not hydrolyse in water. ClO₂ remains as a stable free radical (ClO₂[•]), where it reacts by radical mechanisms with electron rich moieties following **Equation (ix)**, where the source of the e⁻ is electron rich moieties (e.g. lone electron pairs on amines or phenolates) present in organic matter, and leads to the formation of chlorite (ClO₂⁻).



This reaction leads to the formation of highly reactive organic radical moieties which may be further oxidised by ClO₂ 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)**.

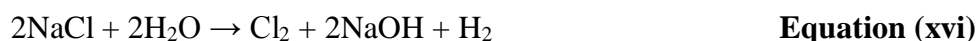


2.4. Electrochemically Generated Mixed Oxidant

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 Cl₂. Electrolysis of water involves an anodic reaction (**Equation xii**) and a cathodic reaction (**Equation xiii**), where the overall process is shown in **Equation xiv**.



Disinfection is achieved by the production of Cl₂, which is formed as a secondary reaction at the anode (**Equation xv**), where **Equation xvi** represents the overall equation.



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.



Ozone and hydrogen peroxide are also formed during EGMO disinfection, although to a much smaller extent than the formation of Cl₂, as per **Equations xviii** and **xix**, respectively. Furthermore, if bromide is present, HOBr may be produced as per **Equation viii**.



3. Disinfection By-Products: Occurrence in Swimming Pool and Spa Waters and the Ambient Air Above Pools

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 the most comprehensive study of DBPs in swimming pools was that of Richardson et al. (2010), who 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 investigation of five chlorinated and two brominated public swimming pools in Spain. Similarly, Daiber et al (2016) identified over 100 DBPs (iodo-THMs, bromoimidazoles, bromoanilines, haloacids, halonitriles, haloamides, halonitromethanes, haloaldehydes, halophenols, halobenzenes, halobenzenediols, bromomethanesulfenic acid esters, aldehydes, ketones, and an organic chloramine), including a range of newly reported DBPs (bromoimidazoles, bromoanilines, bromomethanesulfenic acid esters), in a range of swimming pools and spas treated by either chlorine or bromine based disinfectants. Although many different types of swimming pools exist, the majority of studies have primarily focused on chlorinated swimming pools, particularly those located indoors. Similarly, the ambient air of indoor 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 discuss overall trends for the occurrence of DBPs in the swimming pool environment: both swimming pool water and the ambient air of indoor swimming pool complexes. **Table 2** summarises the range of average concentrations for selected DBPs in swimming pool waters, with **Tables S1-S11** providing a

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

299 **3.1. Occurrence in Swimming Pool and Spa Waters**

300 **3.1.1. Trihalomethanes**

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

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

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

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.

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

337 **3.1.2. Haloacetic Acids**

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

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

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

358 **3.1.3. Inorganic Halamines**

359 Chloramines have been investigated in swimming pools and spas, with their average occurrence
360 summarised in **Table 2** and a more complete summary provided in **Table S3**. Regardless of pool type or
361 treatment method, trichloramine was generally the dominant chloramine, followed by di- and mono-
362 chloramine, although, as discussed in **Section 5.5**, pH plays an important role in DBP occurrence,
363 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 $\mu\text{g/L}$ and between 110 to 490 $\mu\text{g/L}$ have been reported, respectively
366 (Chowdhury et al., 2016; Wang et al., 2014; Weaver et al., 2009). Generally (**Table 2**), brominated pools
367 had lower concentrations of chloramines compared to chlorinated pools, where maximum concentrations
368 between 18 and 300 $\mu\text{g/L}$ have been reported (Daiber et al., 2016; Richardson et al., 2010). Brominated
369 spas contained slightly higher concentrations of chloramines than brominated pools, up to 363 $\mu\text{g/L}$
370 (Daiber et al., 2016), which is likely due to the higher release of human derived chloramine precursors
371 and an increased formation due to the higher operating temperature used in spas, as discussed in **Section**
372 **5.5**.

373 Bromamines are known to form in the presence of ammonia in chlorinated waters (NRC, 1980).
374 Despite the possibility that other halamines (e.g. bromamines, mixed bromochloramines) may be present
375 in the swimming pool environment, their occurrence has yet to be investigated due to the lack of suitable
376 analytical methods. Further work is required to develop such analytical methods in order to fully
377 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
380 reported to date and they have mainly focused on bromochloro-, dibromo-, dichloro- and trichloro-
381 acetonitrile (BCAN, DBAN, DCAN and TCAN, respectively), as summarised in **Tables 2** and **S4**.
382 Chlorinated and brominated species dominated pools treated with chlorine and bromine, respectively,
383 with BCAN concentrations reported higher in chlorinated pools compared to those treated with bromine.
384 Of the HANs investigated, DCAN and DBAN were generally the most abundant in pools treated with
385 chlorine and bromine, respectively, with maximum concentrations of 89 and 39 $\mu\text{g/L}$ being reported
386 (Daiber et al., 2016; Hang et al., 2016). Where disinfection was achieved by bromine, Daiber et al. (2016)
387 reported a higher concentration of DBAN in spas compared to pools, which is likely due to the higher
388 release of nitrogen containing anthropogenic chemicals due to the elevated temperatures, as discussed in
389 **Section 5.5**. As shown in **Table S4**, limited reports of other HANs have been published, although
390 concentrations are much lower, up to 3.0 $\mu\text{g/L}$ (Carter et al., 2015; Kanan, 2010), compared to those
391 discussed above.

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

393 Few studies have investigated the occurrence of *N*-nitrosamines in swimming pool waters, as summarised
394 in **Table 2**, with a more complete summary of the studies provided in **Table S4**. Walse and Mitch (2008)
395 were the first researchers to investigate *N*-nitrosamines in chlorinated swimming pool waters, reporting
396 maximum concentrations of *N*-nitrosodimethylamine (NDMA) of 44, 6.9 and 429 ng L^{-1} in indoor pools,
397 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
399 anthropogenic NDMA precursors from swimmers due to the higher water temperature (discussed further
400 in **Section 5.5**). Although similar average concentrations have been reported for NDMA, maximum
401 concentrations have been reported between 6.9 and 208 ng/L for pools treated by chlorination (Kim and
402 Han, 2011; Wang et al., 2011). Other nitrosamines, *N*-nitrosodiethylamine, *N*-nitrosomorpholine and *N*-
403 nitrosoethylmethylamine have been detected in chlorinated pools at concentrations up to 72, 34 and 26
404 ng/L, respectively (Kim and Han, 2011; Wang et al., 2011), with *N*-nitrosopyrrolidine reported at
405 concentrations up to 127 ng/L (Pozzi et al., 2011), although information regarding pool type or treatment
406 method was not presented.

407 **3.1.6. Haloacetaldehydes**

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

420 **3.1.7. Haloketones**

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

431 **3.1.8. Halonitromethanes**

432 As summarised in **Tables 2** and **S8**, few studies have investigated halonitromethanes (HNMs) in pool or
433 spa waters. Trichloronitromethane (TCNM) is the most investigated HNM, where concentrations up to 5
434 $\mu\text{g/L}$ have been reported for chlorinated pools (Tardif et al., 2015). Daiber et al. (2016) is the only known
435 study of HNMs in spas or brominated pools, although TCNM was not detected in any waters investigated.
436 Several other HNMs (tribromo-, bromochloro- and bromo-nitromethane) have been investigated, where
437 maximum concentrations between 1.2 and 11 $\mu\text{g/L}$ were reported (Kanan, 2010; Yeh et al., 2014).

438 **3.1.9. Haloacetamides**

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

444 **3.1.10. Inorganic Anions**

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

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

463 Although reported at higher concentrations in pools treated with ozone, chlorate has also been
464 detected in pools where ozone was not employed as a secondary treatment. For example, Michalski and
465 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
468 occurrence of chlorate in pools can be explained by (i) the direct addition as a DBP in pre-treated filling
469 water, (ii) the direct addition as a degradation product of hypochlorite stock solutions (Garcia-Villanova
470 et al., 2010), (iii) formation in pools due to the degradation of hypochlorite which has been shown to
471 increase in the presence of metal oxides (Liu et al., 2012), (iv) or in cases where ozone is employed as
472 secondary treatment, formation due to oxidation of hypochlorite by ozone and hydroxyl radicals via a
473 several step mechanism (Von Gunten, 2003). Similarly, chlorite has been detected in pools treated with
474 chlorine and chlorine dioxide, where concentrations up to 2.5 mg/L have been reported (Michalski and
475 Mathews, 2007).

476 3.1.11. Total Organic Halogen

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

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

496 3.1.12. Cyanogen Halides

497 A limited number of studies have investigated cyanogen halides in swimming pools or spas. All
498 known studies have focused on the two cyanogen halide species, cyanogen chloride (CNCl) and cyanogen
499 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 µg/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 µg/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).

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

3.2.1. Trihalomethanes

Several studies have investigated the occurrence of THMs in the ambient air of indoor swimming pool facilities, with a summary provided in **Table S12**. Unless otherwise stated, all reports of THMs in 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 pools, is generally reported to be between 12 and 320 µg/m³ (Aggazzotti et al., 1998; Aprea et al., 2010; Cammann and Hübner, 1995; Caro and Gallego, 2008; Catto et al., 2012b; Lévesque et al., 2000; Silva et al., 2012; Tardif et al., 2015, 2016), although other studies have reported significantly lower concentrations (12 to 81 µg/m³) (Font-Ribera et al., 2010b; Lourencetti et al., 2012; Richardson et al., 2010; Thiriart et al., 2009). Compared to other reported studies, Aggazzotti et al. (1990) reported much higher chloroform concentrations (66 to 650 µg/m³), although these are consistent with concentrations reported in their later investigations (16 to 853 µg/m³) (Aggazzotti et al., 1995), as well as those reported in a study of sixteen chlorinated whirlpool spas (4 to 750 µg/m³) (Benoit and Jackson, 1987). Other THMs, bromodichloro-, dibromochloro- and tribromo-methane, have been reported in the ambient air above indoor chlorinated swimming pools at concentrations of below detection to 24, below detection to 26 and 0.2 to 23 µg/m³, respectively (Aggazzotti et al., 1998; Cammann and Hübner, 1995; Caro and Gallego, 2008; Catto et al., 2012b; Font-Ribera et al., 2010b; Lourencetti et al., 2012; Richardson et al., 2010), with a few studies reporting higher concentrations, up to 155, 205 and 103 µg/m³ for bromodichloro-, dibromochloro- and tribromo-methane, respectively (Tardif et al., 2015, 2016). Lahl et al. (1981) measured trichloro- and bromodichloro-methane in the ambient air above eight chlorinated pools in concentrations between 10 to 384 and 0.1 to 39 µg/m³, respectively, although whether the pools were located indoors or outdoors was not specified. Similarly, trichloro-, bromodichloro-, dibromochloro- and tribromo-methane have been found in the ambient air of other indoor swimming pools in concentrations of 11 to 13000, 8.7, 3.1 and 0.8 µg/m³, respectively, although the disinfection methods of these pools were not provided (Chen et al., 2011; Erdinger et al., 2004; Fantuzzi et al., 2001; Hsu et al., 2009; Lévesque et al., 1994).

