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Risk assessment of exposure to chlorine and its by-products in public/ private swimming pools

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Abstract

The increasing concern about the effect of chlorine used to disinfect swimming pools allows research to focus on the effect of chlorine and its derivates on the development on cancer among bathers/swimmers but also workers.

A reaction between chlorine and compounds already present in the swimming pool water and those chemicals brought in by the bathers/swimmers e.g. sweat, urine, dirt, saliva, cells and all kind of lotions produce products called “disinfection by-products” (DBPs). These DBP are mainly composed of trihalomethanes including mainly chloroform, chloramines, haloacetic acids and nitrosamines. These products can be carcinogenic at certain concentrations.

The risks assessments for swimmers/bathers and workers are assessed with the NOAEL (No Observed Adverse Effect Level) given by authorities. These data were compared with earlier studies and French government analyses of swimming pool water. These risks assessments show that the concentrations of chloroform and chloramines are mainly lower than the NOAEL. Compared to a concentration considered as a discomfort concentration by the French government, results showed chloramines concentrations above that threshold. Swimmers/bathers and also workers can experience some discomfort like irritations in the eyes, and coughing making the time spend in the swimming pool less pleasant. Furthermore, the risk of developing cancer by going to the swimming pool is significant for the inhalation of chloroform.

A comparison between two countries was made, France and Australia. The guidelines were compared. For most of the criteria, the guidelines allow almost the same concentrations. There are also some differences; e.g. it is not allowed to use any stabilizer in indoor swimming pools in Australia, which is allowed in France. The concentration of chlorine should be minimal 3 g/L in Australia when there is stabilizer present while in France this concentration must be minimal 2 mg/L. The concentration of DBPs maybe higher in Australia than in France because there is more chlorine present in the water, while the disinfectant effect is not necessary higher because of the presence of stabilizer.

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List of abbreviations

DBPs	Disinfection by-products
DNA	Desoxyribonucleic Acid
HAA	HaloAcetic Acid
IRIS	Integrated Risk Information System
LOAEL	Low Observed Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
THM	TriHaloMethane
US EPA	United States Environmental Protection Agency
UV	Ultra-Violet
WHO	World Health Organisation

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I- Introduction

The majority of the populations in the industrialized countries enter a swimming pool at least once in their life. Either only to bath, refresh or learn how to swim and/or swimming for pleasure or competition. Swimming pools can either be public or private and have been experiencing growth in attendance during the past three decades. The European Union is ranked second with about 4.5 million swimming pools with the United States being first (about 9 million) (Francesco, 2010).

These swimming pools have to be disinfected; something crucial for the safety of the bathers/swimmers. This can help to prevent possible microbiological, fungal, parasitic and also viral infections. To do this, different types of disinfectants can be used: chlorine, bromine, Ultra-Violet light (UV), active oxygen and ozone. The most used worldwide is chlorine, followed by bromine. The physical and chemical properties are similar but their stability is different. Chlorine is more stable than bromine. UV, active oxygen and ozone are also often used as disinfectants, but they cannot be used alone. They have to be combined with chlorine or bromine (WHO, 2006).

Chlorine, which is added to swimming pool water, can react with other products also present in the water. These are, among others, brought by the people who are coming to swim or generated during the bath. For example: sweat, urine, dirt, saliva, cells and all kind of lotions brought by the swimmers/bathers themselves. Their components such as ammoniac, urea and other amino acids can react with chlorine to form what is called “disinfection by-products” (DBPs) ((Kanan & Karanfil, 2011); Tricker, 1992;(Judd & Bullock, 2003); WHO, 2006). In case of outdoor swimming pools, leaves and others materials from surrounding trees, etc. can also fall in the water. These materials can also react with the disinfectant (WHO, 2006). An individual swimmer who would bath alone, continuously for an hour, the flux of pollution provided by him would be between: 0.55 and 1.0 g of total organic carbon; 0.8 and 0.9 g of Kjeldahl nitrogen; 0.15 and 0.20 g of nitrogen as ammonia; 1.0 and 1.6 g of urea (Seux et al., 1988)

These by-products are composed mainly of trihalomethanes also called THM, of chloramines and of haloacetic acids also named (HAA) (table 1).

Table 1: Summary of DBPs for chlorinated disinfectants (WHO, 2006)

Disinfectant	Organohalogenic disinfection by-products	Non-halogenic organic disinfection by-products	Inorganic disinfection by-products
Chlorine (Cl_2)/hypochloric acid (HOCl)	Trihalomethanes, haloacetic acids, halocetonitriles, chloral hydrate, chloropicrin, halophenols, N-chloramines, halofuranones, and bromohydrins	Aldehydes, alkanic acids, benzene, and carboxylic acids	Chlorate (particularly the application of hypochloric acid)

Swimmers/bathers and workers are exposed to all these products. These by-products and their risks of causing cancer will be explained below.

I-1- The trihalomethanes

The trihalomethanes include principally chloroform/bromoform and chlorodibromomethane/bromodichloromethane.

Chloroform, with a chemical formula of $CHCl_3$, is a colorless, highly refractive, heavily volatile liquid (Lewis, 2007). It seems to have a pleasant odor (NIOSH, 2005). It is highly soluble in water: $7{,}95.10^3$ mg/L at 25°C (Mackay et al., 1980). It can be absorbed essentially through the lungs; this is its primary source of exposure, because it is heavily volatile. It can also be absorbed through the gastrointestinal track and to some extent through the skin (Doull, 1998). It can even cross the placenta barrier and enter the fetal circulation (The Chemical Society, 1975). The rate of absorption through the lungs is from 77 to 94 %, and through the gastrointestinal tract it is approximately 100% (USEPA, 1980). After crossing barriers and being in the blood stream, the chloroform can go in the organ/tissue with which it has the biggest affinity. From the blood stream, the chloroform can accumulate in high concentrations in the nervous tissue, and the organs (IRAC, 1979). During the post-exposure period, the chloroform is redistributed and goes to the body fat with increased levels in the liver (Cohen, 1969). The post-exposure period has a blood concentration peak after 1.5 hours which declines in a two compartment model with half-lives of 13 and 90 minutes. This holds true for a single oral dose of 0.5g of chloroform (WHO, 2004).

Regarding the toxicity of chloroform, it results in a nephrotoxicity in a variety of species. Some of them are more sensitive than others. Among all the different targets of chloroform, the most important ones are the kidney cells in the proximal tubules, with no primary damage in the glomerulus or the distal tube. The nephrotoxicity induced by chloroform is linked to its metabolism by renal cytochrome P450 and the formation of a reactive intermediate that binds covalently to nucleophilic groups on cellular macromolecules. Cytochrome P450 biotransforms chloroform to trichloromethanol which is unstable. It releases HCl and then, form phosgene. The latter can, among others, react with cellular macromolecules to initiate toxicity (Casarett & Doull, 2008). However, according to the US EPA, available data on the mutagenic and genotoxic potential of chloroform are conflicting, but the majority of tests are negative, and some of the positive results are observed only at extreme exposure conditions. Thus, the weight of the evidence indicates that chloroform is not a strong mutagen and that neither chloroform nor its metabolites readily bind to DNA. Based on these results and the results of studies that evaluated other endpoints of genotoxicity, it seems likely that, even though a role for mutagenicity cannot be excluded with certainty, chloroform does not produce carcinogenic effects primarily by a specific genotoxic mechanism (IARC, 1999a). Furthermore, according to the IARC, after several cohort studies on drinking water on humans and oral exposure to chloroform on mice, it shows that there are "*inadequate evidence* in humans and *sufficient evidence* in experimental animals for the carcinogenicity of chloroform" (IARC, 1999b). IARC conclude that chloroform is possibly carcinogenic to humans (Group 2B).

