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Occurrence, origin and toxicity of disinfection byproducts in chlorinated swimming pools: An overview

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Abstract

Disinfection treatments are critical to conserve the microbiological quality of swimming pool water and to prevent water-borne infections. The formation of disinfection byproducts (DBPs) in swimming pools is an undesirable consequence resulting from reactions of disinfectants (e.g. chlorine) with organic and inorganic matter present in pool water, mainly brought by bathers. A considerable body of occurrence studies has identified several classes of DBPs in swimming pools with more than 100 compounds detected, mainly in chlorinated freshwater pools. Trihalomethanes (THMs), haloacetic acids (HAAs), haloacetaldehydes (HALs) are among the major DBPs in swimming pools. Other DBPs such as haloacetonitriles (HAN), haloamines, nitrosamines, and halobenzoquinones have also been detected. Researchers have been interested in identifying the precursors responsible for the formation of DBPs. In swimming pools, anthropogenic organic loads brought by swimmers increase the complexity of pool water chemistry. When human inputs (e.g. sweat, urine, hair, skin and personal care products) containing very diverse organic compounds are introduced to pools by swimmers, they react with chlorine resulting in the formation of complex mixtures of DBPs. The overwhelming majority of the total organic halide (TOX) content is still unknown in swimming pools. Exposure of swimmers to DBPs can take place through multiple routes, depending on the chemical properties of each DBP. Toxicological studies have shown that swimming pool water can be mutagenic with different potencies reported in different studies. Many DBPs have been shown to be genotoxic

and carcinogenic. DBPs were also shown to induce reproductive and neurotoxic adverse effects in animal studies. Epidemiologic studies in humans have shown that exposure to DBPs increases the risk of respiratory adverse effects and bladder cancer. Association between DBPs and other health effects are still inconclusive. Data gathered in the present review (occurrence, toxicity, and toxicological reference values) could be used in conducting chemical risk assessment studies in swimming pools.

Introduction

Disinfection of drinking water was one of the major public health advances of the twentieth century. The adoption of water chlorination as a standard treatment technique caused a large drop in mortality from infectious disease around the world (Boorman, 1999). The efficiency of chlorination in conserving the quality of drinking water from microbiological deterioration has contributed to the extrapolation of its application to include swimming pools and recreational water venues (WHO, 2006). Disinfection of swimming pool water is essential to kill pathogenic microorganisms and prevent outbreaks of infectious diseases (ANSES, 2012). Chlorination represents the most commonly used disinfection treatment in swimming pools (Lakind et al., 2010). Chlorine can be added in the form of compressed chlorine gas, sodium hypochlorite solution (NaOCl), or solid calcium hypochlorite (Ca(OCl)₂). Alternative disinfectants include other chlorine-based disinfectants (e.g. chlorine dioxide, stabilized chlorine), chloramines, and ozone. As in drinking water, disinfection of swimming pool water leads to the undesirable formation of disinfection byproducts (DBPs). Evidence from toxicological and epidemiological studies about adverse health effects for DBPs have raised concerns about the chemical safety of swimming pool waters. The first studies investigating the occurrence of DBPs in swimming pools date back to 1980 (Beech et al., 1980; Weil et al., 1980). Since then, many studies have been performed to examine the occurrence of DBPs in pools in different countries (Aggazzotti and Predieri, 1986; Chu and Nieuwenhuijsen, 2002; Judd and Jeffrey, 1995; Kim et al., 2002). Today, after more than 35 years of research, more than 100 DBP have been detected in swimming pools (Chowdhury et al., 2014; Daiber et al., 2016; Richardson et al., 2010; Teo et al., 2015). The formation of DBPs in swimming pool waters is attributed to precursors that can be derived from the filling water as well as from pool users. Human inputs into swimming pools are diverse and include constituents of urine, sweat, rhino-pharyngeal secretions, skin particles, skin lipids

(sebum), hair, cosmetics, sunscreens and other personal care products (Keuten et al., 2012, 2014; Kim et al., 2002; Lakind et al., 2010; Richardson et al., 2010; Weisel et al., 2009). Chlorine, mainly in the form of hypochlorous acid and hypochlorite ions, reacts with these organic compounds resulting in the formation of complex mixtures of DBPs. Many classes of DBPs including haloamines, trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halodiacids, haloacetaldehydes (HALs), haloketones (HKs), haloaldehydes, haloamides, halophenols, halobenzoquinones and *N*-nitrosamines, have been identified in swimming pools (Chowdhury et al., 2014; Richardson et al., 2010; Teo et al., 2015; Wang et al., 2013; Zwiener et al., 2007). However, the continuous inputs of organic loads by swimmers results in the formation of complex mixture of DBPs that have not been identified yet. In drinking water, more than 50% of the halogenated DBP material formed during chlorination are still not accounted for (Krasner et al., 2006; Richardson and Postigo, 2011; Weinberg et al., 2002). Taking into consideration the complexity of anthropogenic inputs, the fraction of unidentified DBPs in swimming pools is even higher (Kim et al., 2002; Lakind et al., 2010; Manasfi et al., 2017b). The following sections present an overview of occurrence data for DBPs in swimming pools, the precursors that have been demonstrated to generate DBPs, and finally the toxicological and human health effects related to the exposure to DBPs.

Occurrence of DBPs in Swimming Pools

In the recent years, many studies have investigated the occurrence of DBPs in swimming pools. The levels and nature of DBPs in swimming pools depend on several factors including the type of disinfectant, characteristics of the pool, pool users' hygiene (Zwiener et al., 2007), use of pools (competition, relaxation, recreational activities) (Weng et al., 2011; Keuten et al., 2014), and nature of water used to fill the pools whether it is tap water, seawater or even thermal water (ANSES, 2013). Most of the studies analyzing the occurrence of DBPs investigated pools that were filled with municipal (tap) water and treated with chlorine (Teo et al., 2015). Very few studies dealt with pools fed with seawater or with bromide-rich water (Huang et al., 2008; Parinet et al., 2012; Manasfi et al., 2016; Font-Ribera, 2016) or with pools treated with bromine for disinfection (Lee et al., 2010; Hoffmann, M., 2015; Chowdhury et al., 2016). Two recent papers have reviewed the major disinfection by-products that have been commonly reported in chlorinated and brominated swimming pools (Chowdhury et al., 2014; Teo et al., 2015). The

detected DBPs included haloamines, THMs, HAAs, haloaldehydes, halonitriles, haloketones (HKs), halonitromethanes, haloamides, haloalcohols, haloacids and other halogenated and non-halogenated DBPs (Chowdhury et al., 2014).

Haloamines

In terms of occurrence levels, chloramines (or bromamines in bromide-rich waters) are the disinfection by-products detected at the highest levels amongst DBPs, with monochloramine (NH_2Cl) mainly found in water (up to $1180 \mu\text{g L}^{-1}$), followed by trichloramine (NCl_3) (up to $800 \mu\text{g L}^{-1}$) and dichloramine (NHCl_2) (up to $650 \mu\text{g L}^{-1}$) (Table 1). Trichloramine, which is four hundred-fold more volatile than its two congeners (Chu et al., 2013), is also found in air with levels strongly inversely correlated to ventilation applied in indoor swimming pools (Lévesque et al., 2015; Gérardin et al., 2015).

