Variability of chlorination by-product occurrence in water of indoor and outdoor swimming pools

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ABSTRACT

Swimming is one of the most popular aquatic activities. Just like natural water, public pool water may contain microbiological and chemical contaminants. The purpose of this study was to study the presence of chemical contaminants in swimming pools, in particular the presence of disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs) and inorganic chloramines (CAMi). Fifty-four outdoor and indoor swimming pools were investigated over a period of one year (monthly or bi-weekly sampling, according to the type of pool) for the occurrence of DBPs. The results showed that DBP levels in swimming pools were greater than DBP levels found in drinking water, especially for HAAs. Measured concentrations of THMs (97.9 vs 63.7 μg/L in average) and HAAs (807.6 vs 412.9 μg/L in average) were higher in outdoor pools, whereas measured concentrations of CAMi (0.1 vs 0.8 mg/L in average) were higher in indoor pools. Moreover, outdoor pools with heated water contained more DBPs than unheated pools. Finally, there was significant variability in tTHM, HAA9 and CAMi levels in pools supplied by the same municipal drinking water network, suggesting that individual pool characteristics (number of swimmers) and management strategies play a major role in DBP formation.

1. Introduction

Swimming is one of the most popular aquatic activities in industrialized countries. During busy periods, the quality of pool water may be compromised. Indeed, swimmers bring microorganisms and organic substances (saliva, sweat, cosmetics, sunscreen and urine) with them into the water, which strongly contributes to water contamination (Sakkas et al., 2003; Kanan and Karenfil, 2011; Keuten et al., 2012). Chlorine is the most common agent used to disinfect pool water. However, using disinfectants in the presence of organic matter (OM) in water may lead to the formation of disinfection by-products (DBPs). More than 600 DBPs have been identified in drinking water (Richardson et al., 2007). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two main groups of DBPs in drinking water and are monitored in many countries. Total THMs (in this paper denoted tTHM) include four compounds: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. HAAs comprise the following nine compounds (HAA9): bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDCAA), bromodichloroacetic acid (BDCAA),...
(TBAA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA).

There are no regulations for THMs and HAAs in recreational water in Canada. However, there are guidelines in some countries in the world. According to the study of the Agence Française de Sécurité Sanitaire de l’Environnement et du Travail (AFSSET, 2010), the United Kingdom, Finland and the World Health Organization (WHO) recommend a maximum concentration of 100 µg/L of tTHMs for all types of pools. In Belgium, the maximum value for chloroform (instead of total THMs) is also 100 µg/L. In Germany, the recommended maximum concentration is 20 µg/L for tTHMs for any type of pool, while in Switzerland the recommended level for tTHMs is 30 µg/L for indoor pools only. In Denmark, the maximum levels for tTHMs are 25 or 50 µg/L depending on the type of pool (www.retsinformation.dk/Forms/R0710.aspx?id=142195). With regard to swimming pools in France, the AFSSET (2010) recommends not exceeding a level of 100 µg/L of tTHMs. A guideline was determined by the WHO to control the presence of chloramines in pool water (WHO, 2006). In its guideline, the WHO proposes a concentration below 0.2 mg/L of combined chlorine (the difference between total residual chlorine and free available residual chlorine) corresponding to total chloramines in pool water (indoor) (MDDEP, 2006). Using the WHO guideline as a benchmark, several countries have regulated this group of by-products. Indeed, the standard for chloramines in indoor pools is 0.6 mg/L in France and 1 mg/L in Australia (MDDEP, 2006). In Canada, the standard is 0.1 mg/L in Alberta, whereas in Quebec, it is 0.5 mg/L for indoor pools and 1 mg/L for outdoor pools (MDDEP, 2006; MDDEP, 2012a). In the Province of Quebec (Canada), in addition to chloramines, the Regulation Respecting Water Quality in Swimming Pools and Other Artificial Pools (MDDEP, 2012a) establishes standards for free residual chlorine (between 0.8 and 2 mg/L for indoor pools and between 0.8 and 3 mg/L for outdoor pools), pH, alkalinity, turbidity and microbiological parameters (faecal coliforms, E. coli, Pseudomonas aeruginosa and Staphylococcus aureus). However, no standards for THMs and HAAs exist yet for pool water in Quebec.