Chlorodibromomethane or dibromochloromethane ($CHBR_2Cl$) is the second most common trihalomethane formed by the interactions of chlorine in the swimming pool water. It is a liquid (IARC, 1991). It is produced by the interaction between chlorine, organic matter and naturally present bromine in the water.

I-2- Chloramines

Chloramines are also a by-product from the reaction between chlorine and organic matter. It is represented by the equation in which R symbolizes side chains:

$HClO + R\text{-}NH_2 \longrightarrow H_2O + R\text{-}NHCl$ (organic monochloramines)

Further reactions with HOCl lead to the formation to di- and trichloramines. The mineral chloramines are soluble in water and have the capacity to transfer to the gaseous phase. The production and the distribution of monochloramines (NH_2Cl), dichloramines ($NHCl_2$) and trichloramines (NCl_3) are highly influenced by the pH, the ratio of chlorine to organic-nitrogen compounds, temperature and contact time. The formation of monochloramines is the most efficient with a pH between approximately 7.5 and 9.0 (Florentin et al., 2011).

Based on inadequate human data and equivocal evidence of carcinogenicity from animal bioassays, chloramines are considered D; not classifiable as to human carcinogenicity (IRIS, 2000). To date, no data on carcinogenicity, genotoxicity, mutagenicity, reproductive toxicity and teratogenicity of chloramines is mentioned in the literature. Chloramines are more suspected to have an effect on respiratory diseases such as asthma and also causing eye irritation (Ferrari et al., 2011)

I-3- Haloacetics acids

The formation of haloacetics acids (HAA) is made a similar manner to the trihalomethanes, with the interaction between organic matter and chlorine/bromine. The HAA are divided in three groups according to the number of hydrogen substituted atoms: monohaloacetic acids, dihaloacetic acids and trihaloacetic acids (Table 2). In this table, the main acids are presented.

Table 2: Representative compounds of the three groups of HAAs (Florentin et al., 2011)

Monohaloacetic acids	Dihaloacetic acids	Trihaloacetic acids
Monochloroacetic acid (MCA)	Dichloroacetic acid (DCA)	Trichloroacetic acid (TCA)
Monobromoacetic acid (MBA)	Dibromoacetic acid (DBA)	Bromodichloroacetic acid
	Bromochloroacetic acid	Chlorodibromoacetic acid
		Tribromoacetic acid

The monochloroacetic acid (MCA) is not considered as a human carcinogen (Santé Canada, 2009). However, changes in the weight of the body, liver, kidneys and testicles were observed on rats. Three adult volunteers drank 300 mL of a aqueous solution of MCA at 0,05% every day for 60 days (which correspond to 2 mg/kg bw/day). They experience no adverse health effects. (Morrison and Leake, 1941; NTP, 1992). In drinking water, the maximum concentration is 0.1 mg/L.

The dichloroacetic acid (DCA) is considered as a probable human carcinogen. Research proves a link between DCA and liver tumors on rats and mice. Consequently, in drinking water, the maximum concentration is 0.01 mg/L in Canada.

The trichloroacetic acid (TCA) is also considered as a probable human carcinogen. Research revealed a link between TCA and liver tumors in mice only, however, no evidence exist in humans. Consequently, in drinking water, the maximum concentration is 0.3 mg/L.

I-4- Types of exposure

During bathing/swimming, or even by being present but not swimming, these persons can be exposed to chlorine, its emanations, and its possible by-products, in three different ways.

Firstly, the swimmer can ingest swimming pool water: the average of water absorption for children is 37 mL whereas for an adult it is only 16 mL during a 45 minutes swim (WHO, 2006). A little boy will ingest the highest amount of swimming pool water while an adult woman will ingest the lowest. This was confirmed by Schets et al. by their study on the intake of water during swimming in the Dutch population (Schets et al., 2011).

Second, swimmers/bathers as well as non swimmers are also exposed to inhalation of aerosol and volatile solutes such as chlorine, chloramines and trihalomethanes (THM). The exposure is less for a non swimmer than a swimmer/bather. For the latter, the exposure depends on his physical condition, the speed of swimming and finally the period of time of swimming.

The third type of exposure to chlorine and its derivatives such as haloacetic acids (HAA) is through dermal contact and absorption. This exposure is exclusively for swimmers because the risks that a non swimmer is exposed to more than a splash are very unlikely.

Chlorine and bromine have positive properties for disease prevention of the bathers, but it can also have an adverse direct or indirect effect due to the use of chlorine/bromine as a disinfectant.

My thesis study assesses the risks for swimmers in general, but also the difference in exposition to carcinogenic products in a swimming pool between France and Australia, with different guidelines being also applied.

II- Methods of disinfection

II-1- Treatment characteristics

The treatment of the swimming pool water is a combination of physical treatments and chemical compounds. Thanks to Archimedes' principle, the swimmer in the swimming pool makes the water goes away on the sides (figure 1). This water goes in a raw water tank where fresh water is added, and then a flocculent is added in order to improve removal of particles. The flocculent binds to the particles to make them larger by agglomeration so they cannot pass through the filter afterwards. This procedure is also recommended for enhanced removal of *Cryptosporidium* oocysts and *Giardia* (Zwiener et al., 2007). The sand/gravel filter purifies the water by eliminating the large particles. The size of these filters depends on the speed of filtration and the volume of the water that has to be filtered. These kinds of filters need to be cleaned about once a week. Furthermore, the pressure difference of between the top and bottom of the filter should not to be higher than 400 grams. With regular cleaning, these filters can last for 8 to 10 years. After the filtration, the water is chlorinated for the disinfection and the pH is checked because of the presence of hypochlorous acids (see II-2-).

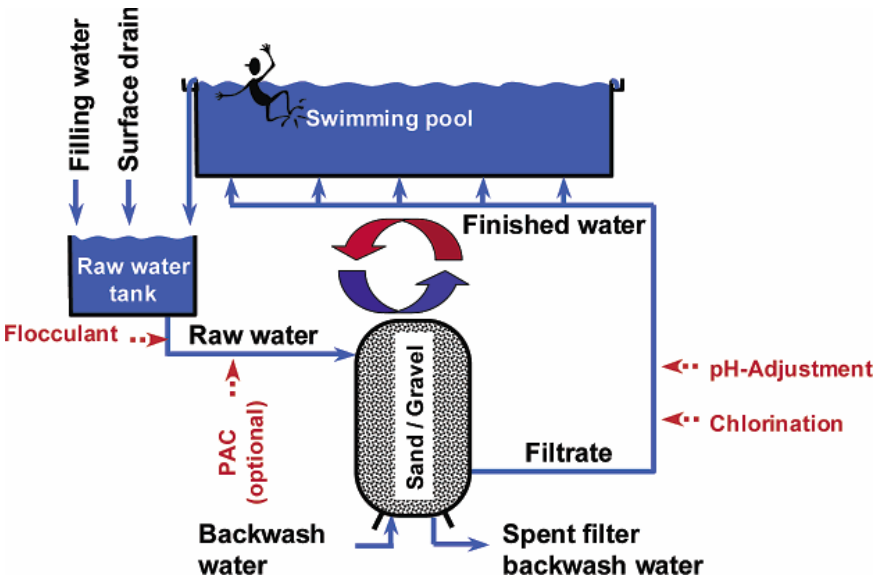

Figure 1: Scheme of conventional pool water treatment with flocculation - filtration - chlorination. PAC powdered activated carbon. (Zwiener et al., 2007)