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
535 concentrations of 1.8 to 6.9, 1.9 to 4.2, 6.4 to 8.7 and 55 to 928 $\mu\text{g}/\text{m}^3$ for trichloro-, bromodichloro-,
536 dibromochloro- and tribromo-methane, in the air above an indoor swimming pool treated by bromination.
537 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
538 $\mu\text{g}/\text{m}^3$ for trichloro-, bromodichloro-, dibromochloro- and tribromo-methane, respectively, in their
539 investigation of an indoor swimming pool treated with BCDMH. As observed in swimming pool water
540 and discussed further in **Sections 4 and 5**, the speciation of THMs in the ambient air is influenced by the
541 water quality of the corresponding swimming pool, particularly by filling water composition and
542 disinfection practices.

543 **3.2.2. Inorganic Halamines**

544 A few studies have investigated halamines in the air above swimming pools, although, to date,
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
547 indoor swimming pool complexes that employ chlorination, at concentrations between 20 and 1340
548 $\mu\text{g}/\text{m}^3$, although on average concentrations are generally between 80 and 637 $\mu\text{g}/\text{m}^3$ (Afifi and Blatchley,
549 2015; Bernard et al., 2011; Bessonneau et al., 2011; Catto et al., 2012b; Chu et al., 2013; Font-Ribera et
550 al., 2016; Fornander et al., 2013; Jacobs et al., 2007; Lévesque et al., 2015; Parrat et al., 2012; Predieri
551 and Giacobazzi, 2012; Richardson et al., 2010; Schmalz et al., 2011a). Richardson et al. (2010) reported
552 an average trichloramine concentration of 80 $\mu\text{g}/\text{m}^3$ in the air of an indoor swimming pool treated with
553 BCDMH, with concentrations varying (70 to 100 $\mu\text{g}/\text{m}^3$) over the twelve samples taken. Monochloramine
554 was investigated in the ambient air of forty-one indoor and chlorinated swimming pool complexes, with
555 concentrations of 70, 320 and 150 $\mu\text{g}/\text{m}^3$ reported for the minimum, maximum and average, respectively
556 (Tardif et al., 2016).

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

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

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.

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

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

603 **Section 5.5.** One study presented even higher concentrations for a whirlpool spas treated with bromine,
604 up to 345 mg/L (Benoit and Jackson, 1987). Only one known study has provided TOC concentrations for
605 indoor pools treated with bromine, where concentrations were generally higher than indoor pools treated
606 with chlorine, being up to 125 mg/L (Plewa et al., 2011). Concentrations of DOC and TOC of 1.0 to 3.6
607 and 1.3 to 8.6 mg/L, respectively, were found in seawater filled, chlorinated swimming pools
608 (Chowdhury, 2015; Parinet et al., 2012), with another study finding more elevated TOC concentrations
609 (up to 12 mg/L) (Manasfi et al., 2016).

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

613 **4.1. Filling Waters**

614 One major factor that influences the occurrence of DBPs in swimming pool waters is the filling
615 water, which can introduce a range of species, e.g. natural organic matter (NOM), trace amounts of DBPs
616 chlorine and bromine, species that are dependent on both the quality and prior treatment of the filling
617 water. The majority of swimming pools are filled with disinfected distributed drinking water (freshwater),
618 however, the use of other natural waters, e.g. seawater, may become the norm in the future for some
619 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
621 pools and spas (Daiber et al., 2016), filling waters may introduce bromide/bromine species, with bromide
622 reported at 65 to 80 and up to 0.5 mg/L, for sea and fresh water, respectively (WHO, 2009), which is
623 consistent with bromide levels reported in seawater filled swimming pools of 68 to 107 mg/L (Manasfi et
624 al., 2016; Parinet et al., 2012). Bromide can also be detected at higher concentrations in freshwaters, with
625 Heeb et al. (2014) detailing a concentration range of ~10 to >1000 µg/L in their critical review of aqueous
626 reactions of bromine and concentrations up to 8.5 mg/L being measured in Western Australian
627 groundwaters (Gruchlik et al., 2014).

628 Although only studied in chlorinated pools, bromide (after quenching the oxidant residual) was
629 reported at significantly lower concentrations than chloride, being below the detection limit in some
630 studies (Cardador and Gallego, 2011; E et al., 2016) and ranging from 0.002 to 1.8 mg/L in other pools
631 located indoors (Michalski and Mathews, 2007; Xiao et al., 2012). Similar results were reported for
632 chlorinated swimming pools located outdoors, where bromide was below detection limits in some studies
633 (Cardador and Gallego, 2011; Yeh et al., 2014) and 0.002 to 0.2 mg/L in others (Manasfi et al., 2016;
634 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
637 in pools treated by BCDMH, sodium bromide in combination with a chlorine based oxidant or EGMO. As
638 the reaction of HOBr with organic compounds in pools results in the formation of Br-DBPs which are
639 generally more toxic than their chlorinated counterparts (Plewa et al., 2004), increasing bromide
640 concentrations in swimming pools will increase the formation of Br-DBPs, an undesired consequence.
641 The predominance of the Br-DBPs despite the lower concentrations of bromine than chlorine is likely due
642 to the higher halogenation reactivity of bromine compared to chlorine, i.e., bromine is incorporated into
643 organic matter at a faster rate (Cowman and Singer, 1996). As discussed in **Section 3**, Br-THMs were
644 generally more abundant in seawater filled swimming pools compared to those filled with freshwater, for
645 pools where treatment methods and location were comparable (Manasfi et al., 2016), consistent with the
646 higher concentrations of bromide entering in the seawater filled pools. Other Br-DBPs, e.g. HAAs
647 (Parinet et al., 2012), have been found in higher concentrations in pools filled with seawater compared to
648 those filled with freshwater. Whilst this section has focused on the input of bromide originating from
649 filling waters, bromide may also be introduced by bromine based disinfectants, which is discussed further
650 in **Section 4.2**. Further discussion on the impact of halide ions on DBP formation is provided in **Section**
651 **5.1**.

652 **4.2. Disinfectants**

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

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

670 the formation of DBPs. Further studies on the impact of fillers on DBP formation are recommended.
671 Naturally, disinfectants themselves can result in DBPs as they are reduced. For example, ClO₂ as a
672 disinfectant introduces chlorite, chlorate and chloride due to the reaction and hydrolysis products of
673 chlorine dioxide (Gordon et al., 1972). Bromide and chloride are introduced by bromine and chlorine
674 based disinfectants, respectively, and can have an effect on DBP formation as discussed in **Section 5.2**.
675 The occurrence of a range of inorganic anions in swimming pools and spas was discussed in **Section**
676 **3.10**.

677 As presented throughout **Section 3**, Br-DBPs are generally detected at higher concentrations in
678 pools treated with bromine based disinfectants compared to their chlorinated counterparts, whilst Cl-
679 DBPs dominate in pools disinfected with chlorine. For example, Kelsall and Sim (2001) investigated
680 THMs in three pools treated with chlorine, chlorine in combination with ozone (Cl₂/Ozone) and sodium
681 bromide in combination with ozone (Br₂/Ozone), in order to assess the disinfectant impact on THM
682 formation. Chloroform was the dominant THM in the chlorinated pools (up to 85 µg/L) but was not
683 detected in the Br₂/ozone treated pool, due to the absence of chlorine, Similarly, bromoform was the
684 dominant THM in the Br₂/ozone treated pool, but was below detection in the chlorinated pools
685 investigated (Kelsall and Sim, 2001). These observations may be explained by the minimal formation of
686 HOCl or HOBr, and therefore minimal formation of the chloro- or bromo-THMs, in the brominated and
687 chlorinated pools, respectively. Daiber et al (2016) compared the DBPs detected in a number of
688 swimming pools and spas employing either bromination or chlorination, reporting the dominance of Cl-
689 DBPs and Br-DBPs in pools treated by chlorination and bromination, respectively. Additionally, on a
690 molar basis, the total DBP concentrations were higher in pools where chlorination (predominantly
691 hypochlorite) was employed, when compared to those where bromination (BCDMH) was employed,
692 although in spas similar total DBP molar concentrations were observed regardless of disinfectant (Daiber
693 et al., 2016). These observations can be explained by the slower dissolution and formation (and hence
694 availability) of free chlorine equivalents from BCDMH compared to the readily available hypochlorite,
695 where the dissolution rate from BCDMH is increased in the spas due to the higher operating temperature.
696 Lourencetti et al. (2012) also reported the dominance of Br-THMs and Cl-THMs in the ambient air at
697 swimming pool sites treated with bromine and chlorine based disinfectants, respectively, with Richardson
698 et al. (2010) reporting a similar finding. Additionally, Richardson et al. (2010) reported a lower maximum
699 dichloramine concentration (<10 µg/L) in a pool treated with BCDMH compared to one where
700 chlorination was employed (650 µ/L).

701 Lee et al. (2009) reported both higher TTHM and Br-THM concentrations in pools treated with
702 EGMO compared to pools where chlorination was employed, although this comparison was of mass
703 concentrations. It is important to note that to accurately compare concentrations of groups of compounds,
704 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
707 a wider range of DBPs: THMs, HAAs, HANs and CH. Considering average concentrations by mass, total
708 THMs and total HANs were higher in pools where EGMO was employed compared to chlorinated pools,
709 which is likely due to the higher abundance of brominated THMs and HANs detected in the EGMO
710 treated pools. Although higher concentrations of Br-HAAs were detected in the pools treated with
711 EGMO, Lee et al. (2010) reported a higher HAA9 concentration in pools treated with chlorination
712 compared to those treated by EGMO. Whilst concentrations varied greatly, compared to where
713 chlorination was employed, on average CH was detected at slightly lower concentrations in the EGMO
714 treated pools (Lee et al., 2010). Zhang et al. (2015) reported substantially lower DBP concentrations in
715 pools treated with chlorine dioxide and TCICA compared to pools treated by chlorination, when
716 comparing molar totals of the sum of TTHMs, HAA9, CH, HAN-4, 1,1-DCP, 1,1,1-TCP and TCNM.
717 Pools treated by chlorination in combination with ozone were also investigated by Lee et al. (2009, 2010)
718 and Zhang et al. (2015), and these are discussed in **Section 5.1**.

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

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

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

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

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

749 **4.3.1. Human Body Excretions**

750 As the name suggests, human body excretions are comprised of any human derived input
751 generally introduced via sweat, urine, saliva, hair or skin cells, and, although differing from person to
752 person, can include urea, ammonia, uric acid, creatinine, creatine, lactic acid, citric acid, hippuric acid,
753 uracil, ornithine, chloride, sulfate, cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} and Zn^{2+} , and amino acids, such as
754 histidine, glycine, cysteine, asparagine, lysine, arginine and guanine (Hirokawa et al., 2007; Montain et
755 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
758 contamination of human origin, as many human inputs contain nitrogenous compounds. In terms of TN,
759 chlorinated pools located indoors have higher reported concentrations than those located outdoors (0.8 to
760 12 and 0.6 to 8.4 mg/L, respectively), although the outdoor pools were treated additionally with ozone
761 (Yeh et al., 2014; Zhang et al., 2015). Additionally, TON concentrations followed the same trend, with
762 reported concentrations of 0.2 to 11 and 0.09 to 1.3 mg/L for indoor and outdoor pools, respectively (Yeh
763 et al., 2014; Zhang et al., 2015). The generally higher concentrations of TN and TON observed in indoor
764 pools (compared to outdoor pools) may be due to (i) indoor pools are often used by a larger number of
765 babies and children (**Section 5.4**), and (ii) indoor pools are generally operated at higher temperatures
766 (**Section 5.5**), both of which would see an increased release of nitrogen containing anthropogenic
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
769 investigation of eight indoor pools treated by chlorination. It should be noted that human inputs differ
770 upon swimmer activity and water temperature, and these aspects are addressed in **Sections 5.4 and 5.5**,
771 respectively.