Many studies have been conducted on the presence of DBPs in swimming pools. Some studies conducted on swimming pool water have served to document tTHM, especially chloroform. Beech et al. (1980) measured an average concentration of 125 µg/L for tTHM (primarily chloroform) in the water of 101 pools in Miami (United States). Fantuzzi et al. (2001), on the other hand, observed a lower average chloroform concentration (33.2 µg/L) in the five indoor pools in Italy. Chloroform was also the subject of studies by Jackson and Rule (2002), who observed average values for this compound between 11.4 µg/L and 236 µg/L in indoor pool water in several regions in Europe. Other studies have focused on chloroform to study its effects on the health of swimmers and target the main routes of exposure by using plasma, blood, urine or alveolar air as exposure biomarkers (Aggazzotti et al., 1990, 1993; Lévesque et al., 1994; Aiking et al., 1994; Aggazzotti et al., 1995; Cammann and Hübner, 1995; Lindstrom et al., 1997; Aggazzotti et al., 1998; Erdinger et al., 2004; Caro and Gallego, 2007, 2008).

Some of these studies have limitations, such as the investigation of a single group of DBPs including THMs (chloroform) or chloramines (Aggazzotti et al., 1990; Aiking et al., 1994; Cammann and Hübner, 1995; Carbonnelle, 2003; Lévesque et al., 2006; Aprea et al., 2010; Schmalz et al., 2011), measurements carried out on pool water on a reduced scale or with samples generated in laboratory-scale simulations (Judd and Jeffrey, 1995; Judd and Black, 2000; Kim et al., 2002; Hansen et al., 2012), the study of a single type of pool, usually indoor (Jackson and Rule, 2002; Lévesque et al., 1994, 2000, 2006; Kanan and Karenfil, 2011), and small numbers of pools studied (Lahl et al., 1981; Fantuzzi et al., 2003; Thacker and Nitnaware, 2003; Cardador and Gallego, 2011). In addition, very little attention has been paid to investigating the seasonal occurrence of DBPs in pool water.

The purpose of this study is to provide a better understanding of the variability of THMs, HAAs and inorganic chloramines (CAMI) in pool water. In particular, the study identifies differences in DBP levels between drinking water and pool water, compares the levels between indoor and outdoor pools and identifies the factors responsible for this variability. The study is based on a large sample of indoor and outdoor pools investigated during a full year.

2. Methodology

2.1. Study cases

The study conducted over a period of one year involved 54 municipal public pools in Québec City (Canada). The pools under investigation included 15 indoor and 39 outdoor pools. These pools are located in eight boroughs of the city. The boroughs are served by five drinking water distribution systems (Québec, Des Îlets, Ste-Foy, Val-Bélair and Lac des Érables) all supplied by water chlorinated during the treatment process. The pools under study were selected according to the water disinfection method. In fact, the water of all the pools is disinfected with chlorine (using online chlorine control). In every case, a hypochlorite-based disinfectant is used. Residual chlorine monitoring is carried out periodically by the swimming pool operator. In most cases, in particular in outdoor pools, water renewal is carried out during the night (with filtration) in order to reduce accumulated contaminants.