II-2- Chlorine

Chlorine, with a chemical formula of Cl_2, is a gas, its boiling temperature is -34.04°C and has a yellowish-green colour (O'Neil, M.J. (ed.), 2001) with a pungent and irritating smell (NIOSH, 2001). It is very corrosive and soluble in water, 6.30 mg/L at 25°C (Amoore JE et al., 1983). Chlorine is used in many different ways; such as a disinfectant, bacteriostatic/bactericide and algaecide in food processing systems, pulp and paper mill systems, and commercial and industrial water-cooling systems. Furthermore, it can be used to wash meat, fresh products and seeds in order to avoid the growth of decay-causing microorganisms (USEPA, 1999)

For the disinfection of swimming pools, chlorine, in its Cl_2 form, is not the active form. When chlorine is in contact with water, there is a chemical reaction:

$Cl_2 + H_2O \longrightarrow HClO + HCl$

One of the products of this reaction, HClO, hypochlorous acid, is a stable product and it has a very important disinfectant power. Consequently, it is also named active chlorine. Its disinfectant properties are the same as Cl_2. However, in an outdoor swimming pool, the water is subjected to UV that breaks down the chlorine faster and would make the use of chlorine double or even triple. In order to solve this problem, a component, named isocyanuric acid, $C_3N_3(OH)_3$, is added to stabilize chlorine. Furthermore, without this stabilizer, the hypochlorous acid decomposes with a certain pH in water:

$HClO \longrightarrow H^+ + ClO^-$ (ARAPH, 1990)

The free ion H^+ induces a decrease of the pH. The stabilizer is necessary to avoid a too important decrease. When the pH is too low, the disinfectant effect of chlorine is rapidly lost. According to Taylor, the pH should not be lower than 7, unless the chlorine is inefficient, this is its optimal pH (Taylor, 1982). However, according to the ARAPH (Association Régionale pour la promotion de la santé par l'hygiène), the pH must be between 6.9 and 7.7 for an efficient disinfection with chlorine products.

In order to have an efficient disinfection and moderate chlorine consumption, different types of stabilizers can be used. These are all solid products contrary to chlorine. The basic product is isocyanuric acid. Being a simple stabilizer, it cannot disinfect water. It must be used in conjunction with a source of chlorine. It exists also as a derived product from that acid: the chlorocyanurates. Three derived products can also be used: trichloroisocyanuric Acid (TCCA), sodium dichloroisocyanurate (NaDCC) and the potassium dichloroisocyanurate (KDCC) (ARAPH, 1990). These products are also a source of chlorine and produce via hydrolyzation, HClO and the stabilizer compound. These are consequently considered as disinfectants. Nevertheless, when they are added in the water, there is a decrease of the concentration of active chlorine and an equivalent augmentation of potential chlorine. This implies a lower disinfectant power with the same concentrations of chlorine without stabilizer (cf. figure 2).

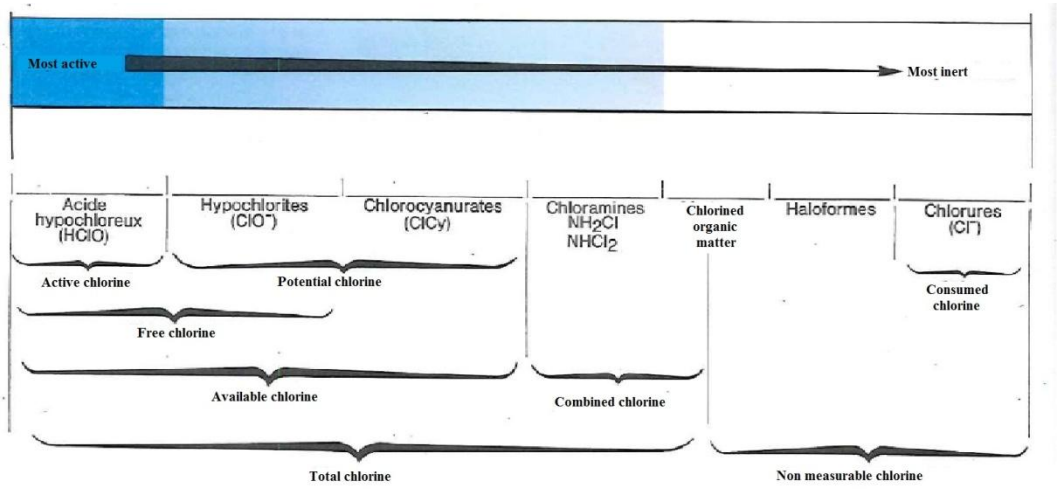

Figure 2: Different types of chlorine (ARAPH, 1990)

The mechanisms involved in the destruction of the microorganisms by chlorine are not completely clear yet. According to the Scientific American, few studies were made on the capacity of chlorine to kill bacteria, viruses and parasites. Research has been more focused on the consequences of chlorine and its derivates on humans health.

However, several theories exist concerning the capacity of chlorine to kill microorganisms. One theory is called “multiple hit”. It consists on the fact that chlorine attacks a variety of bacteriological surface molecules or targets, including enzymes, nucleic acids and lipid membranes. Another theory is based on the fact that chlorine could destroy the cell wall of the bacterium by altering it physically, and (bio)chemically. This would work in several steps going from a disruption of the cell wall barrier by reactions of chlorine with target sites on the cell surface, added to a release of vital cellular constituents from the cell, and with a termination of membrane-associated functions, to finish with a termination of cellular functions within the cell. This would cause the death of the bacterium. In details, researchers studied the effect of chlorine on the gram-negative bacteria like *Salmonella enterica – typhi/paratyphi* (typhoid fever) or *Vibrio cholerae*. The investigation revealed that, for each bacterial species, chlorination significantly increased the permeability of the outer membrane, leaving the bacterium vulnerable to destruction. How chlorine inactivates other types of bacteria has not been determined.

For viruses, the inactivation by chlorine is not understood yet, as well as for parasites. Chlorine kills parasites but the best method for removing parasites is filtration, chlorine. Unfortunately, some parasitic protozoans like *Cryptosporidium parvum* and *Gardia lamblia* are becoming resistant to chlorine (Scientific American, 2011).

II-3- Bromine

Bromine is another disinfecting compound. It has a chemical formula of Br_2, is a liquid, its boiling temperature is 59.47°C, and its colour is reddish with a suffocating odour close to bleach. It is corrosive and soluble in water, 33.6 g/L at 25°C (O'Neil, M.J. (ed.), 2001). Bromine is used because of its same properties as chlorine.
However the efficiency of bromine is lower than chlorine. Consequently, bromine is less and less used to disinfect swimming pools (WHO, 2006). In some countries, e.g. France, the use of bromine as a disinfectant in public swimming pools is forbidden (ARAPH, 1990), bromine being more toxic for the environment than chlorine.
The latter is the major reason why my study focuses on the effect of chlorine and its derivates on humans and does not include bromine.

II-4- Other types of disinfectants

Ozone and UV radiation can also be used in a swimming pool to clean the water. These methods purify the water as it passes through the plan room and neither method leaves residual disinfectant in the water. However it cannot be used alone, but always in combination with chlorine or bromine (WHO, 2006). The disinfectant properties of ozone are not sufficient to destroy all the pathogens in the water.