772 The quantity of contamination due to human input has been investigated in various studies. The
773 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,
775 respectively, during a 30 minute swim time. Urea, a component of urine and sweat (Mosher, 1933), has
776 been detected in a range of pools in concentrations up to 3.7 mg/L (De Laat et al., 2011; Parrat et al.,
777 2012; Schmalz et al., 2011a, 2011b; Tachikawa et al., 2005; Weng and Blatchley, 2011), with a full
778 summary provided in **Table S14**. Afifi and Blatchley (2016) also investigated urea in swimming pools,
779 reporting that it was correlated to the number of swimmers. Nitrate concentrations were found to vary,
780 with no trends observed for swimming pool type (ind88 mg/L found (Beech et al., 1980; Zhang et al.,
781 2015). Concentrations varied greatly between pools located indoors, with nitrate levels reported between
782 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
783 dioxide, chlorination in combination with ozone and EGMO, respectively (E et al., 2016; Lee et al., 2010;
784 Michalski and Mathews, 2007; Spiliotopoulou et al., 2015; Zhang et al., 2015).

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

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

805 Additionally, a range of DBPs including halo(nitro)phenols were detected in pool waters, which
806 were later confirmed to form from the chlorination of human derived precursors, particularly urine (Xiao
807 et al., 2012). Although the formation of HAAs, THMs and HANs were observed upon chlorination of

808 BFA (Hansen et al., 2012a), formation was dependent on pH. This is discussed in more detail in **Section**
809 **5.5**.

810 A mixture including hair, saliva, skin, urine and moisturising body lotion, as well as the individual
811 components, was investigated for potential formation of chloroform, bromodichloromethane, CH₂Cl₂, DCAN
812 and 1,1,1-TCP upon chlorination in a study by Kim et al. (2002). Chloroform was the most abundant
813 DBP (on a mass concentration basis) in all cases, with DCAN formation higher upon chlorination of
814 components of human origin, which is likely due to the formation of nitrogen containing degradation
815 products which enhance DCAN formation (Kim et al., 2002). Additionally, the chlorination of skin
816 specimens by Xiao et al. (2012) led to the formation of HAAs and THMs, with Br-DBPs increasing with
817 increasing bromide concentrations.

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

830 UV treatment and chlorination of three amino acids, L-arginine, L-histidine, and L-glycine, led to
831 the formation of chloramines and cyanogen chloride (Weng and Blatchley, 2013). The formation of
832 chloramines was suggested to be due to rapid *N*-chlorination, with UV irradiation and hydrolysis then
833 promoting cleavage and subsequent formation of ammonia, which formed chloramines upon further
834 chlorination. The formation of CNCl was proposed to occur through a similar pathway of *N*-chlorination
835 followed by UV promoted hydrolysis, where reactions and by-products were found to be dependent on
836 both the chlorine to precursor ratio (Cl/P) and UV dose (Weng and Blatchley, 2013). Lian et al. (2014)
837 reported the formation of CNCl from the chlorination of uric acid, with reactions found to be not only
838 dependant on the Cl/P ratio, but also on pH and temperature. Additionally, at Cl/P ratios greater than 1
839 (i.e. conditions reflective of real swimming pools), the formation of other intermediates and their
840 subsequent DBPs (due to ring cleavage and subsequent chlorination) were observed, which was likely due
841 to the lower stability of these products promoting decarboxylation or hydrolysis reactions (Lian et al.,
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
845 Blatchley (2007) reported the formation of cyanogen chloride upon chlorination of L-histidine, also
846 observing the formation of other DBPs. Creatinine, urea, L-histidine and L-arginine all produced
847 trichloramine upon chlorination, with DCAN and dichloromethylamine observed in some cases (Weng
848 and Blatchley, 2013). Complex mechanisms were proposed for all compounds, and hypothesised to
849 involve several chlorine substitution, hydrolysis, and/or decarboxylation reactions, with several
850 intermediate species (Li and Blatchley, 2007). In a study of the reaction mechanism of the chlorination of
851 urea in a swimming pool context, molecular chlorine, Cl₂, was found to be the chlorine species involved
852 in the rate-determining first step of *N*-chlorination of urea, with HOCl being the chlorine species involved
853 in the subsequent steps to ultimately form trichloramine and nitrate (Blatchley and Cheng, 2010).

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

874 **4.3.2. Pharmaceuticals and Personal Care Products**

875 Although recent reviews by Bottoni et al. (2014), Sharifan et al. (2016) and Haman et al. (2015)
876 discuss some potential issues of pharmaceuticals and personal care products (PPCPs) in aquatic
877 environments, this review will present studies of PPCPs applicable to swimming pools (especially UV

878 filters, antifungal agents and parabens that are commonly added to sunscreens and other cosmetic
879 products), with a particular focus on the potential for DBP formation. Although known by various
880 chemical and trade names, for the purpose of this review, some commonly reported PPCPs will be
881 abbreviated as per **Table 3**, with full lists of names provided in **Table S15**.

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

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

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

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

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

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

958 Although only limited studies exist, a range of other DBPs likely introduced via PPCPs have been
959 investigated in pools. Swimming pool water is suggested to increase the leaching of nanoparticles (TiO₂
960 and ZnO) during swimming (Virkiute et al., 2012), which have the potential to accumulate in swimming
961 pools (Jeon et al., 2016). A range of aliphatic and aromatic aldehydes (glyoxal, methylglyoxal, 2,5-
962 dihydroxybenzaldehyde, butyraldehyde, propionaldehyde, acetaldehyde, 3-hydroxybenzaldehyde,
963 benzaldehyde, formaldehyde, valeraldehyde, 3-methylbenzaldehyde, 2-ethylbenzaldehyde and 2,5-
964 dimethylbenzaldehyde) have been detected in both indoor and outdoor swimming pools in concentrations
965 up to 12 µg/L (Fernandez-Molina and Silva, 2013; Serrano et al., 2013). Halobenzoquinones (2,6-
966 dichloro-, 2,3,6-trichloro-, 2,3-dibromo-5,6-dimethyl- and 2,6-dibromo-1,4-benzoquinone) have also
967 been detected in swimming pool waters, at concentrations up to 299, 11, 0.7 and 3.9 ng/L, respectively
968 (Wang et al., 2013). Only 3-chloro-, 4-chloro- and 2,4,5-trichloro-aniline were detected in swimming pool
969 waters (160, 200 and 40 ng/L, respectively) in an investigation of twenty seven amines, being aliphatic
970 amines, anilines and *N*-nitrosamines (Jurado-Sánchez et al., 2009). Daiber et al. (2016) detected several
971 halogenated DBPs previously not reported in swimming pool waters, including 4,5-dibromo-1-methyl-
972 1H-imidazole and 2,4,5-tribromo-1-methylimidazole, which likely result from the use of BCDMH as a
973 disinfectant in these waters. Although found to be unlikely to pose a health risk, organophosphate flame
974 retardants (tributyl-, tris(2-chloroethyl)-, tris(1-chloro-2-propyl)-, tris(1,3-dichloro-2-propyl)- and
975 triphenyl-phosphate) were detected in a range of indoor and outdoor pools (treated by chlorination or UV
976 in combination with chlorine) at concentrations between 5 and 1180 ng/L (Teo et al., 2016b). The
977 investigated organophosphate flame retardants were generally measured at higher concentrations in the
978 indoor swimming pools compared to the concentrations measured in the outdoor pools, and were found to
979 leach from swimsuits in laboratory studies (Teo et al., 2016b).

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

982 pharmaceuticals, were subject to chlorination in a series of laboratory-scale studies, in which chloroform
983 was produced in all cases (Rose and Herckes, 2014). Pharmaceuticals containing amine groups were the
984 centre of a study by Shen and Andrews (2011) who reported all pharmaceuticals investigated produced
985 NDMA upon chloramination. Based on molar concentrations, ranitidine led to the highest NDMA
986 formation, with NDEA detected in some cases (Shen and Andrews, 2011). Two salicylates commonly
987 found in several personal care products, benzyl salicylate and phenyl salicylate, were found to produce
988 mono- and di-chloro substituted by-products upon their chlorination (de Oliveira e Sá et al., 2014).

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

1003 Although the aforementioned studies have provided some insight to the possible transformation
1004 by-products of both PPCPs and human body excretions, much is still unknown. Controlled laboratory and
1005 real pool investigations of human body excretions and PPCPs are required in order to fully understand
1006 their impact on DBP formation in the swimming pool environment. Human body excretions have been
1007 shown to be a major source of DBP formation in swimming pools, with TON reported to be the main
1008 precursor of N-DBPs (Shah and Mitch, 2011), and, as such, human body excretions in pools should be
1009 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
1017 chlorine prior to UV treatment is undesired, as although some contaminants are decreased by UV, so is
1018 the disinfectant residual (Rand and Gagnon, 2008). Due to this, a chlorination step post UV treatment is
1019 commonly adopted in the treatment of swimming pool waters. UV treatment is known to degrade
1020 chloramines (Cimetiere and De Laat, 2014; Soltermann et al., 2014), however many factors, particularly
1021 turn-over rate, affect the efficiency of this degradation. In addition, post-chlorination is reported to
1022 increase trichloramine stability (Soltermann et al., 2014). In a study of *N*-nitrosamine formation and
1023 degradation during UV treatment of pool water, UV treatment of monochloramine and chlorinated
1024 dimethylamine was found to lead to a substantial increase in NDMA formation, proposed to occur
1025 through reaction of nitric oxide or peroxyxynitrite with the dimethylaminy radical, species produced by UV
1026 photolysis of monochloramine and chlorinated dimethylamine, respectively (Soltermann et al., 2013).
1027 Despite the problematic NDMA being generally efficiently degraded by UV treatment, in the swimming
1028 pool environment where high levels of nitrogen containing NDMA precursors exist, the rate of formation
1029 of NDMA outweighed that of its degradation, resulting in a net increase in NDMA concentration
1030 (Soltermann et al., 2013). Removal of *N*-nitrosamines from swimming pool waters requires UV doses
1031 over thirty times those currently employed at swimming pool sites (Soltermann et al., 2013) . Soltermann
1032 et al. (2013) concluded that UV treatment would only be useful for reduction in *N*-nitrosamine
1033 concentrations if the pool water contained high *N*-nitrosamine concentrations compared to the
1034 concentrations of chloramines and chlorinated secondary amines.