Table 1: Occurrence of haloamines in swimming pools around the world

Country	Air ($\mu\text{g}\cdot\text{m}^{-3}$)	Water ($\mu\text{g L}^{-1}$)			References	
	NCl_3	NCl_3	NHCl_2	NH_2Cl		
France	20-1260	5-1700*			indoor	Anses, 2010; Bessonneau et al., 2011
Switzerland	38-520	-			indoor	Parrat et al., 2012
Québec	300-510	102-568	38-206	171-948	indoor	Simard et al., 2013; Lévesque et al., 2015
	-	2.6-280	1.3-137	4-430	outdoor	Simard et al., 2013
	80-350	<LOD-650	<LOD-593	<LOD-450	indoor	Catto et al., 2012
USA	-	<LOD-377	<LOD-147	<LOD-1180	indoor	Weaver et al., 2009
		100-800**	80-180	180-320	indoor	Weng et al., 2011
Taiwan	17-150	100-1650*			indoor	Chu et al., 2013
Sweden	1-640	-			indoor	Westerlund et al., 2015
Italy	200-1020	-			indoor	Fantuzzi et al., 2013
Spain	170-430	<LOD-377	<LOD-650	100-640	indoor	Richardson et al., 2010
	248-858	<lod-1600	<lod-700	<lod-700	indoor	Font-Ribera et al., 2016
*these values represent the sum of inorganic chloramines determined using the DPD method						
** these high values can be explained because of sampling during a swimming competition						
<LOD : below the limit of detection						

Chloramines are often determined as a global parameter (combined chlorine or total inorganic chloramines) by the use of the colorimetric N,N-diethyl-p-phenylenediamine (DPD). However, only membrane introduction mass spectrometry (MIMS) has demonstrated its performance not only to avoid interferences encountered using the DPD method (due to organic chloramines) (Weaver et al., 2009) but also to discriminate the three inorganic chloramines (Kinani et al.,

2012) and to analyze cyanogen halide compounds, such as cyanogen chloride (CNCl) and cyanogen bromide (CNBr) (Yang and Shang, 2005).

Trihalomethanes (THMs)

THMs have been detected at high concentrations in swimming pools, representing between 5 to 10% of total organohalogens as determined by the adsorbable organic halide (AOX) method, with chloroform (CHCl₃) being the dominant species (Aggazzotti and Predieri, 1986; Beech et al., 1980; Erdinger et al., 2004; Fantuzzi et al., 2001; Lee et al., 2009; Nieuwenhuijsen et al., 2000; Simard et al., 2013; Weaver et al., 2009), or bromoform (CHBr₃) when bromide present in high concentrations or used as disinfectant (Lourencetti et al., 2012; Parinet et al., 2012; Manasfi et al., 2016). THMs also include dichlorobromomethane and bromodichloromethane. Table 2 gives an overview of the levels of THMs found in water and air of some swimming pools spread over the world.

Table 2: Occurrence of trihalomethanes (THM) in indoor swimming pools

		n	Water (µg.L ⁻¹)				Air (µg.m ⁻³)				References
			CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	
Chlorine-based disinfectant	Italy	5	6.1-68.4	2-5.3	0.4-5.4	<lod	19-58.6	2.9-13	0.3-6	<lod-0.8	Fantuzzi et al., 2001
		1	8.5-20	9.4-25	6.7-23	3.1-16	18-61	8.2-23	6.4-22	5.9-22	Lourencetti et al., 2012
		24	2.5-122	1.4-18.3	0.2-11.7	<lod-3.6					Righi et al., 2014
	Korea	30	<lod-45.8	<lod-7	<lod	<lod			-		Lee et al., 2010
	Spain	1	24-61.6	3.8-12.9	0.9-4.7	0.2-1.9			-		Font-Ribera et al., 2016
		16	22.3-217	3.6-25.2	0.4-5.3	0.2-2.8			-		Font-Ribera et al., 2010
		12	8.4-20.8	9.3-26.8	6.5-22.6	3-16.5	11.9-61.6	7.5-23.4	6.1-26.2	4.4-22.6	Richardson et al., 2010
	USA	11	<lod-173	<lod-150	<lod-54	<lod-67.9			-		Weaver et al., 2009
Canada	41	6.7-126.5	<lod-30.1	<lod-51.3	<lod-45.6	20.3-320.4	1.3-154.6	<lod-204.8	<lod-102.8	Tardif et al., 2016	
	15	12.9-215	<lod-23.9	<lod-27.1	<lod-19.2					Simard et al., 2008	
Bromine-based disinfectant or chlorinated bromide-rich waters	France	8	0.03 - 0.3	0.05-1.1	13.6-63.6	28-930		-			Parinet et al., 2012
		3	<lod	<lod	1.6-3.9	48.9-62.5			-		Manasfi et al., 2016
		3	<lod	<lod	2.1-5.5	49.7-101.3	<lod	<lod	3.6-20.7	21.7-240.1	Manasfi et al., 2017b
	Italy	1	0.08-0.29	0.23-0.6	2.1-2.6	52-61	1.8-6.9	1.9-4.2	6.4-8.7	55-92	Lourencetti et al., 2012
	Spain	4	0.5-2	0.3-2.5	1.2-5.1	78.6-146.6			-		Font-Ribera et al., 2010
	7	0.08-0.3	0.22-0.43	2.1-2.5	52-64	1.7-4.8	1.7-2.8	6.0-7.7	53-77	Marco et al., 2015	
		n = number of pools analyzed	- : not determined; <lod : below the limit of detection								

Haloacetic acids (HAAs)

HAAs have also been detected as predominant DBPs (25 to 30% of total organohalogens, determined by the AOX method) with dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) occurring at the highest concentrations in most of the analyzed pools (Cardador and Gallego, 2011; Lee et al., 2010; Sá et al., 2012; Wang et al., 2014; Yeh et al., 2014). Simard et al.

analyzed 39 outdoor and 15 indoor public pools in Canada and found that HAAs were higher in outdoor pools compared to indoor pools (Simard et al., 2013). In bromide-rich waters, chlorinated HAAs are shifted to their brominated analogues, with tribromoacetic acid (TBAA), chlorodibromoacetic acid (CDBAA) and dichlorobromoacetic acid (DCBAA) mostly found (Parinet et al., 2012; Manasfi et al., 2017b, 2016). HAA concentrations reported in swimming pool water are always higher than those for THMs. This can be explained partially by the higher volatility of THMs as compared to HAAs (Table S1, in supporting information). In addition, the higher formation potential of bather organic loads to form HAAs than THMs and the stability of HAAs towards chlorine and pH variation tend to favor their accumulation in water (Kanan and Karanfil, 2011; Lakind et al., 2010). Table 3 gives an overview of HAAs detected in chlorinated tap water swimming pools, chlorinated seawater swimming pools, and brominated swimming pools and spas.