In smaller pools other disinfectants can also be used. Hydrogen peroxide used with silver and copper ions will normally provide low levels of the silver and copper ions in the water (WHO, 2006). However, with these methods it is essential to refresh water frequently to prevent excessive build-up of these metal ions.

III- Formation of compounds, adverse/non adverse effects

In a swimming pool, first fresh incoming water goes through a pipe where chlorine is added. This addition of chlorine in the water starts reactions with natural compounds such as bromine or organic compounds. As a result new compounds are formed in the disinfected water that is used by swimmers. Here it is relevant to note that in some countries showering before swimming is mandatory, but in other countries it is not. The swimmers release in the water many different compounds such as sweat, urine, saliva, dirt and lotions (sunscreen, cosmetics, soap residues, etc.) (Kim et al. 2002). Especially, the urea, ammonia, amino acids and creatine contained in sweat as well as in urine can react with chlorine to produce potential hazardous DBPs (Disinfection by-products) (WHO, 2006).

III-1- Formed compounds

The most abundant of all DBPs are trihalomethanes (THMs). These are volatile in nature and can be released from the surface of the water and also found in the air above the pool (WHO, 2006). The major newly formed trihalomethanes is chloroform ($CHCl_3$) which is a probable human carcinogen (USEPA; IARC, 1999). In the case of disinfection with bromine the main trihalomethane by-product is bromine. According to ToxNet, no studies on the possible carcinogenic effects of bromine were found at the time of this review (ToxNet, 2012). However, according to the IARC and Richardson et al., bromoform can induce sister chromatid exchanges and micronuclei (MN) (IARC; Richardson, 2007) indicating genotoxicity.
Other less abundant by-products with disinfection with chlorine are bromodichloromethane ($CHBrCl_2$) and chlorodibromomethane ($CHClBr_2$). According to Leavans, bromodichloromethane can induce mutagenic activity after crossing the kidneys and present in human urine (Leavans, 2007). On the other hand, chlorodibromomethane can generate chromosomal aberration and sister chromatid exchanges (Kogevinas et al., 2010).

The reaction between chlorine and humic and fulvic acids creates also other by-products such as haloacetic acids (HAAs), which di- and trichloroacetic acid are generally present in the highest concentrations (WHO, 2000). The steady-state permeability coefficients of HAAs varied from 1.1 to $2.6.10^{-3}$ cm/h (Xu et al., 2002). For the three categories of DBPs examined - THMs, Haloketones and HAAs - , HAAs were the least permeable on the skin barrier, with *Kp* (permeation coefficient) values at 40°C that were two orders of magnitude smaller than those of THMs at 25°C. In order to verify a long term exposure, a 6-h permeation study of tritiated water was conducted with receptor samples collected at various time point from 10 to 360 min. Xu et al. discovered that no increasing flux rate of tritiated water across the skin was observed after 360 min, indicating that the skin integrity can be maintained for a 6-h incubation with water (Xu et al, 2002) meaning that a 6 hours exposure to HAA does not result into the presence of HAA in the blood stream via the skin.

According to Wasle et al., dichloroamines are formed by some specific reactions in the water. It starts with the chlorination of ammonia originating from sweat or urine, which forms the basis of inorganic chloramines, such as dichloramines. Dichloramines can react further with amines such as dimethylamine to form a chlorinated unsymmetrical dimethylhydrazine intermediate (UDMH-Cl) (Figure 3). The chlorinated hydrazine intermediate can react with dissolved oxygen to form NDMA or with chloramines to form other products (Walse & Mitch, 2008).

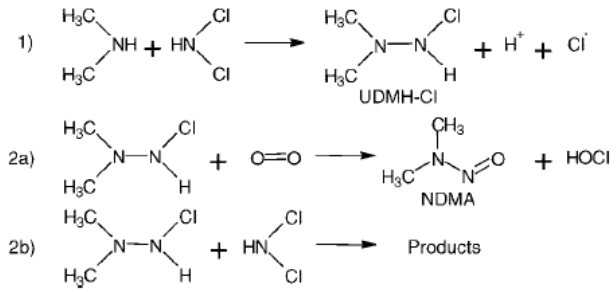

Figure 3: Formation of NDMA and other products from chlorine (Walse & Mitch, 2008)

Alternatively, the nitration of dialkylamines could originate from a pathway involving nitrite, a readily oxidized nitrogen species that can be introduced into pool water via urine, sweat, or the photolysis of nitrate. The chlorination of nitrite forms nitrile chloride ($ClNO_2$) (Figure 4).

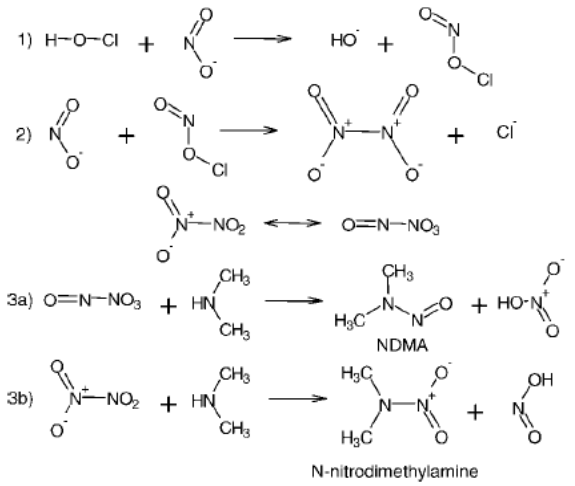

Figure 4: Formation of N-nitrodimethylamine from hypochlorous acid (Walse & Mitch, 2008)

III-2- Adverse/non adverse effects

From all the compounds that are found in the swimming pool water, some are considered dangerous for the health of the swimmer, while others have no or even a beneficiary effect on health.

The DPBs are the compounds that are considered to have the highest carcinogenic potential. In view of the swimming behavior of humans it is not possible to avoid the production of these by-products. However, the formation of these potential hazardous compounds may be reduced to a minimum in the swimming pool by applying several methods.
Several of the by-products mentioned above may be able to induce several types of cancer. The major form of cancer that could be induced by these by-products is considered to be bladder cancer. Indeed, according to Villanueva et al., there is an increased risk of bladder cancer for people who swim regularly in a swimming pool. The risks ratio for swimming up to 165 hours in a swimming pool was 1.50 and for swimming for more than 165 hours was 1.52 relative to never swimming in a pool (Villanueva et al., 2007).

Kogenivas et al. studied the effect of THMs on micronuclei (MN) in humans. The MN assay has been shown to be a predictive biomarker of cancer risk within a population of healthy subjects (Bonassi et al. 2007). A significant increase of MN has been found with exposure to bromodichloromethane (Kogevinas et al., 2010). However, no associations were found between THMs in the pool and DNA damage in peripheral blood lymphocytes (PBLs).

Chen et al. suggest that exposure to THMs could be associated with increased risks of colon/rectum and brain cancers (Chen et al., 2011). They also suggest that THMs can cause reproductive health effects including intrauterine growth retardation, low birth weight, preterm birth, congenital malformations and stillbirth. Unfortunately, their study did not show if the concentration of THMs present in swimming pools is the same that can induce all the reproductive health effects.

Nonetheless, according to the IRIS system from the USA Environmental Protection Agency, the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP) and considering the lack of data, chlorine is not considered to be human carcinogen (IRIS a, 2012; IARC 2006; IRIS 2007; NTP 2005). However, by inhalation, the effect of chlorine is focused on the irritation of the nose and throat, followed by coughing and wheezing, shortage of breath, sputum production and chest pain. Larger exposures may lead to heart and lung failure. Concerning the skin contact, chlorine can cause irritation, pain, redness, blister and burns. To finish, concerning the eye contact, chlorine can cause irritation and inflammation (WHO, 2003).