2.2. Sampling strategy

The pools under study were sampled once a month over one year for indoor pools and every two weeks during the summer (June, July and August) for outdoor pools. All indoor and outdoor pools were sampled during weekdays in the morning or in the afternoon in the presence of swimmers. Sampling consisted of collecting water in the less frequented area of each pool 30 cm under the surface of the water and between the outlet of the filtration system and the backflow. During each visit, two 250 ml water samples per pool were collected in Nalgene bottles and refrigerated at 4 °C in order to carry out the following physical-chemical analyses in the laboratory: UV absorbance at 254 nm, conductivity, turbidity, ammonia, total organic carbon (TOC) and CAMI. For each pool, four water
samples were collected in borosilicate vials (40-mL) containing 332 µL of ammonium chloride at 30 °C for neutralizing free chlorine. The samples were then refrigerated at 4 °C for chromatographic analysis of HAA9 and tTHM in the laboratory. In addition to the samples, on-site measurements were conducted for free residual chlorine, total residual chlorine, pH and temperature on site. All techniques for sampling, sample conservation and delays between sampling and analysis were carried out based on the guidelines described in the Guide des méthodes de prélèvement, de conservation et d’analyse des échantillons relatifs à l’évaluation de la qualité de l’eau des piscines et autres bassins artificiels (MDDEP, 2012b). Moreover, in order to ensure the representativeness of water quality in the pools, employees working at the pools were not informed of the specific time of the sampling visits. In total, more than 400 samples were collected during this study, and nearly 5800 analyses were conducted to measure the different DBPs and other water quality parameters.

2.3. Analytical methods

UV absorbance was measured at a wavelength of 254 nm using a 50-mm quartz cell and UV–visible spectrophotometer (Pharmacia LKB Ultraspec III). TOC was measured using high-sensitivity infrared spectrophotometry (ASI Shimadzu Analyzer, Model 5000) based on the 5310B Standard Method (American Public Health Association, American Water Works Association, Water Environment Federation, 1998). Free and total residual chlorine “in-situ” measurements were carried out based on a colorimetric method (Method 8021 and Method 8167: 0–2.00 mg/L) using a HACH colorimeter (DR890 model). Turbidity was measured using a turbidimeter (HACH 2100 N model). Water conductivity was analyzed using a portable multimeter (WTW model). The various inorganic chloramines forms (monochloramine, dichloramine and trichloramine) were measured using the DPD 4500-Cl-G Standard Method (American Public Health Association, American Water Works Association, Water Environment Federation, 1998) and a UV visible spectrophotometer (Pharmacia LKB Ultraspec III model) at a wavelength of 515 nm and with a 10-mm quartz cell. Solid DPD (chlorine-free HACH pouch) was used instead of liquid DPD, as described in the 4500-Cl-G Standard Method (American Public Health Association, American Water Works Association, Water Environment Federation, 1998). For ammonia analysis, a distiller (Kjeltec model) was used to distill samples and a potentiometer with a nitrogen-selective electrode and reference electrode (Orion reference) was used for dosing.

The analysis of THMs was conducted using Method 524.2 of the United States Environmental Protection Agency (USEPA, 1995b). Samples were analyzed using gas chromatography (Varian GC 3900) with DB1-MS 30 m × 0.25 mm ID × 0.25 µm thickness column and mass spectrometer (Varian MS 2100T ion trap). The detection limits for THMs were set to 0.3 µg/L for chloroform, 0.4 µg/L for bromodichloromethane (BDCM) and dibromochloromethane (DBCM) and 0.5 µg/L for bromoform. For HAA analysis, the EPA 552.2 method (USEPA, 1995a) was used. Samples were analyzed using gas chromatography with ZB-1701 30 m × 0.32 mm ID × 0.25 µm thickness column and ECD detector (Perkin Elmer Autosystem XL). Regarding the HAA analysis, the detection limits were set to 1.3, 0.9, 0.4, 1.0, 0.7, 0.8, 4.6, 4.2 and 6.4 µg/L for MCAA, DCMA, TCAA, MBAA, DBAA, BCAA, CDBAA, BDCAA and TBAA, respectively. To ensure the validity of the THM and HAA results, internal controls, duplicates and blanks (validation parameters) were analyzed.