Table 3: Occurrence of haloacetic acids (HAA) in swimming pools

Nature of water	Country	n	DCAA		TCAA			References
Freshwater	Korea	30	14.1-246		19.7-636			Lee et al., 2010
	Switzerland	4	0.9-240		17.1-94.7			Berg et al., 2000
	USA	25	67-166		93-136			Cardador et al., 2010
	France	8	12-247		16-461			Anses, 2013; Manasfi et al., 2016
	Canada	41	27.4-500		24.1-249.6			Tardif et al., 2016
	Italy	24	<lod-291		<lod-403			Righi et al., 2014
	Spain	30	15.4-51.7		39.2-83.4			Font-Ribera et al., 2016
	Australia	11	230-2400		110-2600			Yeh et al., 2014
			BCAA	DBAA	BDCAA	CDBAA	TBAA	
Bromine-disinfectant	USA	6	<lod-294	90.5-1795	6.3-117	2.5-13.5	26.2-175	Daiber et al., 2016
Seawater	France	10	3.5-216.1	11.3-1088	1.1-20.2	4-427.6	39-53.2	Parinet et al., 2012; Manasfi et al., 2016
<lod : below the limit of detection								
DCAA : dichloroacetic acid; TCAA : trichloroacetic acid; BCAA : bromochloroacetic acid; BDCAA : bromodichloroacetic acid;								
CDBAA : Chlorodibromoacetic acid; TBAA : Tribromoacetic acid								
All concentrations are expressed in $\mu\text{g L}^{-1}$								

Table S1: Physico-chemical properties of main DBPs found in swimming pools

Compound	CAS number	Dissociation constant (pKa)	log P (octanol-water)	Solubility in water (in g L ⁻¹ . 25°C)	Vapour pressure (mm Hg. 25°C)	Henry' constant value (atm.m ⁻³ /mole, at 24 °C)	
THM	Chloroform	67-66-3	nd	1.97	7.95	197	0.00367
	Chlorodibromomethane	124-48-1	nd	2.16	2.7	5.54	0,000783
	Bromodichloromethane	75-27-4	nd	2	3.03	nd	0.00212
	Bromoform	75-25-2	nd	2.4	3.1	nd	0.000535
HA	Monochloramine	10599-90-3	14	nd	4.44.10 ^{4**}	nd	0.45*** (H)
	Dichloramine	3400-09-7	7	nd	1.45.10 ^{3**}	nd	1.52*** (H)
	Trichloramine	10025-85-1	nd	nd	0.412**	nd	435*** (H)
HAA	Monochloroacetic acid (MCAA)	79-11-8	2.866	0.22	858	0.065	0.0000000942
	Dichloroacetic acid (DCAA)	79-43-6	1.26	0.92	1000	0.179	0.000000352
	Trichloroacetic acid (TCAA)	76-03-9	0.512	1.33	44	nd	0.000000135
	Bromoacetic acid	79-08-3	2.89	0.41	93.8	0.119	0.0000000631
	Dibromoacetic acid (DBAA)	631-64-1	nd	0.7	nd	nd	nd
Chloral hydrate	75-87-6	9.66	0.99	30	50	0.0000000291	
HAN	Dichloroacetonitrile	3018-12-0	nd	0.29	33.5	2.82	0.00000379
	Dibromoacetonitrile	3252-43-5	nd	0.47	9600	0.301	0.000000406
	Trichloroacetonitrile	545-06-2	nd	2.09	715	74.1	0.00000134
N-nitrosodimethylamine (NDMA)*	62-75-9	nd	-0.57	290 g (20°C)	nd	0.0000338	
References: ToxNet (National Library of Medicine. USA)							
*Sax. N. et R. Lewis. Sr. 1987. Hawley's condensed chemical dictionary. 11e édition. Van Nostrand Reinhold Co. New York (N.Y.). p. 832.							
** Solubility coefficients at 25°C	D.R. Lide, H.P.R. Frederikse (Eds.), Handbook of Chemistry and Physics (76th ed.), CRC Press, Boca Raton, FL (1995)						
*** Dimensionless Henry constants	Holzwarth, G., Balmer, R.G., Soni, L., 1984. The fate of chlorine and chloramines in cooling towers Henry's law constants for flashoff. Water Res. 18 (1984), 1421-1427						

Haloacetaldehydes (HALs)

HALs represent one of the major chemical class of DBPs found in swimming pools, accounting for 15 to 20% of total organohalogens, as determined by the AOX method (ANSES, 2011). Among HALs, chloral hydrate (trichloroacetaldehyde, CH) is the most often encountered compound followed by dichloroacetaldehyde, in chlorinated swimming pools. CH is relatively stable in chlorinated swimming pools, with a hydrolysis rate of around 30% within 6-8 days at a pH of 7.6, resulting in chloroform and formic acid (Freyfer, 2012). CH has been found in French

swimming pools at levels varying from 31.8 and up to 497 $\mu\text{g L}^{-1}$ ($n=37$; mean : 180.3 $\mu\text{g L}^{-1}$; median: 118.9 $\mu\text{g.L}^{-1}$) (Freyfer, 2012), in Korean Swimming pools between 5 and 35 $\mu\text{g L}^{-1}$ (Lee et al., 2010), and in outdoor Australian swimming pools between 19.4 and 23.8 $\mu\text{g L}^{-1}$ (Yeh et al., 2014). In chlorinated bromide-rich water or when bromine is used as disinfectant, bromal hydrate (BH) is the predominant trihaloacetaldehyde (Daiber et al., 2016; Manasfi et al., 2017b, 2016). In a recent study, BH was detected as one of the degradation byproducts of benzophenone-3, a UV filter commonly used in sunscreens, in chlorinated swimming pools filled with seawater (Manasfi et al., 2015a). BH was detected in seawater swimming pools at low levels (0.35-2.22 $\mu\text{g L}^{-1}$) (Manasfi et al., 2015b), probably due to its increased instability at the slightly basic pH of seawater (8.2-8.6) (Koudjonou and LeBel, 2006).

Haloacetonitriles (HANs)

The most commonly reported HANs include dichloroacetonitrile (DCAN, CNCHCl_2), trichloroacetonitrile (TCAN, CNCCl_3), bromochloroacetonitrile (BCAN, CNCHBrCl) and dibromoacetonitrile (DBAN, CNCHBr_2). HANs are soluble substances, even if lipophilic, which are susceptible to degradation due to hydrolysis reaction or by reaction with the residual chlorine. HANs are purgeable substances, so they are volatile, but they are less volatile than chloroform (Table S1). HANs are also byproducts of degradation of THMs and HAAs in certain conditions (Weaver et al., 2009; Lee et al., 2010). HAN production is directly related to the content of nitrogen compounds (urea, ammonium, creatine, amino acids) (Li and Blatchley, 2007; Weaver et al., 2009; Deiber et al., 2016). DCAN and BCAN are the two compounds mostly encountered in freshwater swimming pools (Tardif et al., 2016). DBAN is the predominant HAN in bromine-disinfected swimming pools (Deiber et al., 2016) and in chlorinated seawater pools (Parinet et al., 2012; Manasfi et al., 2017b, 2016). Table 4 presents HAN concentrations reported in swimming pools.

Table 4: Occurrence of haloacetonitriles (HAN) in swimming pools

Nature de l'eau	Pays	n	DCAN	BCAN	DBAN	References
Eaux du réseau	Corée	30	0.5-12.2	<lod-1.9	<lod-0.9	Lee et al., 2010
	France	11	2.8-74.6	0.8-6.4	0.2-0.6	Cimetiere et al., 2014; Manasfi et al., 2016
	Canada	41	2.3-22.4	0.28-29.4	<lod-30.8	Tardif et al., 2016
	USA	14	<lod-160	<lod-24.8	<lod-15.8	Daiber et al., 2016
	Espagne	30	3.8-12.2	1.8-4.7	1.1-3.6	Font-Ribera et al., 2016
Désinfectants bromés ou eaux riches en bromures	USA	6	<lod	<lod-1.8	35.3-219	Daiber et al., 2016
	France	3	<lod	0.9-1.0	13.1-27.6	Manasfi et al., 2016
<lod : sous la limite de détection						
DCAN : dichloroacetonitrile; BCAN : bromochloroacetonitrile; DBAN : dibromoacetonitrile						
Toutes les concentrations sont exprimées en µg L ⁻¹						