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

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).

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

1082 Like UV treatment, ozonation is often employed prior to chlorination, as a secondary treatment in
1083 swimming pools. As discussed in **Section 3**, swimming pools treated with ozone generally contained
1084 lower concentrations of the investigated DBPs than pools where ozone was not employed. For example,
1085 TTHM concentrations were lowest in swimming pools where ozone/chlorination was used, compared to

1086 those treated exclusively by chlorination, which the authors attribute to the oxidation of long chained
1087 organic molecules by hydroxide ions (introduced by use of sodium hypochlorite) at the relatively high pH
1088 (up to 8.5) found in these pools, leading to a higher formation of THMs compared to that observed in the
1089 ozone/chlorine pools where ozone is the more dominant oxidant and hence oxidation by hydroxide ions
1090 would be less prevalent (Lee et al., 2009). Similar results were reported by Kelsall and Sim (2001), where
1091 lower TTHMs (13 to 24 µg/L) were detected in swimming pools treated by chlorination in combination
1092 with ozone than pools treated only by chlorination (21 to 87 µg/L).

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

1105 The use of an ozone-bromine treatment, the formation of HOBr by oxidation of bromide by ozone,
1106 for pools has been suggested by Hoffmann et al. (2015), who successfully applied this treatment method
1107 to a hydrotherapy pool for three years, in which microbiological parameters were found to meet guideline
1108 values. In waters rich in bromide, ozone has the potential to form bromate, but bromate formation was
1109 controlled by pH in the pool (Hoffmann, 2015). Although this study demonstrated the potential use of an
1110 ozone-bromine treatment in pools, DBP formation was not closely examined and future work should
1111 assess the impact of ozone-bromine treatment on the formation of DBPs, particularly Br-DBPs.

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

1120 waters, however further studies should assess the impact of continual precursor input on this combined
1121 treatment method, which would be more reflective of real swimming pools.

1122 In addition, pools where UV treatment was combined with chlorination are reported to be less toxic,
1123 with up to 3x less cytotoxicity observed (Liviak et al., 2010b; Plewa et al., 2011). Whilst secondary
1124 treatments have been shown to increase the overall quality of swimming pool water, further studies are
1125 required to fully understand the chemistry underpinning secondary treatment methods under conditions
1126 more reflective of swimming pools, e.g. continual chlorine residual and continual precursor input. Further
1127 studies should investigate a wider range of DBPs under these conditions, in both laboratory and
1128 swimming pool studies.

1129 **5.2. Halide Anions: Bromide and Chloride**

1130 One major impact of the disinfectant is the introduction of halide ions, which in turn can affect the
1131 formation of DBPs. As previously discussed in **Sections 2.1** and **4.2**, after oxidation reactions in the pool,
1132 chlorine based disinfectants introduce chloride (Cl^-), whilst bromine based disinfectants introduce
1133 bromide (Br^-), and these ions can often accumulate due to the continual recirculation in pools.
1134 Highlighting the impact of the disinfectant on the ionic composition of pool waters, chloride has been
1135 reported at concentrations up to 3233 mg/L for freshwater chlorinated swimming pools (E et al., 2016).

1136 E et al. (2016) presented a linear correlation of the concentrations of three volatile DBPs,
1137 trichloramine, trichloromethane and DCAN, with chloride concentrations, in both bench scale
1138 experiments and real swimming pool waters. The authors attributed this relationship to chloride
1139 promoting speciation shifts of free chlorine from HOCl to the more reactive Cl_2 (Voudrias and Reinhard,
1140 1988), hence a higher formation of these chlorinated DBPs (E et al., 2016). Additionally, oxidant
1141 consumption was shown to increase with increasing chloride levels (E et al., 2016).

1142 **5.3. Swimming Pool Location**

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

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

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

1161 Indoor swimming pools are often operated at higher temperatures than those located outdoors and,
1162 as discussed in **Section 5.5**, the increased temperature can have several effects on DBP formation. Factors
1163 such as higher reaction rates and increased volatilisation of some DBPs will impact their occurrence in
1164 indoor swimming pools. On the one hand, higher volatilisation would lead to lower concentrations of
1165 DBPs in the water but would increase their concentration in the ambient air, but on the other hand, DBPs
1166 in the ambient air of indoor pools may become trapped and hence be observed at higher concentrations,
1167 compared to outdoor pools where volatile DBPs can easily disperse.

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

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

1187 swimmers, such as lap pools, competition pools and pools designated for exercise (e.g. water
1188 aerobics/aquafitness), would differ from those used mainly by recreational swimmers, e.g. leisure pools,
1189 paddling pools. Additionally, although more reflective of bather load input (**Section 4.3**), pools used by
1190 specific people (e.g. babies, toddlers or children) may have different water chemistry and hence DBP
1191 formation.

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

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

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

1222 activity and THM removal from water has been found (Kristensen et al., 2010; Marco et al., 2015). The
1223 trichloramine concentrations in the ambient air was found to increase (0.11 to 0.36 mg/m³) when school
1224 children entered a pool compared to when no swimmers were present, which was suggested to be a result
1225 of the increased mass transfer coefficient due to increased water agitation (Zwiener and Schmalz, 2015).
1226 An earlier study showed increase in mass transfer coefficients of trichloramine by swimming activity,
1227 (1.8x10⁻³ to 7x10⁻³ g/(h m²)), and by splashing or water jets (up to 12.6x10⁻³ g/(h m²)) (Schmalz et al.,
1228 2011a). This trend is likely to extend to other volatile DBP classes, with agitation leading to decreased
1229 concentrations in swimming pool waters, and increased concentrations in swimming pool air. This
1230 transfer of volatile DBPs to the gas phase is of high importance due to the inhalation uptake mechanism
1231 and further studies are required to fully understand the water-to-air relationship in terms of volatile DBPs
1232 and water activity.

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

1255 5.5. Temperature and pH

1256 As mentioned in throughout this review, swimming pool water temperature has been shown to
1257 affect (i) the release of human derived input, (ii) volatilisation rates of volatile DBPs and (iii) reaction
1258 rates of DBP formation, all of which are interrelated. In addition, pools operated at elevated temperatures
1259 are required to maintain a higher disinfectant residual, which may also affect the formation of DBPs.

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

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

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

1293 Although knowledge has been gained from these studies, the difference in laboratory to real pool
1294 studies highlights the need for further investigation at both the laboratory scale and real pool scale. Future
1295 laboratory studies should encompass a wider range of DBPs and be conducted at conditions more suited
1296 to swimming pool waters. Additionally, the impact of temperature should be assessed for all DBP classes,
1297 in both laboratory and full scale studies, to provide a better understanding of the role of temperature on (i)
1298 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**

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

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

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

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

1359 the breathing zone for swimmers is the water-air interface, where high concentrations of volatilised
1360 THMs have been reported (Catto et al., 2012a).

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

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

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

1393 children who attended swimming pool complexes at an early age (Voisin et al., 2014). Additionally,
1394 children who did not swim until a later age had lower cases of ear infections (Schoefer et al., 2008).

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

1412 Similarly, brominated HAAs have been shown to be more toxic than their chlorinated counterparts
1413 (Liviak et al., 2010a; Plewa et al., 2008). DeAngelo and McMillan (1990) found both DCAA and TCAA
1414 produced liver cancer in mice, with DCAA more potent than TCAA. Yeh et al. (2014) suggests that
1415 HAAs may be the decomposition products of other compounds, but has shown that HAAs degrade to the
1416 equally toxic THMs. Despite HAAs having low skin permeability (Xu et al., 2002), they are still of high
1417 importance due to the transformations suggested by Yeh et al. (2014) giving rise to a wider variety of
1418 uptake mechanisms and therefore a wider range of health issues.

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

1428 et al., 2004). Even at low concentrations, HAAs are of high importance as they have reportedly shown
1429 much 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.

1434 Despite the many studies of the health impacts of swimming pools, as summarised by Lubick
1435 (2007) and Richardson et al. (2010), no definitive answers can yet be drawn in regards to the potential
1436 health effects. Many studies are only suggestive, reporting health issues that may be correlated with
1437 attending swimming pools, particularly those that are indoors and disinfected with chlorine. The lack of
1438 certainty and conflicting reports suggest that further investigation into the health impacts of swimming
1439 pools is warranted.

1440 **7. Conclusions**

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

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

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 health effects of many DBPs at the concentrations reported in swimming pool waters and under swimming pool exposure conditions are yet to be defined. Apart from Germany and Denmark, no known 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 Standardization, 2012) and Danish (Lovtidende, 2012) swimming pool guideline values for THMs are approximately five times lower than that recommended by the World Health Organisation for THMs in drinking waters (WHO, 2011), demonstrating the need for swimming pool specific guidelines. Further investigation into DBPs and anthropogenic chemicals within the swimming pool environment should aim to support development of swimming pool specific guidelines in the future.

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2122

2123 **List of Tables**

2124 **Table 1:** Recommended minimum free chlorine equivalent concentrations (mg/L) and pH values for
 2125 swimming pools and spas by selected organisations.

Disinfectant	pH Range	Swimming Pools		Spas	Reference
		Unstabilised	Stabilised*		
Chlorine	7.2-7.8	1	2	3	(NHMRC, 2008)
Bromine		2	-	6	
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	7.2-7.8	1	2	3	(CDC, 2016)
Bromine		3	-	4	
Chlorine	7.2-7.8	0.5-1.2	0.5-1.2	2-3	(WHO, 2006)
Bromine		4-6	-	4-6	

2126 *Stabilised refers to the use of cyanuric acid. Stabilisation not possible with bromine based disinfectants.

2127 **Table 2:** Summary of the occurrence of disinfection by-products in swimming pool and spa waters. Unless otherwise stated, concentrations are
 2128 presented in µg/L and represent a range of the average concentrations reported. Where only one value is present, either only one known report exists or, of
 2129 the existing reports, only one presented data regarding average concentrations. Where no data is included, either the concentration(s) were below the limit of
 2130 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**.