IV- Risks assessments

IV-1- Risks assessments chloroform

A swimmer has a risk to be exposed to chloroform, which is very different depending on the country and type of swimming pool. Chloroform is present mainly in gaseous form in swimming pools, and is formed by the reaction between chlorine and organic matter in the water. Consequently, the concentration of this compound in the air depends on the concentration of chlorine in the water, the regulations in the country and the behaviour and the number of swimmers in the water. In inside swimming pools it also depends on the efficiency of the air conditioning (WHO, 2006).

In the literature, several no observed adverse effect levels were found. According to the American Conference of Governmental Industrial Hygienists, the NOAEL of chloroform for eight hours Time Weighted Average (TWA) is: 10 ppm (ACGIH, 2008). Furthermore, the World Health Organization gives a NOAEL of 30 mg/kg body weight (WHO, 2008) or 50 mg/m^3 (WHO, 2000).

According to the case study by Aggazzoti et al., the concentration of chloroform in plasma is different for swimmers being at the edge and the centre of the swimming pool. In an indoor swimming pool in Italy, after resting one hour on the swimming pool edge, the concentration of chloroform in the plasma was 29.4 ± 13.3 µg/m^3. This is clearly lower than the concentration after one hour swimming, which was found to be 75.6 ± 18.6 µg/m^3 (Aggazzotti et al., 1998).

According to the case study of Caro et al. in Spain, the exposure concentration to chloroform differs significantly between the workers and swimmers. (Caro & Gallego, 2007). For a swimmer, after an hour swimming, with a concentration of 110,000 ± 6600 ng/L of chloroform in the water, the concentration of chloroform rises from 468 ± 21 ng/L to 1400 ± 63 ng/L in 12 mL of urine. That is why the worker and the swimmers are separated for the risk assessments.

Several studies were made to measure the chloroform concentrations in indoor swimming pools. In the following table (table 3), the levels of chloroform are gathered.

Table 3: Levels of chloroform measured in indoor swimming pools

City/Country	Chloroform concentration (µg/L)			Reference
	In the water	In the boundary layer	In the air	
Kaohsiung/Taiwan	9.81 ± 1.36	609 ± 85	13.97 ± 1.94	Chen et al. 2011
Seoul/South Korea	32.9			Lee et al. 2009
Modena/Italy	15.42 ± 12.38			Cammann et al. 1995
Modena/Italy	34 ± 9			Aggazzotti et al. 1998
Modena/Italy	32.02 ± 15.05			Aggazzotti et al. 1990
Heidelberg/Germany	15.95 ± 8.85			Erdinger et al. 2004
Nakhon Pathom/Thaïland	23.23 ± 13.73			Mallika et al. 2008

The concentrations of chloroform differ from one study to another. Thus, for the risk assessment, the concentrations of the Chen et al. paper will be used thanks to their measurements in the boundary layer and in the air. To know the quantity of chloroform inhaled during leisure/professional swimming and for the workers, the inhalation rates are needed. US EPA inhalation rates are used and gathered in the following table (table 4).

Table 4: Human inhalation rates for men and women by activity levels (USEPA, 1985)

Exposure route	Units	Value	
		Male	Female
Inhalation resting	m^3/h	0.7	0.3
Inhalation swimming	m^3/h	0.8	0.5

In order to know the quantities of chloroform inhaled during the time spend in the swimming pool, some calculations are needed. The values used for these calculations are from Chen et al. study for the concentrations of chloroform in the boundary layers and in the air and the exposure times, Derelanko et al for the body weight concentration (Derelanko et al. 1995), and the table 4 for the inhalation rates.

$$Chloroform = Inhalation\ rate\ x\ time\ of\ exposure\ x\ chloroform\ concentration\ x\ body\ weight$$

The concentration of chloroform inhaled (µg/kg bw) are shown in the table 5.

Table 5: Human chloroform inhalation for men and women by activity levels

	Time of exposure (h/event)	Inhalation rate (m^3/hour)		Concentration of choloform ($\mu g/m^3$)	Total chloroform Inhalation (µg/kg bw)	
		Man	Woman		Man	Woman
Leisure swimming	1.92 ± 1.73	0.8	0.5	609.10^{-3}	65.48	40.92
Swimming professional	6	0.8	0.5	609.10^{-3}	204.62	127.89
Resting	2	0.7	0.3	609.10^{-3}	59.68	25.58
Shift for workers	8	0.7	0.3	$13.97.10^{-3}$	5.48	2.35

The concentration in µg/kg bw found during the case studies are between 250 and 2500 lower than the NOAEL given by the WHO (WHO, 2008). Swimming two hours or more does not reach the NOAEL concentration. Considering these values, the swimmer and the worker do not occur any risk concerning the exposure to chloroform.

These results are confirmed by other studies. Lévesque et al. made a study in Québec city where they made the difference between the young competitive swimmer and the adult leisure swimmer (Lévesque et al., 2000). At first, they found a significant association between the concentration of chloroform in the water and the concentration of chloroform in the alveolus. Then, they discovered that a young competitive swimmer is twice more exposed than the adult leisure swimmer. Indeed, the concentration of chloroform after fifteen minutes swimming for the young competitive swimmer is 144 $\mu g/m^3$ whereas for the adult leisure swimmer the concentration is 82 $\mu g/m^3$. This is the same for thirty minutes swimming, 183 $\mu g/m^3$ and 96 $\mu g/m^3$ respectively and for sixty minutes 201 $\mu g/m^3$ and 100 $\mu g/m^3$ respectively. But, unfortunately, they did not study more than an hour swimming. However, these results are lower than the NOAEL.
Furthermore, according to the case study of Kogenivas et al. also in Spain, the concentration of chloroform in the exhaled breath of swimmers after a 40 min swim was researched and compared to the concentration before swimming. Before swimming the concentration is 0.7 $\mu g/m^3$ and after forty minutes swimming, the concentration is 4.5 $\mu g/m^3$.
According to the data from the different measurements of chloroform and the Aggazzoti et al. and Kogenivas et al. case studies, a swimmer does not incur risks by swimming in the water for two hours or more.

According to the USEPA and IRIS, chloroform is a probable human carcinogen (USEPA, 2006; IRIS, 2000b). To study the risks more, cancer risks calculations were made. According to the US EPA, these results have to be under 10^{-6} to be considered as negligible (see table 6 and 7).