Other (or emerging) DBPs

DBPs presented above account for the largest components of identified DBPs found in chlorinated swimming pools (by weight), as assessed by comparison of the sum of their concentrations with their adsorbable organic halide (AOX) concentrations (Yeh et al., 2014). However, few recent studies have revealed the presence of other compounds that could have a health impact, even at the ng L⁻¹ level. Among these emerging compounds, nitrogenous DBPs are of the greatest concern for human health because of their higher genotoxicity, cytotoxicity, and carcinogenicity (Richardson et al., 2010). Halonitromethanes (HNMs), including trichloronitromethane (TCNM or chloropicrin or nitrochloroform), bromonitromethane (BNM), bromochloronitromethane (BCNM) and dibromonitromethane (DBNM), have been detected in chlorinated swimming pools at concentrations between 0.8 and 7 µg L⁻¹, and up to 11 µg L⁻¹ for BCNM (Kanan, 2010). Recently, TCNM was detected at levels varying between 0.07 and 1.43 µg L⁻¹ (Tardif et al., 2016). Among nitrosamines, *N*-nitrosodimethylamine (NDMA) has been reported in few studies at levels varying from 32 ng L⁻¹ (Walse and Mitch, 2008) to 210 ng L⁻¹ (Kim and Han, 2011) and up to 310 ng L⁻¹ in a hot tub (Walse and Mitch, 2008). NDMA has also been reported in Canada by Tardif et al. (2016) with levels varying between 2.4 and 25.4 ng L⁻¹. This compound may result either from the reaction between dichloramine and dimethylamine (present in urea and sweat), or by the reaction of N₂O₄ (resulting from the reaction of chlorine and nitrites) with dimethylamine (Walse and Mitch, 2008). Other nitrosamines (*N*-nitrosodiethylamine (NDEA), *N*-nitrosomorpholine (NMor), *N*-nitrosopyrrolidine (NPyr), *N*-nitrosopiperidine (NPip) and *N*-nitrosodibutylamine (NDBA) have also been reported but at very lower levels (Teo et al., 2015). Cyanogen compounds (CNCl and CNBr) are also formed in

swimming pools, due to the reaction of nitrogenous compounds of body fluids with chlorine, and from the reaction of chloramines with ammonium (Lian et al., 2014). The reported levels ranged between 1 to 21 $\mu\text{g L}^{-1}$ for CNCl and 1 to 25 $\mu\text{g L}^{-1}$ (Weaver et al., 2009). Dichloromethylamine (DCMA, CH_3NCl_2) was detected as a byproduct of creatinine chlorination (Li and Blatchley, 2007). DCMA was found in hot tub waters in USA by Weaver et al. (2009) at concentrations between 0.05 and 50.98 $\mu\text{g L}^{-1}$ and in atmosphere of indoor pools in France at concentrations varying between 16 and 70 $\mu\text{g.m}^{-3}$ (Cimetiere et De Laat, 2009). Recently, several halobenzoquinones were detected in chlorinated swimming pool waters (Wang et al., 2013). Authors conducted chlorination experiments that showed that halobenzoquinones were formed from the chlorination of sunscreens and lotions. Very recently, an extensive study analyzed the occurrence of DBPs and the mutagenicity of water in pools and spas treated with chlorine, bromine or ozone (Daiber et al., 2016). Authors identified more than 100 DBPs including a new class of DBPs, bromoimidazoles. Occurrence data for these emerging DBPs in seawater pools are very limited.

Formation of DBPs in Swimming Pools

Reactivity of chlorine

Chlorine is used in the form of gaseous chlorine, liquid sodium hypochlorite (NaOCl), or solid calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). The different forms of chlorine, when applied to water, generate hypochlorous acid (HOCl) which is a weak acid with a pK_a of approximately 7.5 at 25 °C. The pH of water affects the dominating chlorine species such that HOCl dominates at pH below 7.5, while hypochlorite ions (OCl^-) dominate at pH above 7.5. Of the two species, HOCl is the stronger oxidant (WHO, 2000). The reactivity of chlorine with inorganic compounds (e.g. ammonia, halides Br^- and I^- , $\text{Fe}(\text{II})$, $\text{As}(\text{III})$, Sulfates SO_4^{2-} , CN^- , NO_2^-) usually results from an initial electrophilic attack. Reactions of chlorine with organic compounds may involve oxidation, addition, and electrophilic substitution reactions as possible pathways. However, only electrophilic attacks are significant from a kinetic point of view (Deborde and von Gunten, 2008). In water containing bromide ions, chlorination results in the formation of hypobromous acid, which is a weak acid ($\text{pK}_a = 8.7$). The speciation of bromine between hypobromous acid and hypobromite ions depends on the pH of water. As a halogenating agent, bromine is usually more reactive than chlorine especially with phenolic compounds leading to the formation of

brominated products (Acero et al., 2005; Gallard et al., 2003; Hua et al., 2006). Thus, bromide levels, pH, and other factors (e.g. temperature, organic content) can affect the composition and levels of DBPs in chlorinated swimming pools (Teo et al., 2015; WHO, 2000)

Precursors of DBPs in swimming pools

Natural organic matter

Natural organic matter (NOM) was the first known precursors to be accounted for the formation of DBPs in chlorinated drinking waters (Bellar et al., 1974; Rook, 1974). Similar to drinking water, DBPs can be formed from reactions of chlorine with NOM present in the filling water of swimming pools (Chowdhury et al., 2014; Kanan and Karanfil, 2011). These reactions result in the formation of THMs, HAAs, HANs, HKs, and halofuranones (Urbansky and Magnuson, 2002). Kanan and Karanfil (2011) conducted a comparative formation potential study and showed that NOM in chlorinated swimming pools formed more THMs than HAAs.

Body fluids released by swimmers

Human body fluids are believed to be major precursors for the formation of DBPs in swimming pools (Kim et al., 2002). It has been estimated that a swimmer releases approximately 25–77 mL in average (De Laat et al., 2011; Weng et al., 2012). In addition, Seux (1985) estimated that every swimmer introduces into the pool 100 to 1000 ml/h of sweat depending on the physical activity. Nitrogen-containing DBPs are generally attributed to nitrogenous organic precursors present in human body fluids (mainly urine and sweat) such as uric acid, urea, creatinine, L-arginine, L-histidine, glycine, and ammonia (Lian et al., 2014; Weng et al., 2012). The reaction pathways leading to the formation of DBPs from the chlorination of these organic compounds have been previously identified (Blatchley and Cheng, 2010; De Laat et al., 2011; Freuze et al., 2005; Hureiki et al., 1994; Jafvert and Valentine, 1992; Joo and Mitch, 2007; Li and Blatchley, 2007; Na and Olson, 2006). Trichloramine has been identified as a byproduct of chlorination of organic nitrogenous compounds present in body fluids (Li and Blatchley, 2007; Lian et al., 2014). The highly toxic cyanogen chloride (CNCl) has been identified as a byproduct of chlorination of glycine (Lee et al., 2006; Li and Blatchley, 2007) and uric acid (Lian et al., 2014). L-Histidine was found to act as precursor for the formation of dichloroacetonitrile (DCAN) and slightly to the

formation of CNCl. Besides nitrogenous DBPs, reactions of chlorine with human body fluids also generates non-nitrogenous DBPs including HAAs, THMs, THA, and HK (Kim et al., 2002). Formation potential studies conducted on body fluid analogs showed their tendency to form more HAAs than THMs (Kanan and Karanfil, 2011).