Disinfection By-Product	Swimming Pools					Spas		Reference(s)
	Chlorine Based	Bromine Based	EGMO	Chlorine & Ozone	Seawater Filled	Chlorine Based	Bromine Based	
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., 2010a; Glauner et al., 2005; Golfinopoulos, 2000; Hang et al., 2016; Kelsall and Sim, 2001; Lee et al., 2009; Lee et al., 2010; Lourencetti et al., 2012; Manasfi et al., 2016; Parinet et al., 2012; Richardson et al., 2010; Weaver et al., 2009; Zhang et al., 2015)
Dibromochloromethane	0.49-120	2.4-2.5	8.9-9.1	0.2-2	3.57-27	0.14	4.67	
Tribromomethane	0.04-44	57-152	4.1-19	47	50-651	0.11	182-1253	
Trichloromethane	8.65-243	0.2-0.21	14-27	7.4-141	0.1-6	19-264 ^b	1.6	
Haloacetic Acids (HAAs)								
Bromoacetic Acid	2-12	4.7		16	3.75-55		46-62	(Catto et al., 2012b; Chowdhury et al., 2016; Daiber et al., 2016; Font-Ribera et al., 2016; Hang et al., 2016; Kanan, 2010; Lee et al., 2010; Manasfi et al., 2016; Parinet et al., 2012; Sarrion et al., 2000; Tang and Xie, 2016; Wang, 2011; Yeh et al., 2014; Zhang et al., 2015)
Bromochloroacetic Acid	1.8-510	2.2		425	4.27-65	2.6 ^b	13-294	
Bromodichloroacetic Acid	2.71-61	8.9			2.03-12	12 ^b	10-117	
Chloroacetic Acid	4.22-109			41	1.25-96	31 ^b	-3.9	
Dibromoacetic Acid	1-28	123			16-307		337-1795	
Dibromochloroacetic Acid	2.7-33	4.05		1.2	3.1-103		4.4-14	
Dichloroacetic Acid	23-982	2.2	34	12-200	1.67-4.79	343 ^b	27-89	
Tribromoacetic Acid	5.6-19	72		8.1	43-186		73-97	
Trichloroacetic Acid	19-978	64	97	17-20	2.56-27	1865 ^b	13-37	
Halamines and Cyanogen Halides								
Dichloramine	11-430	51			220		40-142	(Afifi and Blatchley, 2016; Catto et al., 2012b; Chowdhury et al., 2016; Daiber et al., 2016; Font-Ribera et al., 2010b; Font-Ribera et al., 2016; Lian et al., 2014; Richardson et al., 2010; Simard et al., 2013; Weaver et al., 2009)
Monochloramine	10-323	67-270			220		48-205	
Trichloramine	7-1500	12			70		91-183	
Cyanogen Chloride	4.4-24	3.7					3.2	
Cyanogen Bromide	3.3-25	19-52					4.9-125	
Haloacetonitriles (HANs)								
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 Blatchley, 2007; Manasfi et al., 2016; Tardif et al., 2016; Yeh et al., 2014; Zhang et al., 2015)
Chloroacetonitrile	1.14-2.4							
Dibromoacetonitrile	0.2-5.8	37	2.6	0.4	19		80-219	
Dichloroacetonitrile	0.1-75		3.8	1.3-5.3	8.99	14 ^b		
Trichloroacetonitrile	0.03-1.2							
N-Nitrosamines								
<i>N</i> -Nitrosodiethylamine	1.2-35 ^d						5.5-313	(Carter et al., 2015; Jurado-Sánchez et al., 2010; Kim and Han, 2011; Walse and Mitch, 2008; Wang, 2011)
<i>N</i> -Nitrosodimethylamine	5.3-52							
<i>N</i> -Nitrosodi- <i>n</i> -butylamine	15-141							
<i>N</i> -Nitrosoethylmethylamine	7.1-16							
<i>N</i> -Nitrosomorpholine	3.1-26							
<i>N</i> -Nitrosopiperidine	4.4							
<i>N</i> -Nitrosopyrrolidine	4.5-77 ^d							
Haloacetaldehydes (HALs)								
Dibromoacetaldehyde	2.4							(Carter et al., 2015; Daiber et al., 2016; Lee et al., 2010; Manasfi et al., 2016; Serrano et al., 2011)
Dibromochloroacetaldehyde	0.3							
Dichloroacetaldehyde	1.8-23 ^c							
Tribromoacetaldehyde					0.4-2.2 ^c			
Trichloroacetaldehyde	17-301		10	3.6	190	405	2.9	
Haloketones (HKs)								
Chloroacetone	1.9							(Carter et al., 2015; Hang et al., 2016; Manasfi et al., 2016; Spiliotopoulou et al., 2015; Yeh et al., 2014)
1,2-Dichloroacetone	0.8							
1,1,1-Dichloropropanone	0.4-21							
1,1,1-Trichloropropanone	1.3-46			11				
Halonitromethanes (HNMs)								
Bromochloronitromethane	4							(Kanan, 2010; Montesinos and Gallego, 2012; Yeh et al., 2014; Zhang et al., 2015)
Bromonitromethane	1.5							
Tribromonitromethane	1.2							
Trichloronitromethane	0.1-1.2			0.4				
Haloacetamides (HAAMs)								
Dibromoacetamide	0.6-1.9							(Carter et al., 2015; Yeh et al., 2014)
Dichloroacetamide	1.5							
Trichloroacetamide	2-2.7							
Inorganic Anions								
Bromate	3	10-900 ^{b,c}						(Chowdhury et al., 2016; E et al., 2016; Lee et al., 2010; Manasfi et al., 2016; Parinet et al., 2012; Righi et al., 2014; Spiliotopoulou et al., 2015)
Bromide	0.2-79 ^a				0.6-86 ^a			
Chlorate	0.04-37 ^a							

Chlorite	20-22 ^c				
Nitrate	0.004-63 ^a	23 ^a	13 ^a		
Total Organic Halogen (TOX)					
Total Organic Halogen (TOX)	140-480	47-1215	880-1080 ^c		
Total Organic....					
Bromine (TOBr)	0.75-200	4897	0.3-16	53-84 ^c	4197-18239
Chlorine (TOCl)	139-3682	1337	47-1198	1081-9512 ^c	1213-13860
Iodine (TOI)	0.63	0.04-1.9			

(Daiber et al., 2016; Font-Ribera et al., 2016; Kelsall and Sim, 2001; Yeh et al., 2014)

2131

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

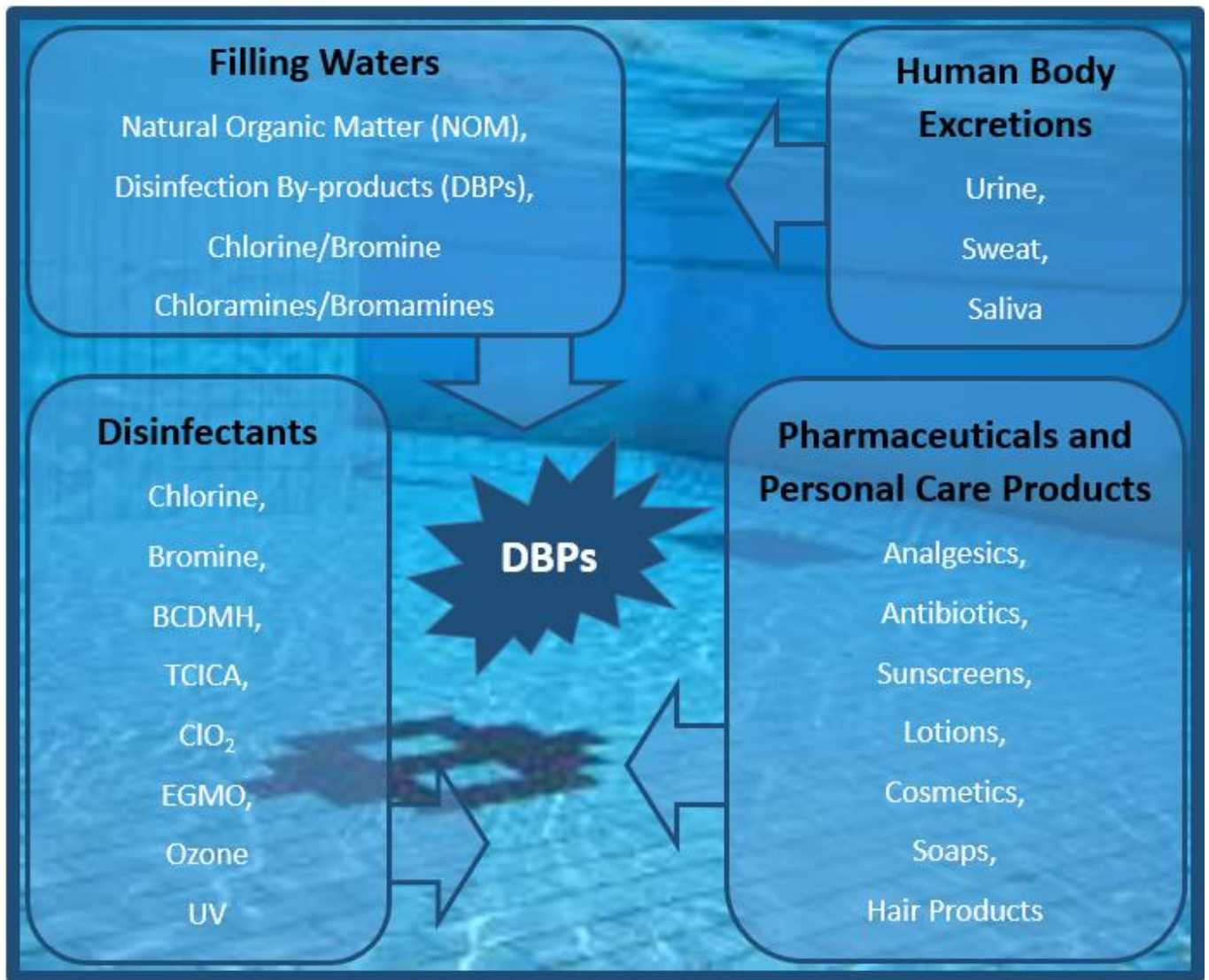
2132

2133 **Table 3:** Commonly used names and abbreviations (Abbr.) for selected components commonly used in
 2134 personal care products.

<u>Antifungal Agents</u>		<u>Parabens</u>			
Common Name	Abbr.	Common Name	Abbr.	Common Name	Abbr.
dichlorophene	dichlorophen	methylparaben	MeP	isobutylparaben	iBuP
5-chloro-(2,4-dichlorophenoxy)phenol	2,4-DCPh	ethylparaben	EtP	pentylparaben	PeP
2,4,6-trichlorophenol	2,4,6-TCPH	propylparaben	PrP	heptaparaben	HeP
		isopropylparaben	iPrP	octylparaben	OcP
		butylparaben	BuP	benzylparaben	BzP
<u>UV Filters</u>					
Common Name	Abbr.	Common Name	Abbr.		
isoamyl 4-methoxycinnamate	Amiloxate	4-hydroxybenzophenone	4-HB		
avobenzene	Avobenzene	1H-benzotriazole	1HBT		
2,4-dihydroxybenzophenone	BP-1	3,3,5-trimethylcyclohexyl-2-hydroxybenzoate	Homosalate		
2,2',4,4'-tetrahydroxybenzophenone	BP-2	4-methylbenzylidene camphor	4-MBC		
benzophenone-3	BP-3	octocrylene	OCR		
2,2'-dihydroxy-4-methoxybenzophenone	BP-8	octyldimethyl-para-aminobenzoic acid	OD-PABA		
benzyl salicylate	BzS	octylmethoxycinnamate	OMC		
4, 4'-dihydroxybenzophenone	4-DHB	2-phenyl-3H-benzimidazole-5-sulfonic acid	PBS		
5,6-dimethyl-1H-benzotriazole monohydrate	DMeBT	phenyl salicylate	PS		
ethyl 4-aminobenzoate	Et-PABA	2,3,4-trihydroxybenzophenone	THB		