Table 6: Total Lifetime Cancer Risk assessment in Taiwan

Exposure route	Units	Value		Total Incremental Lifetime Cancer Risk (ILCR)		Reference
Taiwan		**Male**	**Female**	**Male**	**Female**	
Inhalation resting	m^3/h	0.40	0.31	$4.16.10^{-7}$ (0.61%)	$3.77.10^{-7}$ (0.69%)	Chen et al. 2011
Inhalation swimming	m^3/h	0.75	0.51	$6.83.10^{-5}$ (99.35%)	$5.42.10^{-5}$ (99.25%)	Chen et al. 2011
Oral ingestion				$4.08.10^{-9}$ (0.01%)	$4.77.10^{-9}$ (0.01%)	Chen et al. 2011
Dermal contact				$2.56.10^{-8}$ (0.04%)	$2.62.10^{-8}$ (0.05%)	Chen et al. 2011
Total ILCR				$6.87.10^{-5}$ (100%)	$5.46.10^{-5}$ (100%)	Chen et al. 2011

Table 7: Cancer Risk assessment in South Korea

Exposure route	Cancer Risk		Reference
South Korea	**Male**	**Female**	
Inhalation	$1.15.10^{-3}$	$1.36.10^{-3}$	Lee et al. 2009
Oral ingestion	$2.77.10^{-8}$	$3.33.10^{-8}$	Lee et al. 2009
Dermal contact	$1.57.10^{-7}$	$1.63.10^{-7}$	Lee et al. 2009

Table 6 and 7 show the cancer risk assessments after an exposure to chloroform in indoor swimming pools. Furthermore, the table 6 shows the main routes of internalisation of chloroform in the body. Inhalation is the man route; more than 99% of the chloroform is going through this route. According to these results, the other routes are negligible for a risk assessment. The values for the cancer risk of the Lee et al. and Chen et al. studies show that there are no risks of cancer through the oral ingestions and dermal contact; the values are lower than 10^{-6}. Chen et al. separated inhalation resting and swimming, for the resting inhalation the value is also lower than 10^{-6}, there are no risks of cancer through this route also. However, the values for the inhalation (Lee et al.) and the inhalation during swimming (Chen et al.) are 10 times to 1000 times higher than the negligible value of the USEPA. By this route, there is a non negligible cancer risk for the swimmers.

To conclude, the concentrations of chloroform do not reach the NOAEL but considering all the parameters like chloroform concentrations, exposure factors, body weight, skin surface, penetration coefficient of chloroform, etc. there is a can risk concerning the inhalation of chloroform during swimming.

IV-2- Risks assessments chloramines

In combination with the exposure of chloroform, the swimmer/bather and the worker are also exposed to chloramines. There are three types of chloramines: monochloramines (NH_2Cl), dichloramines ($NHCl_2$) and trichloramines (NCl_3). Trichloramines is the most volatile one, so easier taken up by inhalation and dermal contact (WHO, 2006). As chloroform, chloramines are mainly present in gas form in swimming pools, and are formed by the reaction between chlorine and organic matter in the water. Therefore, the concentration in the air also depends on the concentration of chlorine, the guidelines in the country and the behaviour and the number of swimmers in the water. It depends also on the efficiency of the ventilation (WHO, 2006).

In the literature, the NOAEL are given by several organizations. At first the WHO gives a NOAEL of 50 mg/L, equivalent to 8.6 mg/kg bw/day for the total chloramines. Then, it gives a NOAEL of 100 mg/L, equivalent to 5.8 mg/kg bw/day for the monochloramines (WHO, 2000). The second organization that gives a NOAEL is the USA Environmental Protection Agency, with a NOAEL of 200 ppm, equivalent to 9.5 mg/kg/day.

The concentrations of chloramines are expressed in mg/m^3; consequently, the NOAEL in ppm must be converted into mg/m^3. According to the French institute, l'institut de veille sanitaire, and the equation (Furetox, 2012):

$$mg/m^3 = \frac{ppm\ x\ molecular\ weight}{24.45}$$

$$mg/m^3 = \frac{200\ x\ (16 + 1x2 + 35.5)}{24.45}$$

$$mg/m^3 = 421.27$$

Then the NOAEL for the monochloramines of the IRIS organization is 421.27 mg/m^3 (IRIS, 2000a).

Héry et al. made a study about the chloramines in the atmosphere of an indoor swimming pool in France. The workers are starting to feel irritation around 0.5 mg/m^3. This study found concentrations of chloramines up to 0.84 mg/m^3 (Héry et al., 1995).

No other studies on the amount of chloramines found in swimming pools were found. The articles in the literature are only referring to Héry et al. when they talk about concentration of chloramines in swimming pools. However, in France, the DDASS (Direction Départementale des Affaires Sanitaires et Sociales) is regularly controlling the levels of chloramines in French swimming pools. As no other scientific studies with the concentrations of chloramines in swimming pools were found, a French study done by the DDASS in collaboration with Atmo Picardie is used in order to evaluate the risks for a swimmer.
The amount of chloramines present in the air of the swimming pool was tested with four air extractors, at each side of the swimming pool and one next to the lockers. The test was done during a week with different attendance in the swimming pool (figure 5)

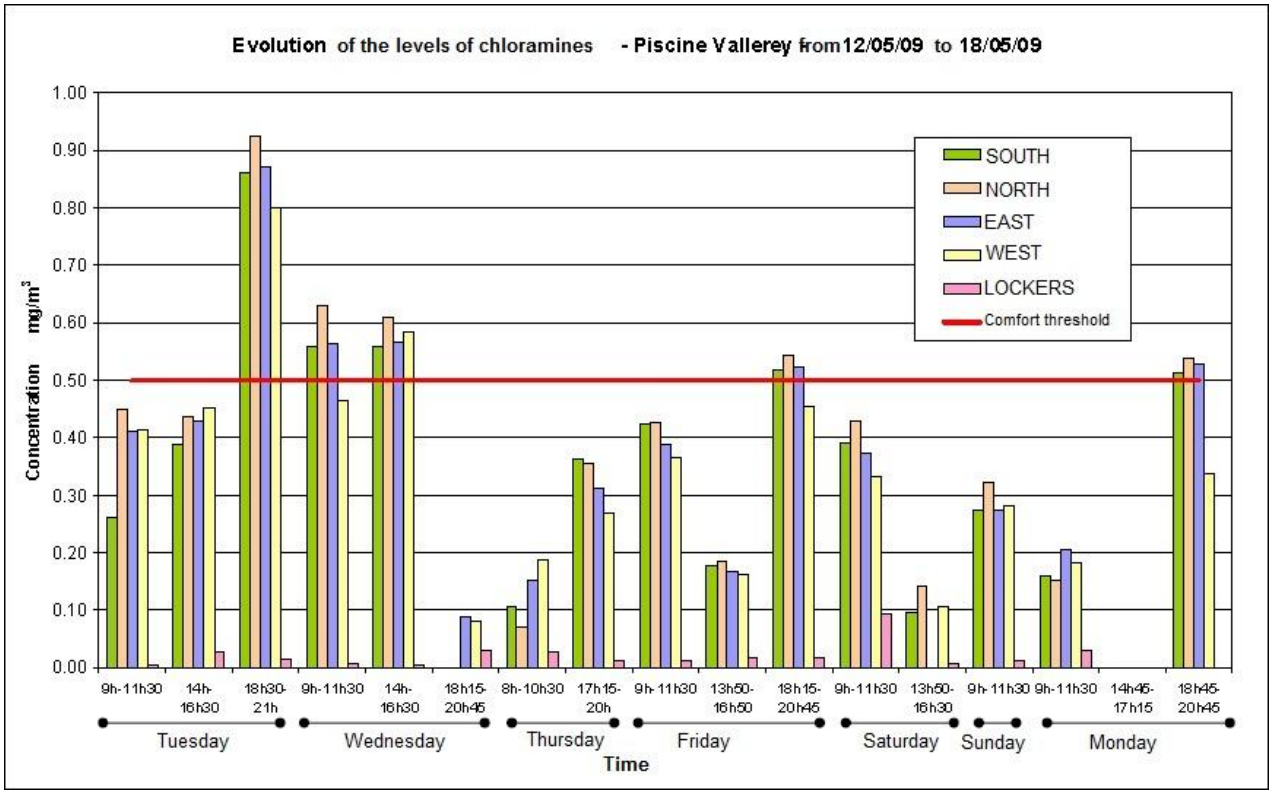

Figure 5: Evolution of the amount of chloramines, Vallerey swimming pool (Amiens), from 12/05-18/05/09 (ATMO, 2009)

All the results are under the IRIS NOAEL. However, it occurs five times that the amount of chloramines is higher than the comfort threshold. This threshold is decided by the government and the amount of chloramines in the air has normally not to be upper than that. Furthermore, in the Héry et al. study, the worker starts to feel some discomfort at the same concentration. With a higher amount of people in the water and with water movements, the concentration of chloramines will rise above that threshold.