Particles released by swimmers

The potential of particles (e.g. skin cells, hair, and microorganisms) to form DBPs in swimming pools has been first demonstrated by Kim et al. (2002). Recently, Hansen et al. (2012b) examined the potential of particles captured by filters in swimming pools to form DBPs. The particles were collected from hot tubs and treated with chlorine in laboratory-controlled experiments. The formation of DBPs from human particles was found to be higher than that reported from other precursors including body fluid analogues (BFA) and natural organic matter (Table S2), probably due to high contents of nitrogenous precursors present in human particles. However, the formation of DBPs from particles released by bathers still merit further research since particles studied in previous investigations have not been fully characterized and discriminated. In the previously conducted studies, there has been no separation of skin and hair particles from microorganisms which themselves have been already shown to acts as precursors for DBPs (Wang et al., 2013).

Table S2: DBP formation from different chlorinated precursors at pH 7.0

	THM ($\mu\text{mol}/\text{mgDOC}$)	HAA ($\mu\text{mol}/\text{mgDOC}$)	HAN ($\mu\text{mol}/\text{mgDOC}$)	Reference
Particles	4	9.6	1.6	Hansen et al., 2012b
BFA	0.077	0.27	0.025	Hansen et al. 2011
BFA	0.25	0.51	N.D	Kanan and Karanfil, 2011a
NOM	0.62	0.26	N.D	Kanan and Karanfil, 2011a

Emerging precursors in swimming pools

Advances in analytical methods have allowed to detect and measure many emerging organic compound originating from human inputs in swimming pools (Richardson and Kimura, 2016). Most of these compounds are ingredients of personal care products (PCPs) and sometimes of pharmaceuticals. Personal care products (PCPs) constitute a diverse group of products including lotions, sunscreens, perfumes, and cosmetic creams. Since PCPs are applied externally on the

human body, their ingredients can be released upon immersion of swimmers into water. Among the ingredients that can be found in PCPs, there are disinfectants (e.g. triclosan), fragrances (e.g. musks), insect repellants (e.g. DEET), preservatives (e.g. parabens) and UV filters (e.g. methylbenzylidene camphor) (Ternes et al., 2004). Parabens or their salts, which are widely used as preservatives in pharmaceuticals and PCPs, have been detected and quantified in swimming pool waters (Alcudia-León et al., 2013; Terasaki and Makino, 2008). In addition, several pharmaceutical compounds including atenolol, carbamazepine, hydrochlorothiazide, metronidazole, ofloxacin, sulfamethoxazole, acetaminophen, ibuprofen, ketoprofen and phenazone were detected in swimming pools and spas in Spain (Ekowati et al., 2016). Teo et al. (2016) reported the detection of ibuprofen and caffeine in Australian swimming pools. Urination in swimming pools can be a potential route for pharmaceuticals into the pool water, especially that certain pharmaceutical are secreted unchanged in urine (Richardson and Bowron, 1985; Weng et al., 2014). Recently, Sharifan et al. (2016) estimated that considerable amounts of UV filters are introduced into pools, prompting a call for an urgent investigation regarding the potential toxic effects of UV filter transformation products and DBPs originating from them. Organic UV filters are increasingly used due to concerns about adverse health effects of exposure to sunlight. Organic UV filters can be found in sunscreens and in other PCPs, such as cosmetics, beauty creams, skin lotions, lipsticks, hair sprays, hair dyes, and shampoos (Ramos et al., 2015; Silvia Díaz-Cruz et al., 2008). Several studies conducted in different countries have reported the occurrence of UV filters in swimming pools. The concentrations of UV filters occurring in the pools varied considerably between different surveys with detected levels ranging from the sub nanogram to the microgram per liter orders (Ekowati et al., 2016; Lambropoulou et al., 2002; Zwiener et al., 2007). The levels of UV filters quantified in pools in different countries so far are summarized in Table 5. PCPs and other emerging contaminants, similarly to other organic precursors, react with chlorine leading to the formation of DBPs. For this reason, the occurrence of pharmaceuticals and PCPs in swimming pool waters has raised concerns about their potentially toxic byproducts (Bottoni et al., 2014). Although several studies have analyzed the occurrence of these compounds in swimming pools, data about their degradation and transformation products in chlorinated media are very limited. Shen and Andrews (2011) demonstrated the potential of a group of pharmaceuticals and PCPs containing amine groups to serve as nitrosamine precursors during disinfection. Kuhlich et al. (2011) investigated the reactions of chlorine with the two

polycyclic musks 6-acetyl-1,1,2,4,4,7-hexamethyltetraline (AHTN) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopentag-2-benzopyran (HHCB), widely used as fragrances in cosmetics. AHTN chlorination generated two new chlorinated DBPs. Studies on the fate of UV filters in chlorinated waters such as swimming pools are rather scarce (Santos et al., 2012). Sakkas et al. (2003) studied the behavior of the UV filter octyl-dimethyl-p-aminobenzoic acid (ODPABA) in various aqueous solutions and identified several chlorinated byproducts originating from the UV filter. Negreira et al. (2008) investigated the fate of the UV filters ethylhexyl salicylate (EHS), ODPABA, and 2-hydroxy-4-methoxybenzophenone (BP-3, OXY) in chlorinated aqueous solutions. EHS showed an acceptable stability whereas BP-3 and ODPABA reacted with free chlorine at significant rates following pseudo-first-order kinetics. The reaction of chlorine with OXY and ODPABA involved electrophilic aromatic substitutions. Monohalogenated and dihalogenated byproducts of OXY were detected. Halogenated 3-methoxyphenol was also detected as a cleavage byproduct.

Table 5: Levels of UV filters in swimming pools detected in previous studies

Country	Type of pool	UV filter Concentrations (ng L ⁻¹)						Reference
		OXY (BP3)	ODPABA	4-MBC	OMC	OC	PBS	
Greece	Swimming pool	2400–3300	2100					Lambropoulou et al. (2002)
Greece	Swimming pool	4.2		6.9	4.5			Giokas et al. (2004)
	Game pool	5.7		5.4	3.0			
Germany	Swimmer pool				1800	7000	0.7	Zwiener et al. (2007)
	Non-swimmer pool				2700	11000	2	
	Baby pool	1200			7000	25000	16	
Slovenia	swimming pool	400	17	330		15		Cuderman and Heath (2007)
Spain	Swimming pool	<LOD–2326		43–4035	107–1462	1421–25967		Negreira et al. (2010)
Italy	Swimming pool (seawater)	25–216			53–86			Nguyen et al. (2011)
Czech Republic	Swimming pool(outdoor)	26–620					240–13000	Grabicova et al. (2013)
Spain	Swimming pool (Indoor)	<0.1–4.87	<0.1	<0.4–5.6				Ekowati et al. (2016)
	Swimming pool (outdoor)	<0.1–15.17	<0.1–2.0	<0.4–35.9				
	Children pool (indoor)	<0.1–1.77	<0.1	8.6–12.1				
	Children pool (outdoor)	<0.1–1.97	<0.1	8.1–45.4				
	Spa	<0.1–1.07	<0.1	<0.4–69.3				