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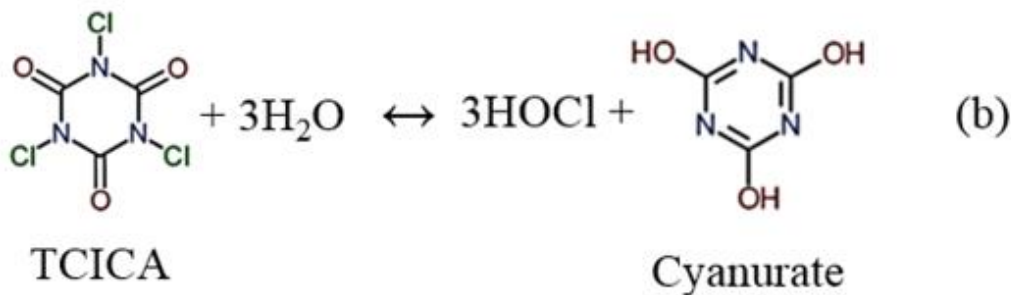
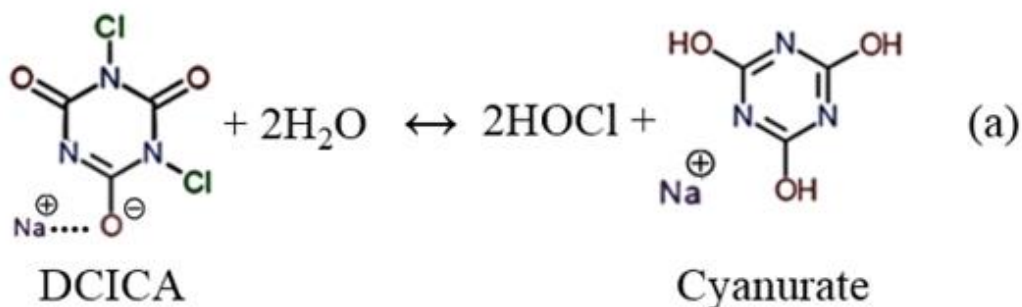


2138

2139 **Figure 1:** Disinfection By-product precursors and disinfectants in swimming pool and spa waters.
2140 Adapted from Carter et al., (2015).

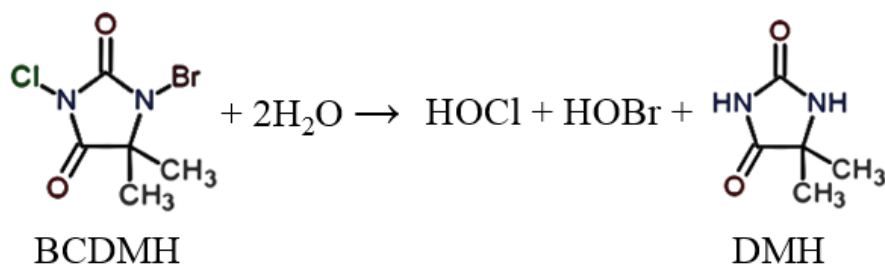
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2144 **Figure 2:** Formation of HOCl by the use of (a) DCICA and (b) TCICA, where DCICA is added as its
 2145 sodium salt.



2146

2147 **Figure 3:** Formation of HOBr and HOCl via the hydrolysis of BCDMH.

Supporting Information

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.

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

Country	Pool(s) Type	Disinfection Method	Trihalomethane Concentration in Swimming Pool Water (µg/L); mean (min-max).				Analytical Method	Reference
			Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane		
USA	Outdoor*	Cl		6 (NR-21)	5 (NR-19)	27 (NR-102)	651 (NR-1166)	LLE GC-ECD (Beech et al., 1980)
	Outdoor	Cl		106 (NR-271)	34 (NR-117)	15 (NR-83)	2 (NR-8)	
	Outdoor	Cl		103 (NR-386)	13 (NR-98)	3 (NR-38)	<1 (NR-6)	
Sweden	NR NR	Cl Br		(50-100)			(NR-400)	LLE GC-ECD (Norin and Renberg, 1980)
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	Cl		256 (43-665)			5.4 (1-14)	PT GC-ECD (Chambon et al., 1983)
	NR	Br		32 (18-45)			289 (177-600)	
Italy	NR	Cl		115 (62-179)	8 (6-10)	1.4 (0.8-2)	nd	HS GC-ECD (Aggazzotti and Predieri, 1986)
Canada	Spa Spa	Cl Br		154 (5-750)				PT GC-MS (Benoit and Jackson, 1987)
Germany	Indoor	NR		95 (41-118)	0.5 (0.2-1.5)	0.1 (0.05-0.3)		GC (Puchert et al., 1989)
	Indoor	NR		81 (44-170)	9 (6-20)	1.5 (1.2-2.2)		
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)
Australia	Indoor	Cl/Oz	(13-24)	(13-24)	(0.1-0.9)	nd	nd	NR (Kelsall and Sim, 2001)
	Indoor	Cl	(21-87)	(20-85)	(0.2-2)	nd	nd	
	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, 2002)
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 (Kozłowska et al., 2006)
USA	Indoor	NR		0.1 (nd-0.14)				MIMS (Li and Blatchley, 2007)
	Outdoor	NR		(0.08-0.13)				
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)
Korea	Indoor	Cl		41 (0.2-102)	3 (nd-11)	0.5 (nd-5.6)	nd	PT GC-MS (Lee et al., 2009)
	Indoor	Cl/Oz		29 (0.2-65)	2.4 (nd-5.7)	0.2 (nd-3.4)	nd	
	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)
Korea	Indoor	Cl		21 (nd-46)	2.1 (nd-7)	nd	nd	PT GC-MS (Lee et al., 2010)
	Indoor	Cl/Oz		7.4 (nd-21)	1.1 (nd-2.5)	nd	nd	

Country	Pool(s) Type	Disinfection Method	Trihalomethane Concentration in Swimming Pool Water (µg/L); mean (min-max).				Analytical Method	Reference
			Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane		
	Indoor	EGMO		15 (nd-40)	10 (nd-34)	8.9 (nd-32)	4.1 (nd-18)	
Italy	Indoor	SDCIC		86 (36-127)	1.9 (1.6-2)	nd	nd	
	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)	
Spain	Indoor	NR	43					
	Outdoor	NR	151					PT GC-MS (Font-Ribera et al., 2010a)
Spain	Indoor	Cl	92 (29-247)	77 (22-217)	11 (3.6-25)	2.4 (0.4-5.3)	1.5 (0.2-2.8)	
	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 GC-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)	
	Indoor	BCDMH		0.2 (0.1-0.3)	0.4 (0.2-0.7)	2.4 (2.1-2.7)	57 (52-64)	PT GC-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)	
	Outdoor	Cl		556 (170-882)	125 (34-315)	10 (6.3-13)	nd	LLE GC-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)
Italy	Indoor	Cl		15 (8.5-20)	14 (9.4-25)	13 (6.7-23)	7.2 (3.1-16)	
	Indoor	Br		0.2 (0.1-0.3)	0.4 (0.2-0.6)	2.4 (2.1-2.6)	60 (52-61)	PT GC-MS (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)	
	Indoor*	DCICA	(32-78)	(0.2-0.3)	(0.3-0.7)	(3-3.2)	(29-74)	HS GC-MS (Parinet 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)					
	Outdoor	Cl	98 (12-311)					LLE GC-MS (Simard et al., 2013)
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)
Italy	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)	
	Indoor	Cl	32 (6.8-98)					
	Indoor	DCICA	54 (14-134)					HS GC-ECD (Righi et al., 2014)
	Indoor	TCICA	32 (12-53)					
China	Outdoor	Cl	55 (27-74)					
	Indoor	Cl/Oz	31 (7.6-57)					LLE GC-ECD (Zhang et al., 2015)
Denmark	NR	Cl		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)					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)	
	Spa	Cl		19	0.1	0.2	0.1	HS-SPME GC-MS (Carter et al., 2015)
Canada	Indoor	Cl	84 (29-140)	63 (22-100)	9.9 (1.2-38)	21 (nd-56)	13 (nd-25)	HS-SPME GC-ITMS (Tardif et al., 2015)
Saudi Arabia	Indoor*	Cl	61 (29-96)	<5 ^a	<5 ^a	<5 ^a	50 (43-58)	LLE GC-MS (Chowdhury et al., 2016)
USA	Spa	Br/TCICA		nd	nd	14	253	
	Indoor	BCDMH		nd	nd	2.5 (2.4-2.6)	152 (118-186)	MIMS (Daiber et al., 2016)

Country	Pool(s) Type	Disinfection Method	Trihalomethane Concentration in Swimming Pool Water ($\mu\text{g/L}$); mean (min-max).				Analytical Method	Reference
			Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane		
	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 (Hang et al., 2016)
	Indoor	Cl/Oz		141 (96-213)	106 (85-141)	2.0 (1.5-4.9)	47 (38-59)	
France	Outdoor	Cl	80	70	7.9	1.9	0.6	LLE GC-ECD (Manasfi et al., 2016)
	Indoor*	Cl	70 (50-92)	nd	nd	3.6 (1.6-5.2)	66 (49-87)	
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 Br₂). **CIC**: Chloroisocyanurate. **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **DCICA**: Dichloroisocyanuric acid. **EGMO**: Electrochemically-Generated Mixed-Oxidant. **Oz**: Ozone. **SDCIC**: Sodium dichloroisocyanurate. **TCICA**: Trichloroisocyanuric acid. **Various Cl**: 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.

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

Country	Pool(s) Type	Disinfection Method	Haloacetic Acid Concentration in Swimming Pool Water (µg/L); mean (min-max).										Analytical Method	Reference	
			THAA	TCAA	DCAA	CAA	BAA	DBAA	TBAA	BDCAA	DBCAA	BCAA			
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) ^a											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)
Korea	Indoor	Cl		156 (20-636)	68 (14-246)									LLE GC-ECD	(Lee et al., 2010)
	Indoor	Cl/Oz		17 (1-86)	12 (nd-32)										
	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)	77 (60-109)	23 (8.5-36)								HS GC-MS	(Cardador and Gallego, 2011)
	Outdoor	Cl		120 (99-146)	151 (130-170)	26 (19-34)									
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) ^b	(0.4-0.9)	(0.1-12) ^b	(0.2-0.9)	(0.4-25)		HS-SPME GC-ECD	(Sa et al., 2012)
Portugal	NR	NR	106 (76-154) ^c	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)											PT GC-ECD	(Simard et al., 2013)
	Outdoor	Cl	808 (155-2224)												
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) ^c	53 (6-90)	34 (5-60)									LLE GC-ECD	(Wang et al., 2014)
	Outdoor	NR	156 (89-332) ^c	53 (33-98)	81 (44-195)										
	Indoor	NR	1613 (70-3980) ^c	890 (20-2970)	727 (50-750)										
USA	Outdoor	NR	1442 (800-2430) ^c	680 (370-1140)	700 (310-1330)										
	Spa	NR	1067 (690-1360) ^c	330 (40-530)	450 (50-750)										

Country	Pool(s) Type	Disinfection Method	Haloacetic Acid Concentration in Swimming Pool Water (µg/L); mean (min-max).									Analytical Method	Reference	
			THAA	TCAA	DCAA	CAA	BAA	DBAA	TBAA	BDCAA	DBCAA			BCAA
Australia	Indoor	Various Cl		893 (110-1700)	983 (230-2100)	43 (32-64)	<0.5	<0.5		17 (<0.5-22)	<0.5	<0.5	LLE GC-ECD	(Yeh et al., 2014)
	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		
	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) ^d	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)
	Indoor	Cl/Oz	102 (14-161)											
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., 2016)
USA	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)	LLE GC-MS	(Daiber et al., 2016)
	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)		
	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)		
	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)
	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)		
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) ^c	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, DBAA 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**: Bromodichloroacetic Acid. **CAA**: Chloroacetic Acid. **DBAA**: Dibromoacetic Acid. **DBCAA**: Dibromochloroacetic Acid. **DCAA**: Dichloroacetic Acid. **TBAA**: Tribromoacetic Acid. **TCAA**: Trichloroacetic Acid. **THAA**: Total Haloacetic Acids: Sum of CAA, DCAA, TCAA, BAA, DBAA, TBAA, BCAA, CDBAA and BDCAA. **BCDMH**: 1-Bromo-3-chloro-5,5-dimethylhydantoin. **Br**: Bromine Based (NaBr in combination with an oxidiser or Br₂). **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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. **SPE**: Solid-Phase Extraction. **SPME**: Solid-Phase Microextraction. **TQMS**: Triple Quadrupole Mass Spectrometry. **UPLC**: Ultra Performance Liquid Chromatography. **UVD**: Ultraviolet Detection.