Another swimming pool, in La Roche-sur-Yon, shared their results of a study made by the DDASS the 24/11/2011. Five devices were put at different places in the swimming pool: A: where the workers are watching the swimmers, B: next to the "river", C: in front of the toboggans, D: on the control consol game, E: above the whirlpool, F: next to the steam room. The results of the concentration of trichloramines found in these places are shown in figure 6.

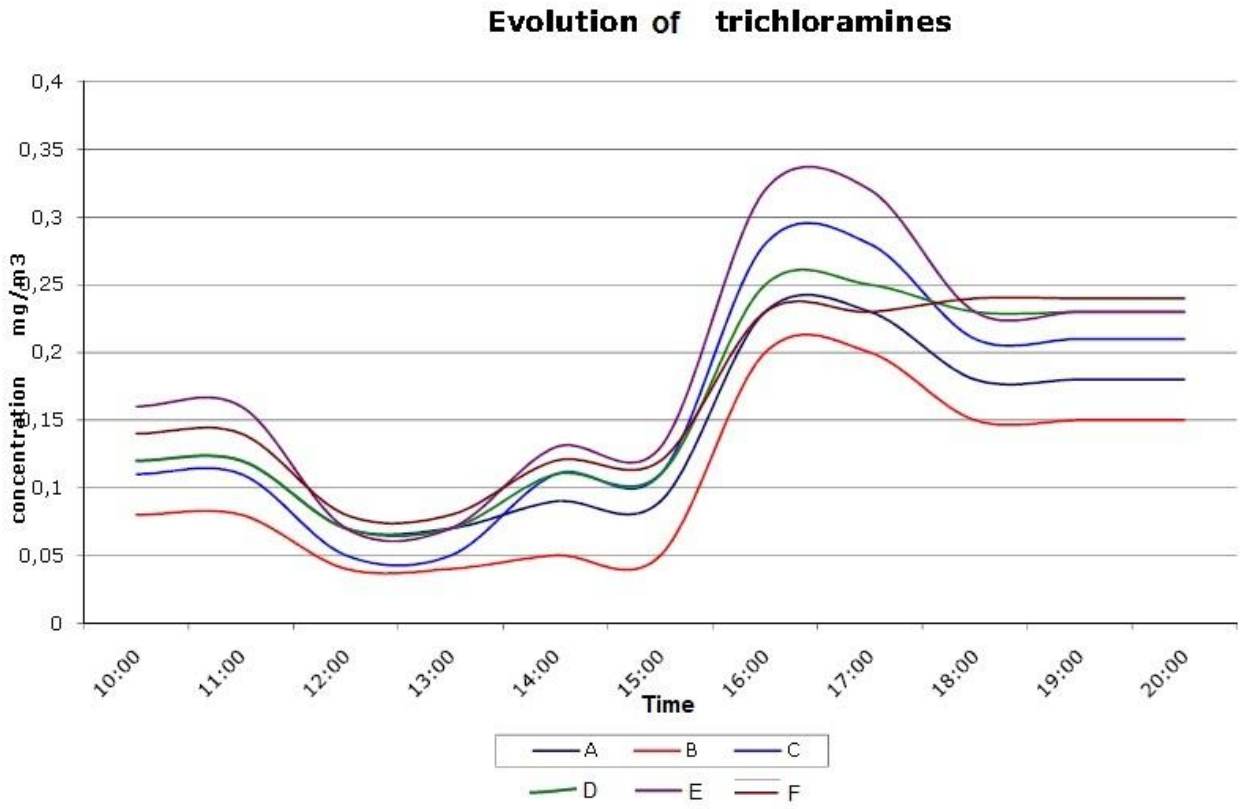

Figure 6: Evolution of the amount of trichloramines, ARAGO swimming pool (La Roche-sur-Yon), from 24/11/2011 (Cédia, 2012)

During the day when these samples were taken, the amount of trichloramines was not above the discomfort threshold of 0.5 mg/m^3. Thus, with the number of swimmers in the pool and the ventilation that day, the swimmer and the worker do not incur any discomfort. However, the sampling was done only on one day during the week, when there are not so much swimmers in the pool. As shown in the Atmo study, the risk is higher when there are more swimmers in the pool. The measurements should be done as in the Atmo study on several days and several times.

According to the NOAEL of the IRIS, the concentrations found in the French swimming pools by Héry et al. are at least 500 times lower than the NOAEL; the maximal concentration is 500 times lower.

Furthermore, the concentrations found in the Amiens' swimming pool are lower than the NOAEL. This does not mean that the swimmer is comfortable in the swimming pool, above 0.5 mg/m^3, the swimmer starts to feel irritation in the eye and pulmonary discomfort. The French government also considers this concentration as the discomfort threshold.

To conclude, the concentrations of chloramines are lower than the NOAEL, so the swimmer does not incur serious risks. However, the swimmer may experience some discomfort as reported in the Héry et al. study (Héry et al., 1995). Indeed, even if there is a threshold, it occurs frequently that the concentration goes above that. As this happens more during busy hours of the swimming pool, a sensitive person should avoid going there during these times in order to avoid any irritations due to high concentrations of chloramines.

Unfortunately, the studies on chloramines are focusing on the consequences of the exposure of chlorine on eyes, lungs and throat. They are based on questionnaires asked to workers and/or swimmers but not on actual measurements. The studies based on actual sampling in the swimming pool air and/or water is focused on the trichloramines. Regrettably for a risk assessment, no NOAEL were found on these compounds neither on IRIS nor ToxNet.

Studies should be made on the three types of chloramines on other things than asthma. Samples should be taken regularly and at different times of the year; when it is cold/warm and crowded or not. The workers should wear a sampling machine when they work and breath samples should be taken from professional and also leisure swimmers. The comparison should be made to be able to see which persons are the most exposed for acute and long term exposure.

IV-3- Comparison of regulations between France and Australia

The exposure of swimmers and workers depends on countries. The legislation differs in each country; e.g. the concentration of products which are allowed in the swimming pool. Here, a comparison between France and Australia will be made in order to see if there is a difference of exposure for the swimmer/worker.

The temperature:

The temperature in a French indoor swimming pool has to be between 25 and 27°C and 24°C for an outdoor one. However, for certain activities (babies, elderly activities), the temperature can be raised to 30-32°C (ARS, 2011).

In Australia, there is no specification about the temperature for an outdoor swimming pool. But for an indoor swimming pool, a differentiation between under and above 26°C is made for the chlorine concentrations.

pH:

In any type of swimming pool, the pH should be between 6.9 and 7.7 in France, and between 7.2 and 7.8 in Australia.

Chlorine:

The difference is made between free chlorine, combined chlorine and total chlorine.