Nakajima et al., 2009 investigated the reactions of the UV filters ODPABA and octyl-4-methoxycinnamate (OMC) with chlorine in aqueous solution under conditions that simulate those found in swimming pools. ODPABA reacted rapidly with chlorine while OMC reacted slowly under the same conditions. The difference in reactivity was attributed to the effect of substituents present on the benzene ring. Both UV filters produced monochlorinated and dichlorinated transformation products. The structures of the chlorinated byproducts were not identified. The chlorination products of OMC exhibited weak mutagenic activity on *Salmonella typhimurium* TA100 strain in the Ames test. Duirk et al. (2013) studied the transformation of the two benzophenone UV filters OXY and DIOXY in the presence of excess aqueous chlorine. Both UV

filters were rapidly transformed by aqueous chlorine in a second-order reaction, first order with respect to each reactant. Authors detected chloroform as a stable transformation product resulting from the reaction of chlorine with OXY and DIOXY. Chloroform yields at pH 8 were 0.221 and 0.212 for OXY and DIOXY, respectively. These yields are similar to the average yields for phenols and substituted phenols (Gallard and von Gunten, 2002). Wang et al. (2013) found that some sunscreens and PCPs produced halobenzoquinones when chlorinated swimming pool water. Li et al. (2016) studied the reactivity of a group of benzophenone-type UV filters with chlorine in aqueous solutions. Second-order reactions were found to take place between chlorine and the UV filters OXY, 4-hydroxybenzophenone, and 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid. Authors identified several transformation products and proposed transformation pathways that include electrophilic substitutions, methoxyl substitutions, ketone group oxidations, hydrolysis, decarboxylation, and ring cleavage reactions. Authors also tested the toxicity of the chlorinated UV filters on the luminescent bacteria *Photobacterium phosphoreum*. Most of the UV filters exhibited higher toxicities after chlorination.

Toxicity and Human Health Effects of DBPs

Swimming pool users can be exposed to DBPs through multiple routes: dermal absorption, inhalation, and ingestion (Chowdhury et al., 2014; Zwiener et al., 2007). Many *in vitro* and *in vivo* toxicological studies have provided evidence about toxic effects induced by DBPs. Epidemiological studies have suggested associations between exposure to DBPs and adverse health effects in humans.

Toxicological studies

Toxicity of pool waters

Few studies have analyzed the mutagenic potential of swimming pool water. Honer et al. (1980) assessed the mutagenic potential of water samples obtained from three public indoor pools in Canada and detected positive mutagenic activity using the Ames test in *Salmonella typhimurium* TA100. Richardson et al. (2010) tested the mutagenicity of water samples obtained from brominated and chlorinated pools. Samples of both pools exhibited mutagenic activity similar to the average mutagenicity of drinking waters. Glauner et al. (2005) evaluated the genotoxicity of different fractions of DBPs present in swimming pool water and found that the strongest

mutagenic activity was induced by the low-molecular-weight fraction. Liviak et al. (2010) analyzed the genotoxicity of water concentrates of recreational pools under different disinfection treatments and that of source tap water used in filling the pools. Authors detected higher genotoxic activity induced by the recreational pool water compared to source tap water. Plewa et al. (2011) compared the mammalian cell cytotoxicity of various recreational pool water samples issued from the same tap water source and showed that the whole disinfected waters samples (indoor and outdoor) were more cytotoxic than raw water. Daiber et al. (2016) studied the progressive increase of water mutagenicity from tap water to swimming pool and spa waters, disinfected by chlorine, ozone or bromine, using the Salmonella assay. In this latter study, the mutagenicity correlated very well with the heavy use of pools, and therefore with the levels of DBPs (especially the nitrogenous brominated compounds).

Toxicity of DBPs

Numerous studies have investigated the toxicological effects induced by DBPs. However, most of these studies focused on few toxicity endpoint, mainly genotoxicity, carcinogenicity, and reproductive effects (Villanueva et al., 2015). Experimental evidence has been provided in many investigations regarding the genotoxicity of numerous DBPs (Guha et al., 2012; Villanueva et al., 2015). Richardson et al. (2007) reviewed comprehensively the reported data about the genotoxicity and carcinogenicity of 85 DBPs. Table 6 summarizes of well-documented genotoxic and/or carcinogenic effects of THMs, HAAs, and trihaloacetaldehydes (ANSES, 2011). Table S3 presents the known Toxicological Reference Values (TRV) of several DBPs, defined as priority substances to be monitored in French swimming pools (ANSES, 2011). Generally, N-containing DBPs exhibit higher genotoxic potencies than C-containing DBPs (Muellner et al., 2007; Plewa et al., 2008). Furthermore, brominated DBPs are more genotoxic than the chlorinated compounds, while iodinated DBPs were the most genotoxic of all (Jeong et al., 2015; Plewa et al., 2010, 2002; Richardson et al., 2007; Yang et al., 2014). In a recent study, CH was shown not to induce genotoxic effects, while BH induced mutations and DNA damage but not chromosomal aberrations (Manasfi et al., 2017a). Plewa et al. (2015) compared the toxicity of six DBP classes by assessing their cytotoxicities to chinese hamster ovary (CHO) cells.

Table S3: Toxicological Reference Values (TRV) of main DBPs

Compound	#CAS	Genotoxicity	IARC evaluation	Carcinogenic risk	Reprotoxic risk	Threshold (yes/no)	Route of exposure	Critical effect	Origin and year of the constructed TRV	TRV	Critical dose	Species
Chloroform	67-66-3	no	2B	yes (in the animal)	Yes	yes	inhalation	renal cell proliferation, precursor of cancer	Afsset (2008)	63 µg.m ⁻³	NOAEL = 5 ppm or 25 mg.m ⁻³	male mice BDF1
						yes	ingestion	hepatotoxicity	US EPA (1998)	0.01 mg.kg ⁻¹ .d ⁻¹	LOAEL = 15 mg.kg ⁻¹ .d ⁻¹	dog
Chlorodibromomethane	124-48-1	yes (IARC)	3	no	no	yes	force-feeding	hepatotoxicity	US EPA (1991)	2.10 ⁻² mg.kg ⁻¹ .d ⁻¹	NOAEL = 21.4 mg.kg ⁻¹ .d ⁻¹	Rats F344 et mices B6C3F1
						no	force-feeding	carcinoma and hepatocellular adenoma	US EPA (1991)	8.42.10 ⁻² mg.kg ⁻¹ .d ⁻¹	LMS model	Rats F344 et mices B6C3F1
Bromodichloromethane	75-27-4	yes (A)	2B	yes (in animals)	No	yes	force-feeding	renal citomegalia	US EPA (1987)	2.10 ⁻² mg.kg ⁻¹ .d ⁻¹	LOAEL = 17.9 mg.kg ⁻¹ .d ⁻¹	Rats F344 et mices B6C3F1
						no	force-feeding	Adenoma and adenocarcinoma of renal tubular cells	US EPA (1987)	6.2.10 ⁻² mg.kg ⁻¹ .d ⁻¹	LMS model	Rats F344 et mices B6C3F1
						no	inhalation	neoplastic lesion in the large intestine	US EPA (1991)	1.10 ⁻⁶ µg.m ⁻³	LMS model	Rats F344 et mices B6C3F1
						yes	force-feeding	liver damages	US EPA (1991)	2.10 ⁻² mg.kg ⁻¹ .d ⁻¹	NOAEL : 17.9 mg.kg ⁻¹ .d ⁻¹	Rats F344 et mices B6C3F1
Bromoform	75-25-2	yes (A)	3	no	yes	no	force-feeding	neoplastic lesion in the large intestine	US EPA (1991)	7.9.10 ⁻³ mg.kg ⁻¹ .d ⁻¹	LMS model	Rats F344 et mices B6C3F1
						yes	force-feeding	liver damages	US EPA (1991)	2.10 ⁻² mg.kg ⁻¹ .d ⁻¹	NOAEL : 17.9 mg.kg ⁻¹ .d ⁻¹	Rats F344 et mices B6C3F1
Trichloramine	10025-85-1					yes	inhalation	increase in serum level of SPA and SPB pncoproteins	EHESP (2009)	4.10 ⁻³ mg.m ⁻³	0.355 mg.m ⁻³	Human
						yes	ingestion	depression of the central nervous system and gastrointestinal irritations	US EPA (2000)	0.1 mg.kg ⁻¹ .d ⁻¹	LOAEL : 10.7 mg.kg ⁻¹ .d ⁻¹	Human
Chloral hydrate	302-17-0	ambiguous	3	yes (in mice)	yes (in animals)	yes	ingestion	Adenoma and hepatic carcinoma	Sante canada (2008)	0.0045 mg.kg ⁻¹ .d ⁻¹	13.5 mg.kg ⁻¹ .d ⁻¹	Rats F344 et mices B6C3F1
N-nitrosodimethylamine	62-75-9	Yes	2A	yes (in mice)	yes (in animals)	no	ingestion	induction of liver tumours	US EPA (1993)	51 mg.kg ⁻¹ .d ⁻¹	Weibull method	Colwoth female rats
Chloroacetic acid	79-11-8	No		no	yes (in animals)	yes	force-feeding	change in body, kidney, liver and testis weight	Sante canada (2008)	0.0117 mg.kg ⁻¹ .d ⁻¹	13.5 mg.kg ⁻¹ .d ⁻¹	Rats
						yes	ingestion	testicular, liver and brain lesions	US EPA (2003)	4.10 ⁻³ mg.kg ⁻¹ .d ⁻¹	LOAEL : 12.5 mg.kg ⁻¹ .d ⁻¹	Beagle dogs
Dichloroacetic acid	79-43-6	yes (IARC)	2B	yes		no	ingestion	liver tumour and hepatocellular carcinoma	Sante canada (2008)	1.02.10 ⁻⁶ mg.kg ⁻¹ .d ⁻¹	model	BCF63F1 male mices
						no	ingestion	hepatoadenoma and hepatocarcinoma	US EPA (2003)	0.015 mg.kg ⁻¹ .d ⁻¹	BMD	BCF63F1 male mices
Trichloroacetic acid	76-03-9	no (IARC)	3	yes (in mice)	yes (in animals)	yes	ingestion	change in body weight and increase in hepatic enzym	Sante canada (2008)	0.0325 mg.kg ⁻¹ .d ⁻¹	32.5 mg.kg ⁻¹ .d ⁻¹	Rats
Bromoacetic acid	79-08-3	no	3	no	yes (in animals)							
						yes	ingestion	malignant mesothelioma	Sante canada (2008)	4.26.10 ⁻⁶ mg.kg ⁻¹ .d ⁻¹	LMS model	BCF63F1 male mices
Dibromoacetic acid	631-64-1	yes		no	yes (in animals)	no	ingestion	hepatoadenoma and hepatocarcinoma	Sante canada (2008)	0.14.10 ⁻⁶ mg.kg ⁻¹ .d ⁻¹	LMS model	BCF63F1 male mices
Dichloroacetonitrile	3018-12-0											
Dibromoacetonitrile	3252-43-5	yes (A)	3	no								
Trichloroacetonitrile	545-06-2											