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

Country	Pool(s) Type	Disinfection Method	Chloramine Concentration in Swimming Pool Water ($\mu\text{g/L}$); mean (min-max).				Analytical Method	Reference
			Total Inorganic Chloramines	Trichloramine (NCl_3)	Dichloramine (NHCl_2)	Monochloramine (NH_2Cl)		
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)
	Outdoor	NR		(70-160)				
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)
Spain	Indoor	Cl		<100	380 (<10-650)	290 (100-640)	DPD/KI Colorimetric	(Richardson et al., 2010)
	Indoor	BCDMH		<100	<10	270 (240-300)		
USA	Indoor	Cl		(100-780)	(180-750)	(180-300)	MIMS	(Weng and Blatchley, 2011)
Canada	Indoor	Cl				40 (10-60)	DPD/KI Colorimetric	(Wang, 2011)
	Outdoor	Cl				10 (9-11)		
Canada	Indoor	Cl	689 (376-981)	341 (nd-650)	25 (nd-593)	323 (188-434)	DPD/KI Colorimetric	(Catto et al., 2012)
	Indoor	Cl	527 (268-802)	232 (nd-557)	11 (nd-70)	284 (nd-450)		
Canada	Indoor	Cl	736 (311-1723)				DPD/KI Colorimetric	(Simard et al., 2013)
	Outdoor	Cl	142 (8-845)					
USA	Indoor	Cl		420 (nd-2190)	65 (nd-250)	89 (nd-620)	MIMS	(Afifi and Blatchley, 2015)
Switzerland	Indoor/Outdoor	Various ^a		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)
USA	Indoor	Cl		319 (66-527)	41 (nd-55)	58 (43-71)	MIMS	(Daiber et al., 2016)
	Indoor	BCDMH		12 (5.6-18)	51 (45-56)	67 (nd-67)		
	Spa	BCDMH		183 (3.7-363)	40 (39-41)	48 (43-52)		
	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)
Spain	Indoor	Cl		50 (nd-300)	300 (180-400)	180 (100-200)	DPD/KI Colorimetric	(Llana-Belloch et al., 2016)
	Indoor	Cl		50 (nd-300)	350 (300-400)	320 (300-400)		
	Indoor	UV only		nd	nd	nd		

*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 , $\text{Ca}(\text{OCl})_2$ or Cl_2). **Oz**: Ozone. **UV**: Ultraviolet. **DPD**: diethyl-*p*-phenylenediamine. **KI**: Potassium Iodide. **MIMS**: Membrane-Inlet Mass Spectrometry.

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

Country	Pool(s) Type	Disinfection Method	Haloacetonitrile Concentration in Swimming Pool Water (µg/L); mean (min-max).						Analytical Method	Reference	
			BAN	CAN	BCAN	DBAN	DCAN	TCAN			THAN
USA	Indoor	NR						100 (100-100)		MIMS	(Li and Blatchley, 2007)
	Outdoor	NR						(20-30)			
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			
	Indoor	EGMO			3.5 (nd-8.0)	2.6 (nd-6.8)	3.8 (nd-9.0)	nd		LLE GC-ECD	(Lee et al., 2010)
	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			
	Spa	Cl					9.0			LLE-GC-MS	(Carter et al., 2015)
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 (4.-24)	0.2 (nd-1.1)		LLE GC-ECD	(Tardif et al., 2015)
China	Indoor	TCICA							5.0 (1.3-13) ^a		
	Outdoor	Cl							3.6 (0.8-8.3) ^a	LLE GC-ECD	(Zhang et al., 2015)
USA	Spa	Br/TCICA			5.6	219	nd	nd			
	Indoor	BCDMH			1.8 (nd-1.8)	37 (35-39)	nd	nd			
	Spa	Cl/Oz			nd	nd	(nd-14)	nd		MIMS	(Daiber et al., 2016)
	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)			
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)

*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 Br₂). **Cl:** Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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.

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

Country	Pool(s) Type	Disinfection Method	<i>N</i> -Nitrosamine Concentration in Swimming Pool Water (ng/L); mean (min-max).								Analytical Method	Reference	
			NDMA	NDEA	NEMA	NDBA	NMOR	NPIP	NDPA	NPYR			
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)	
	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)	
	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)

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)₂ or Cl₂). **FLD:** Fluorescence Detection. **GC:** Gas Chromatography. **HPLC:** High Performance Liquid Chromatography. **LLE:** Liquid-Liquid Extraction. **MS:** Mass Spectrometry. **SPE:** Solid-Phase Extraction.

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

Country	Pool(s) Type	Disinfection Method	Haloketone Concentration in Swimming Pool Water (µg/L); mean (min-max).					Analytical Method	Reference
			Trichloroacetaldehyde (CH)	Dichloroacetaldehyde (DCAL)	Dibromoacetaldehyde (DBAL)	Dibromochloroacetaldehyde (DBCAL)	Tribromoacetaldehyde (TBAL)		
Korea	Indoor	EGMO	10 (nd-23)					LLE GC-ECD	(Lee et al., 2010)
	Indoor	Cl/Oz	3.6 (nd-10)						
	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)					LLE GC-ECD	(Zhang et al., 2015)
	Indoor	Cl	47 (6.0-132)						
Australia	Indoor	Cl	301 (177-400)		2.4	0.3		LLE GC-MS	(Carter et al., 2015)
	Spa	Cl	405						
France	Outdoor*	Cl	190					LLE GC-ECD	(Manasfi et al., 2016)
	Indoor*	Cl	nd				(0.4-2.2)		
USA	Indoor	Cl	120 (68-165)					MIMS	(Daiber et al., 2016)
	Indoor	BCDMH	nd						
	Spa	Cl/Oz	(nd-101)						
	Spa	Br	2.9 (1.3-3.9)						

*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 Br₂). **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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.

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

Country	Pool(s) Type	Disinfection Method	Haloketone Concentration in Swimming Pool Water (µg/L); mean (min-max).				Analytical Method	Reference
			1,1-Dichloropropanone (1,1-DCP)	1,1,1-Trichloropropanone (1,1,1-TCP)	1, 2-Dichloroacetone (1,2-DCA)	Chloroacetone		
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)
	Outdoor	Cl		2.4 (0.9-6.3) ^a				
USA	Spa	Br/TCICA	nd	nd			MIMS	(Daiber et al., 2016)
	Indoor	BCDMH	nd	nd				
	Spa	Cl/Oz	nd	(nd-9.7)				
	Spa	BCDMH	nd	nd				
USA	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)			LLE GC-MS	(Hang et al., 2016)
	Indoor	Cl	0.7 (nd-7.7)	46 (1.9-180)				
France	Indoor*	Cl	nd	nd			LLE GC-ECD	(Manasfi et al., 2016)
	Outdoor	Cl	21	72				
Canada	Indoor	Cl		1.9 (0.3-7.3)			LLE GC-MS-MS	(Tardif et al., 2016)

*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 Br₂). **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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.

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

Country	Pool(s) Type	Disinfection Method	Halonitromethane Concentration in Swimming Pool Water (µg/L); mean (min-max).					Analytical Method	Reference
			Total halonitromethanes (THNMs)	Trichloronitromethane (TCNM)	Tribromonitromethane (TBNM)	Bromochloronitromethane (BCNM)	Bromonitromethane (BNM)		
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	(Zhang et al., 2015)
	Outdoor	Cl		nd					
USA	Indoor	BCDMH		nd				MIMS	(Daiber et al., 2016)
	Indoor	Cl		nd					
	Spa	NR		nd					
	Spa	BCDMH		nd					
	Spa	Cl/Oz		nd					
China	Indoor	Cl		1.0 (nd-4.5)				LLE GC-ECD	(Hang et al., 2016)
	Indoor	Cl/Oz		0.4 (nd-2.1)					
France	Indoor	Cl		nd				LLE GC-ECD	(Manasfi et al., 2016)
	Outdoor	Cl		4.5	nd				
Canada	Indoor	Cl		0.3 (0.02-3.7)				LLE GC-ECD	(Tardif et al., 2016)

*Seawater filled. **nd**: Not Detected. **NR**: Not Reported. **BCDMH**: 1-Bromo-3-chloro-5,5-dimethylhydantoin. **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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) Type	Disinfection Method	Haloacetic Acid Concentration in Swimming Pool Water (µg/L); mean (min-max).									Analytical Method	Reference	
			TCAAm	DCAAm	TBAAm	DBAAm	BCAAm	BDCAAm	DBCAAm	BIAAm	CIAAm			DIAAm
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. **CIAAm**: Chloroiodoacetamide. **DIAAm**: Diiodoacetamide. **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **ECD**: Electron Capture Detector. **GC**: Gas Chromatography. **LLE**: Liquid-Liquid Extraction. **MS**: Mass Spectrometry.

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

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

*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 Br₂). **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **ClO₂**: Chlorine dioxide. **DCICA**: Dichloroisocyanuric acid. **EGMO**: Electrochemically-Generated Mixed-Oxidant. **Oz**: Ozone. **SDCIC**: Sodium dichloroisocyanurate. **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 Br₂) and/or ultraviolet (UV). **Various Cl**: Refers to any of the following individually or in combination: Cl Based, SDCIC, chloroisocyanurate (CIC), DCICA, TCICA and/or ultraviolet (UV).