For a swimming pool which does not contain any stabilizer, the concentration of free chlorine authorized in France, for every type of swimming pool, is between 0.4 and 1.4 mg/L. In Australia, the concentration should be above 1.0 mg/L for an outdoor swimming pool, above 1.5 mg/L for an indoor one with a temperature under 26°C and above 2.0 mg/L for an indoor one with a temperature above 26°C. In a swimming pool which contain stabilizer, the concentration should be more than 2 mg/L for France and more than 3.0 mg/L for Australia.

For combined chlorine and total chlorine, an equation is used in France to know the concentration of combined chlorine: [total chlorine – free chlorine] = combined chlorine. No total chlorine regulation exists. In Australia, the maximum concentration of combined chlorine is 1 mg/L but it is not specified how this concentration is obtained. Furthermore the maximum concentration of total chlorine is 10 mg/L.

Stabilizer:

Only a minimum concentration is given in France, 75 mg/L. In Australia, the maximum concentration is 100 mg/L. It is also not allowed to use stabilizer in indoor swimming pools in Australia which is allowed in France.

Despite a few differences, the guideline of the chlorine concentrations is more or less the same for the two countries. Even if the concentrations of free chlorine are higher in Australia, the risk may not be significantly higher. This means that even if each country has its own laws about it, the swimmer does probably not incur more risks in France than in Australia or the other way around.

V- Discussion

The aim of this study was to assess the risks of swimmers in public/private swimming pools. For this purpose, the possible effects of chlorine by-products on the health of both swimmers and workers have been examined, in relation to the concentrations found by researchers and French government officials.

The risk for a worker or a swimmer depends on the swimming pool, but after analysing several studies in different parts of the world, the risks for swimmers (leisure and professional) to develop cancer through inhalation of chloroform is significant. However, the concentrations of by-products (chloramines and chloroform) are not above the NOAEL in the studies analysed.
For professional swimmers and workers the risks are higher because they can spend respectively up to eight hours per day in the water and eight hours at the edge of the swimming pool. The risks are higher with a chronic exposure than with an acute exposure.

This study shows that the analyses to know the quantities of chloroform in the swimming pool are not sufficient to assess the risk of cancer for the swimmers and workers. Indeed, even with concentrations of chloroform lower than the NOAEL, the risk of developing cancer after inhalation of chloroform for swimmers is significant. Through the other routes (dermal and ingestion) the risk of developing cancer is not significant. Focus has to be put on the inhalation of chloroform and solutions to reduce the exposure to a 10^{-6} risk of cancer have to be applied. Further studies have to be made to know if the solutions are efficient to decrease the exposure and hence the risk.

To reduce the risk of developing cancer for swimmers, the swimmers can take more breaks after a few hours of swimming. These breaks should be made outside the water to be out of the high concentration layer of chloroform above the water. Furthermore, there should be a better understanding of why showering is necessary before entering the water. Education for the workers and the visitors has to be provided. If there would be a better understanding among the public of the need to shower before swimming, the addition of products to the water could be lower. This would reduce the concentration of by-products (chloroform but also chloramines).

The studies made in the swimming pool, e.g. by the French government, are sometimes made in such a way that the concentration of trichloramines never surpasses the NOAEL limit, especially the government decided discomfort threshold. In the study in La Roche-sur-Yon's swimming pool, the measurements were made only on one day, which was a day with a low amount of swimmers. The study should be made for at least a week continuously with low and high amount of swimmers; the problems are starting to occur with a higher number of swimmers in the water.
In the studies published, the questionnaires serve to evaluate the discomfort of the swimmers and workers but the actual concentrations when they experience a discomfort are not measured.

During the comparison of Australia and France it was shown that the concentration of chlorine is higher in Australia, the maximum concentration in France is the minimum concentration in Australia. There are, consequently, probably more by-products in the Australian swimming pools. This could be studied by comparing the amount of chloramines in the water and in the air in different swimming pools in both countries.

Alternative methods

There are alternative methods to avoid the risks of chlorine. For example certain companies specialise in the production of devices to prevent swimmers to be exposed to chlorine and its derivates.

The first method is with oxidation and copper ions. As shown in the following figure (figure 7), the oxidation is achieved by water passing through the chamber while low voltage electrical current is sent to the coated titanium plates in the chamber. The copper ions are added to the water once a week.

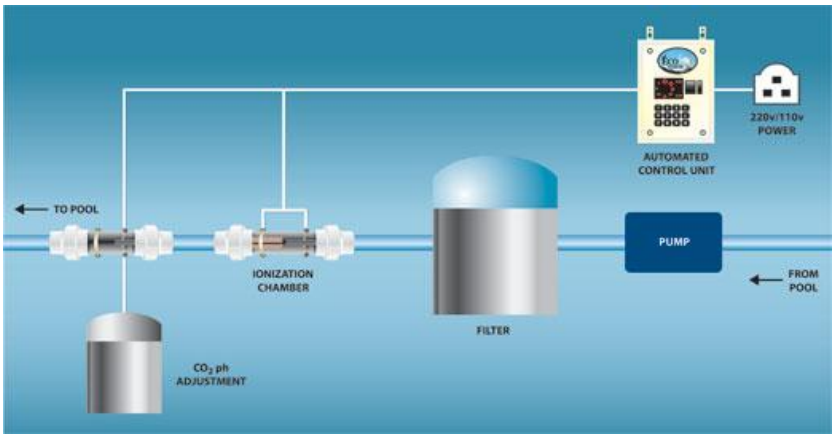

Figure 7: Alternative method to chlorine (Ecosmartepool, 2012)

According to the WHO the oxidation should not be used as the only disinfectant in the water because it is not sufficient to kill the microorganisms brought by swimmers/bathers (WHO, 2006). Here it is used in combination with copper ions. The company does not say at which concentration the copper ion are added to the water, it is not possible to know if this concentration is safe. Indeed, according to Piriou et al., at an acute concentration of copper ion of 4.10^{-4} M, haemolysis, a dramatic decrease of glutathione and an increase of methemoglobin were observed.

Another alternative is to use polyhexamethylene biguanide, also called PHMB. According to Arch chemicals, this product is used as a sanitizer or preservative to kill bacteria and viruses, and to control algae in a wide range of applications globally. However, this product does not oxidize so hydrogen peroxide has to be used alongside it.

To conclude, the cheapest and easiest product that can kill bacteria as well as viruses and parasites is chlorine. It will probably stay the main disinfectant product in swimming pool for a long time.

VI- Conclusion

Each time a leisure swimmer goes to the swimming pool, the chloroform exposure is a cancer risk. For a professional swimmer, the risks are higher due to more time spend swimming and these events occurs more often. A worker has no risk of developing cancer by watching the swimmers.

Concerning the exposure to chloramines, there are not enough data to evaluate a cancer risk but a discomfort and a higher risk for them to develop respiratory problems is known for leisure, professional swimmer and workers. These persons should be aware of the risks in case of higher concentrations of by-products in the water.

A suggestion for the measurements would be to make them during a week at different time of the year, summer as well as winter. Some swimming pools obtain good results for these measurements because they are not made during a day with a lot of swimmers. The ventilation of the swimming pool cannot be verified if there are no measurements during busy hours where a high strain is put on the renewal of the air.

There are not enough measurements on the different types of chloramines in the air. Furthermore, there are no exposure studies made in order to know the NOAEL and LOAEL concentrations for the trichloramines, the by-product which is considered the most dangerous.

Concerning the alternative methods, these methods are not proven to be as effective as chlorine. In my opinion, chlorine should maybe used less and in combination with more ecological products until there is a mix of products, that are not dangerous for the health of swimmers and workers, which can be used.

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