NOAEL : No Observable Adverse Effect Level; LOAEL : Lowest Observed Adverse Effect Level

IARC : International Agency for Research on Cancer; EHESP : Ecole des Hautes Etudes en Santé Publique; Afsset : Agence française de sécurité sanitaire, de l'environnement et du travail; US EPA : Unites States Environmental Protection Agency

(A) Richardson, S., Plewa, M., Wagner, E., Schoeny, R., Demarini, D., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutat. Res. 636, 178–242

The rank order of cytotoxicity was haloacetamides > HALs > halonitromethanes > HAAs > HANs > THMs. Among HALs the rank order of cytotoxicity was tribromoacetaldehyde (TBAL) \approx chloroacetaldehyde (CAL) > dibromoacetaldehyde (DBAL) \approx bromochloroacetaldehyde (BCAL) \approx dibromochloroacetaldehyde (DBCAL) > IAL (iodoacetaldehyde) > bromoacetaldehyde (BAL) \approx bromodichloroacetaldehyde (BDCAL) > dichloroacetaldehyde (DCAL) > trichloroacetaldehyde (TCAL). However, despite these studies, there are still data gaps with regard to the cytotoxicity and genotoxicity of DBPs (Richardson et al., 2007; Richardson and Postigo, 2011). Experiments conducted *in vivo* have shown that certain DBPs are carcinogenic (Boorman, 1999; Melnick et al., 2007; Richardson et al., 2007). In addition, investigations conducted in animals have provided evidence about the potential of DBPs to induce a range of adverse reproductive effects such as reduced fetal growth, sperm toxicity, and teratogenicity (Tardiff et al., 2006).

Table 6: Genotoxicity and carcinogenicity of THMs and HAAs

Genotoxicity						
Compounds	Gene mutation		Chromosomal mutation		DNA damage	
	Bacteria	Mammalian cells	<i>In vitro</i>	<i>In vivo</i>	<i>In vitro</i>	<i>In vivo</i>
Bromodichloromethane	+		-		+	-
Bromoform	+	+	+	+	+	-
Chlorodibromomethane	+	+	+		-	
Chloroform	-	-	-	-	+	
Monochloroacetic acid	-	+			-	-
Monobromoacetic acid	+				+	
Dibromoacetic acid	+				+	
Dichloroacetic acid	+	+	+	+	-	
Trichloroacetic acid	-	-			-	-
Chloral hydrate*	-	-	-		-	
Bromal hydrate*	+	+	-		+	

Carcinogenicity				
Compounds	Rodents		Classification in Humans	
	Mices, B6C3F1	Rats F344	IARC	EPA
Bromodichloromethane	+, -, -	+, -, -	2B	B2
Bromoform	-	+	3	B2
Chlorodibromomethane	+	-	3	C
Chloroform	+, -	+, +, +	2B	
Monochloroacetic acid	-	-, -		
Monobromoacetic acid				
Dibromoacetic acid	+	+		
Dichloroacetic acid	+	+	2B	B2
Trichloroacetic acid	+	-	3	C

All references come from the ANSES' review, except for compounds marked with *, coming from Manasfi et al., 2017a

Few studies focused on the neurotoxicity of DBPs. Dichloroacetic acid (DCAA) and dibromoacetic acid (DBAA) were found to induce neurotoxic effects in rats (Moser et al., 2004, 1999). More recently, THMs and tetrachloroethylene were shown to induce autistic-like behaviors in male mice (Guariglia et al., 2011). HAAs have been identified as being genotoxic and cytotoxic and able to induce cellular DNA damage and oxidative stress response via several pathways. Some toxicological studies showed that HAAs are more carcinogenic than THMs with DCAA and TCAA producing liver tumors in rodents (Righi et al., 2014). DCAA has been classified by IARC as possibly carcinogenic to humans (group 2B). Moreover, DCAA and TCAA induce both developmental and teratogenic effects in rats including low birthweight, cardiovascular and urogenital malformations and reproductive effects, such as lower sperm numeration (Righi et al., 2014).