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

Country	Pool(s) Type	Disinfection Method	Total Organic Halogen in Swimming Pool Water (µg/L); mean (min-max).				Reference
			TOX	TOCl	TOBr	TOI	
Australia	Indoor	Cl/Oz	(880-1080)				(Kelsall and Sim, 2001)
	Indoor	Cl	(930-1380)				
	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)
China	Indoor	Cl		246	4		(Xiao et al., 2012)
	Outdoor	Cl		213	4		
Australia	Indoor	Cl	1508	1490	15	3.2	(Yeh et al., 2014)
	Outdoor	Cl	699 (194-1150)	680 (193-1117)	18 (1.6-32)	0.6 (nd-1.3)	
	Indoor	EGMO	1538	1524	12	1.3	
	Outdoor	EGMO	1049	1039	8	2.5	
	Baby	EGMO	(2894-3015)	(2825-2907)	(69-107)	(nd-1.3)	
USA	Indoor	Cl		3682 (1428-4828)	200 (137-280)		(Daiber et al., 2016)
	Indoor	BCDMH		1337 (1162-1511)	4897 (4106-5688)		
	Spa	BCDMH		1213 (950-1394)	4197 (2198-5444)		
	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)

nd: Not Detected. **TOBr**: Total organic bromine. **TOCl**: 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 Br₂). **Cl**: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **EGMO**: Electrochemically-Generated Mixed-Oxidant. **Oz**: Ozone. **TCICA**: Trichloroisocyanuric acid.

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

Country	Disinfection Method	Trihalomethane Concentration in Swimming Pool Air ($\mu\text{g}/\text{m}^3$); mean (min-max).					Collection height above water's surface (cm)	Collection Method	Analytical Method	Reference
		Total THMs (TTHMs)	Trichloromethane (Chloroform)	Bromodichloromethane	Dibromochloromethane	Tribromomethane (Bromoform)				
Germany	Cl		117 (10-384)	9.5 (0.1-39)			Directly	XAD ₂ -Resin	LD GC-MS/ECD	(Lahl et al., 1981)
Canada	Cl ^a Br ^a		154 (4-750)			747 (nd-1910)	10-20	Tenax	PT GC-MS	(Benoit and Jackson, 1987)
Italy	NR		214 (66-650)				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) ^a 170 (135-195) ^b	11 (7-14) ^b 20 (16-24) ^c	5.2 (4-7) ^b 11 (9-14) ^c	0.2 ^b 0.2 ^c	150	Glass Vial	DI GC-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	(Thiriart et al., 2009)
Italy	Cl		85 (21-182) ^d 52 (12-127) ^e				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)
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) ^f	148 (54-241) 53 (2.7-134) ^f	25 (3.8-86) 4.9 (0.1-16) ^f	16 (0.2-95) 1.9 (nd-4.8) ^f	9.6 (nd-36) 1.2 (nd-1.8) ^f	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)

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 Br₂). Cl: Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). ATD: Automatic Thermal Desorption. DI: Direct Injection. ECD: Electron Capture Detector. FTIR: Fourier Transform 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.

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

Country	Disinfection Method	Trichloramine (NCl ₃) Concentration in Swimming Pool Air (µg/m ³)	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 ^a	560 (130-1340)	30	Quartz Fibre ^c	LD-IC-MS	(Jacobs et al., 2007)
		660 (380-1100) ^b	150			
Spain	Cl	290 (170-430)	60	Quartz Fibre ^c	LD-IC-MS	(Richardson et al., 2010)
	BCDMH	80 (70 -100)	60			
France	Cl	190 (20- 1260)	NR	Quartz Fibre ^c	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 ^c	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 Fibre ^c	LD-IC-MS	(Chu et al., 2013)
Sweden	NR	200 (40-360)	130	Quartz Fibre ^c	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 ^d	IC	(Lévesque et al., 2015)
Canada	Cl	270 (60-450) ^b	150	Teflon ^e	LD-IC-MS	(Tardif et al., 2015)
Sweedeen	Cl	130 (20-290)	130	NR ^e	IC	(Johannesson et al., 2016)
Canada	Cl	230 (nd-560) ^b	150	Teflon ^e	LD-IC-MS	(Tardif et al., 2016)
		150 (70-320) ^f				
Spain	Cl	473 (249-858)	150	Quartz Fibre ^c	LD-IC-MS	(Font-Ribera et al., 2016)

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)₂ or Cl₂). **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.

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

Country	Pool(s) Type	Disinfection Method	Total Carbon, Total Nitrogen and Urea in Swimming Pool Water (mg/L); mean (min-max).			Reference
			Total Organic Carbon (TOC)	Total Nitrogen (TN)	Urea	
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)
	Outdoor	Cl	(1.6-2)			
Thailand	NR	NR	1.1 (0.6-1.5) 0.9 (0.6-1.5) ^a			(Panyakapo et al. 2008)
Korea	Indoor	Cl	4.4 (0.2-71)			(Lee et al. 2009)
	Indoor	Cl/Oz	3.7 (0.2-82)			
	Indoor	EGMO	3.5 (0.4-12)			
USA	Indoor	Cl	7.1 (3-24)	3.6 (0.8-12)		(Kanan 2010)
Korea	Indoor	Cl	2.3 (0.5-7)			(Lee et al. 2010)
	Indoor	Cl/Oz	1.7 (0.7-3)			
	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	1.3 ^a		0.8	(Schmalz et al., 2011b)
Germany	Various	NR			1.3 (0.5-2.1)	(Schmalz et al., 2011a)
USA	Indoor	Cl/UV	(5.2-18)			(Plewa et al., 2011)
	Indoor	BCDMH	125			
	Indoor	Cl	23 (13-33)			
	Outdoor	Cl	33			
	Spa	Cl	12			
Portugal	Indoor	Cl	4 (1.13-6.7)			(Sa et al., 2011)
Canada	Indoor	Cl	2.1 (0.02-4.4)			(Wang, 2011)
	Outdoor	Cl	6.2 (0.02-16)			
USA	Indoor	Cl			(<0.1-0.3)	(Weng and Blatchley, 2011)
France	Indoor	Cl	4.8 (3.6-8.6)	3 (0.7-7.7)		(Parinet et al., 2012)
	Indoor	DCICA	(2.8-3.3)	(1.3-2.7)		
China	Indoor	Cl	3.2			(Xiao et al., 2012)
	Outdoor	Cl	2.8			
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)
Canada	Indoor	Cl/UV	12 (10-15) 7.3 (4.9-9.5) ^a			(Wang et al., 2013)
			13 (11-16)			
	Indoor	Cl	7.9 (5.9-11) ^a			
Australia	Outdoor	Cl	3.4 (3.1-3.9)	2.9 (0.6-4.6) 0.4 (0.1-0.7) ^b		(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)
USA	Indoor	NR	4.7 (1.3-8.4)			(Wang et al., 2014)
	Outdoor	NR	2.5 (0.9-8.5)			
	Spa	NR	8.1 (3.7-11)			
China	Indoor	NR	11 (2.7-27)			(Wang et al., 2014)
	Outdoor	NR	9.5 (nd-13)			
Australia	Indoor	Cl	5.7 (3.6-7.2)			(Carter et al., 2015)
	Spa	Cl	12			
Denmark	NR	Cl	1.9 (1.6-2.2)			(Spiliotopoulou et al., 2015)

China	Indoor	Cl/Oz	8.9 (2.5-27)	2.2 (0.2-11) ^b	(Zhang et al., 2015)
	Outdoor	Cl	9.5 (3.2-13)	0.9 (0.2-1.3) ^b	
Saudi Arabia	Indoor*	Cl	2.1 (1.3-3.9) 1.9 (1.0-3.6) ^a		(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) ^a		(Hang et al., 2016)
	Indoor	Cl	22 (4.2-39) ^a		
France	Indoor	Cl	11 (10-12)		(Manasfi et al., 2016)
	Outdoor	Cl	11		
China	Outdoor	Cl	1.1 (NR)		(Tang and Xie, 2016)
Canada	Indoor	Cl	1.0 (1.4-10) ^a		(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 Br₂). **Cl:** Chlorine Based (NaOCl, Ca(OCl)₂ or Cl₂). **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: Cl Based, Br Based.

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

Antifungal Agents	
Dichlorophen	Dichlorophene; 4-chloro-2-[(5-chloro-2-hydroxyphenyl)methyl]phenol; eptiphen; <i>o</i> -benzyl- <i>p</i> -chlorophenol; <i>ortho</i> -benzyl- <i>p</i> -chlorophenol; benzylchlorophenol; 5-chloro-2-hydroxydiphenylmethane; 4-chloro- α -phenyl- <i>o</i> -cresol; chlorofene; 4-chloro-2-(phenylmethyl)phenol; benzyl- <i>p</i> -chlorophenol; 4-chloro- α -phenylcresol; 2-benzyl-4-chlorophenol; 4-chloro-2-(phenylmethyl)phenol; 5-chloro-2-hydroxydiphenylmethane; <i>o</i> -benzyl- <i>parachlorophenol</i> ; <i>p</i> -chloro- <i>o</i> -benzylphenol; ketolin-h; santophen 1; neosobenil; sentiphen clorofenum
2,4-DCPh	5-chloro-(2,4-dichlorophenoxy)phenol; 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; Dowicide 2S; omal
Parabens	
MeP	methylparaben; methyl-4-hydroxybenzoate; methyl <i>p</i> -hydroxybenzoate; methyl parahydroxybenzoate; Nipagin M; E218; Tegosept; Mycocten
EtP	ethylparaben; ethyl-4-hydroxybenzoate; ethyl <i>parahydroxybenzoate</i> ; ethyl <i>para</i> -hydroxybenzoate; ethyl- <i>p</i> -hydroxybenzoate; 4-hydroxybenzoic acid ethyl ester; E214
PrP	propylparaben, propyl-4-hydroxybenzoate; 4-hydroxybenzoesäurepropylester; propyl- <i>p</i> -hydroxybenzoate; propyl <i>parahydroxybenzoate</i> ; nipasol; E216
iPrP	isopropylparaben
BuP	butylparaben; butyl-4-hydroxybenzoate; butyl- <i>parahydroxybenzoate</i> ; butyl- <i>p</i> -hydroxybenzoate
iBuP	isobutylparaben
PeP	pentylparaben; pentyl-4-hydroxybenzoate; amyl-4-hydroxybenzoate; pentyl- <i>p</i> -hydroxybenzoate; n-pentyl-4-hydroxybenzoate
HeP	heptaparaben; 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; <i>n</i> -octyl-4-hydroxybenzoate; octyl- <i>p</i> -hydroxybenzoate
BzP	benzylparaben; benzyl-4-hydroxybenzoate; benzyl <i>p</i> -hydroxybenzoate; benzyl <i>parahydroxybenzoate</i> ; phenylmethyl 4-hydroxybenzoate; nipabenzyl; parosept; benzyl parasept
UV-Filters	
Amiloxate	isoamyl 4-methoxycinnamate; 3-methylbutyl-(2 <i>E</i>)-3-(4-methoxyphenyl)acrylate; isopentyl 4-methoxycinnamate; isoamyl- <i>p</i> -methoxycinnamate
Avobenzone	avobenzone; 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	benzophenone-3; 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	1 <i>H</i> -benzotriazole
Homosalate	3,3,5-trimethylcyclohexyl-2-hydroxybenzoate; Eusolex HMS
4-MBC	4-methylbenzylidene camphor; enzacamene; (3 <i>E</i>)-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 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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