Epidemiological studies in Humans

Respiratory effects

Several epidemiological studies have investigated the respiratory effects of chronic swimming pool attendance for workers, elite swimmers, and children. Exposure to DBPs was associated with higher prevalence of adverse respiratory effects among pool workers (Fantuzzi et al., 2010; Jacobs et al., 2007; Massin et al., 1998). Some studies have described higher prevalence of asthma among elite swimmers (Fisk et al., 2010). Some surveys have demonstrated associations between regular attendance at chlorinated pools and increased risk of asthma in children (Bernard et al., 2006, 2003; Langerkvist et al., 2004; Nickmilder and Bernard, 2006). Also, investigations have suggested increased risk of recurrent respiratory tract infections and otitis media linked to baby swimming (Nystad et al., 2007). Exposure to trichloramine, a volatile irritant DBP in indoor pools, has often been associated with an increased risk of respiratory effects in highly exposed populations (Florentin et al., 2011; Villanueva et al., 2015). Recent studies clearly demonstrated uptake of DBPs during swimming, by measuring levels of THMs in exhaled breath of swimmers, before ($0.5 \mu\text{g}\cdot\text{m}^{-3}$, median level found in 116 bathers) and after swimming ($14.4 \mu\text{g}\cdot\text{m}^{-3}$, median level). Moreover, a direct correlation between levels of brominated THMs measured in air levels found in exhaled breath was detected, despite variations observed according to sex, physical activity and polymorphisms in key metabolic enzymes (Marco et al., 2015; Font-Ribera et al.,

2016). Exposure of swimmers and workers to THMs had been also previously reported in several past studies (Caro and Gallego, 2008; Kogevinas et al., 2010; Lourencetti et al., 2010; Nieuwenhuijsen et al., 2000; Xu and Weisel, 2005). However, some studies have claimed that swimming is beneficial for children and adolescents with asthma (Matsumoto et al., 1999; Rosimini, 2003). Current evidence of an association between childhood swimming and new-onset asthma is suggestive but not conclusive (Weisel et al., 2009). Inconsistent findings have been continuously reported in studies that are more recent. In a prospective longitudinal epidemiologic study, no significant association was found between increased risk of asthma or allergic symptoms and swimming pool attendance in British children. The study suggested that swimming was associated with increased lung function and lower risk of asthma symptoms, especially among children with preexisting respiratory conditions (Font-Ribera et al., 2012). On the other hand, a more recent study conducted in Sweden supported the proposed link between indoor swimming pool attendance and asthma in sensitized children (Andersson et al., 2015). Further well-designed studies with defined asthma outcomes are still needed to provide conclusive evidence about the relationship between swimming pool attendance and childhood asthma.

Cancer

Several epidemiological studies have demonstrated evidence for a relationship between exposure to DBPs and increased risks of bladder cancer (Cantor et al., 2010; Nieuwenhuijsen et al., 2009; Villanueva et al., 2004). Two studies evaluated specifically the exposure to DBPs through swimming pool attendance and found increased risk of bladder cancer among attending subjects mainly related to THM exposure through showering, bathing, and swimming (Villanueva et al., 2007). Panyakapo et al. (2008) showed that the risk of developing cancer exists in swimmers exposed to THM from pool and tap water, and that the dermal route accounts for 94.2% of the total THM exposure for swimmers. Some studies have suggested associations between exposure to DBPs and other types of cancer including colorectal and skin cancer (Nelemans et al., 1994; Rahman et al., 2010). However, evidence about such associations remains inconclusive and inconsistent (Hrudey, 2009; Nieuwenhuijsen et al., 2009; Villanueva et al., 2015).

Reproductive effects

Because of toxicological studies detecting adverse reproductive effects in animals, reproductive health outcomes such as low birthweight, prematurity, spontaneous abortion, congenital anomalies and stillbirth have been the focus of epidemiological studies. Studies have provided some evidence for a relationship between exposure to DBPs and small for gestational age/intrauterine growth retardation and preterm delivery. However, evidence for other outcomes such as low birthweight, stillbirth, congenital anomalies and semen quality appears to be inconclusive and inconsistent (Hinckley et al., 2005; Hrudey, 2009; Nieuwenhuijsen et al., 2009, 2000; Tardiff et al., 2006; Villanueva et al., 2015).

Conclusion

This paper reviewed the occurrence, origin, and toxicity of DBPs in swimming pools disinfected with chlorine. In terms of occurrence, haloamines, HAAs, THMs, HANs and HALs are the byproducts largely present in water of swimming pools treated with chlorine. Recent studies have provided evidence about the occurrence of other emerging DBP that are toxic, even at low concentrations, including nitrogenous DBPs such as N-nitrosamines, HNMs, nitramines, nitramides, and cyanogen halides as well as carbonaceous DBPs such as halobenzoquinones, haloketones, halofuranones. Although more than 100 DBPs have been identified so far (Richardson et al., 2010), we have to keep in mind that these compounds represent only a small fraction of the total organic halide (TOX) contents detected in chlorinated swimming pool waters (Richardson et al., 2010; Freyfer, 2012; Manasfi et al., 2017b). It is thus important to continue to investigate the nature and levels of occurrence of DBPs in pool waters so that the unknown DBPs contributing to the TOX contents could be determined. In addition, further research is required to analyse the exposure of bathers to the emerging DBPs in swimming pools and to investigate their potential health effects. Indeed, if ocular, respiratory, and cutaneous irritations seem well correlated with the presence of trichloramine and dichloromethylamine in swimming pool water, relationships between pool attendance and other adverse health effects such as asthma, different cancers, and reproductive outcomes prompt further investigations (Kogevinas et al., 2010; Font-Ribera et al., 2012).

The identification and quantification of DBPs in swimming pools is analytically challenging given the complexity of swimming pool water chemistry. The nature of human inputs varies considerably not only as a function of bathers' hygiene but also as a function of activities carried out in pools (relaxing, sport, therapeutic pools ...). Furthermore, pool location (indoor or outdoor) as well as maintenance conditions applied by pool operators, such as ventilation, rates of water renewal, adjustment of chlorine or chlorine-based disinfectant levels (depending on local regulations), and use of additives (e.g. stabilizers) can all have an impact on the occurrence of DBPs in pool water and ambient air. Moreover, the nature and levels of DBPs are clearly modified when treatments other than chlorine-based disinfection, such as ozone, ozone/chlorine, ozone/UV or UV/chlorine, are applied. Few papers compared the impact of different disinfection treatment on the toxicity of generated DBPs in swimming pools. However, the reported findings with regard to toxicity variation from one treatment to another were often conflicting (Plewa et al., 2011; Hansen et al., 2013; Solterman et al., 2013; Cimetiere and De Laat, 2014; Spiliotopoulou et al., 2015).

Data presented in this review with regard to the occurrence, toxicity, and toxicological reference values of DBPs could be used in conducting risk assessment studies for swimming pools. However, to be robust, these studies need to be correlated to daily exposure doses, and to the characteristics of people attending swimming pools (occasional swimmers, elite swimmers, baby swimmers, pregnant women, technical staff ...). Volatile DBPs can be inhaled and the inhaled amounts depend on the mode of breathing, oral or nasal (Bernard et al., 2007). Swimmers can be also exposed to DBPs when water is accidentally ingested. The average ingested volume varies largely as a function of swimmer categories and for the same category considerable differences have been reported in different studies (from 25 mL h⁻¹ to 50 mL h⁻¹ for babies, from 20 to 25 mL h⁻¹ for swimmers, and from 170 to 225 mL h⁻¹ for elite swimmers) (Dufour et al., 2006; WHO, 2000). Another route of exposure of swimmers to DBPs is through dermal absorption. Some DBPs can cross the cutaneous barrier but the limited data available make difficult determining the contribution of the dermal exposure route to the overall exposure. Biomonitoring and investigations about the pharmacokinetic profiles of DBPs would provide data that is vital to improve risk assessment studies. In addition, a better understanding of the occurrence of DBPs in swimming pools, their formation and transformation mechanisms, and their toxicity, is required

so that efficient preventive measures could be taken to reduce their formation and to minimize the exposure of swimmers to these chemical contaminants.

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