2.4. Data analysis

The results of this study were subjected to comparative analyses to determine the statistically significant differences that existed based on various scenarios. Data analysis was carried out using the SPSS (Statistical Package for the Social Sciences) software, version 13.0. Given that all data produced in the study did not follow a normal distribution (Kolmogorov–Smirnov, theoretical distribution), non-parametric statistical tests were used. A variance analysis using the Kolmogorov–Smirnov test was carried out to show significant differences in DBP levels between indoor and outdoor pools (Section 3.3) and heated and unheated outdoor pools (Section 3.4). Moreover, a Pearson correlation test was also carried out to study existing correlations between indoor and outdoor pools (Section 3.3). A Kruskal–Wallis test (n > 2) was also carried out to evaluate inter-pool variations in DBP levels by observing the differences between average DBP concentrations for three indoor pools and three outdoor pools supplied by the same municipal distribution system (Section 3.5).

3. Results and discussion

3.1. Occurrence of DBPs in pools

The average concentrations of tTHM were 63.7 µg/L and 97.9 µg/L in the water of indoor and outdoor pools, respectively. For HAA9, the average levels measured were 412.9 µg/L for indoor pools and 807.6 µg/L for outdoor pools, whereas the levels of CAI were 0.8 mg/L and 0.1 mg/L, respectively. The levels of tTHM observed in this study are comparable to those observed in others studies on indoor pools (Aggazzotti et al., 1990, 1993, 1995, 1998; Fantuzzi et al., 2001). However, some authors measured far higher levels, even more than 200 µg/L (Lahl et al., 1981; Chambon et al., 1983). In the case of chloramines, the average concentrations measured in indoor pools in this study were higher (nearly two times higher) than those found in the study of Lévesque et al. (2006). For outdoor pools, although there are fewer studies, the levels of THMs and HAAs measured in this study were very different from those obtained in other studies. Indeed, THM (chloroform) concentrations measured in the studies reported by the WHO (2006) were higher than those obtained in the present study. For HAAs, the average concentrations measured of DCAA and TCAA in outdoor and indoor pools in our study were much higher (two to eight times higher) than those obtained in recent studies (WHO, 2006; Cardador and Gallego, 2011).

Chloroform was the most prevalent THM found in the pools under study. This compound alone corresponded on average to nearly 97% of the tTHM found in the pool waters. Other studies also observed the predominance of chloroform in recreational waters (Thacker and Nitaware, 2003; Judd and
3.2. Comparison of DBP levels in pools and drinking water

Table 1 compares the average levels of tTHM and HAA9 in the water of the five municipal distribution systems and the pools supplied by these systems. The average levels of HAA9 in the pools were considerably higher than those observed in drinking water (4 to 80 times greater, on average, depending on the network). Such was not the case for tTHM, for which levels in pool water were comparable to those in drinking water (more or less high, depending on the network).

In fact, unlike HAAs, THMs are highly volatile, as reported by various authors (Beech et al., 1980; Lahl et al., 1981; Aggazzotti et al., 1987, 1995; Aiking et al., 1994; Lévesque et al., 1994; Weisel and Shepard, 1994; Cammann and Hübner, 1995). Furthermore, certain authors noted that THM volatility is especially high when swimmers cause turbulence in the water (Aggazzotti and Predieri, 1986; Aggazzotti et al., 1995, 1998; Weng and Blatchley III, 2011). Moreover, according to certain studies, the contribution of drinking water from distribution systems supplying the pools would be minimal in terms of DBPs (Lahl et al., 1981; Kim et al., 2002).

The relatively high formation of DBPs in pools versus drinking water (especially for HAA9) is mainly associated with chlorination at relatively high water temperature conditions. The temperatures in the pools under study (25 °C–35 °C) exceeded those of the water in the distribution system (1 °C–23 °C). The quality of water in swimming pools can also have an impact on the occurrence of DBPs. Indeed, on average, TOC concentrations in pool waters exceeded two to five times that of drinking water from corresponding municipal networks (Fig. 1). Chu and Nieuwenhuisjen (2002), Kanan (2010) and Liviac et al. (2010) also observed that levels of TOC were much higher in pools than in drinking water (or filling water). Generally speaking, drinking water contains DBP precursors of humic origin such as fulvic acid, whereas in pools, more exogenic precursors predominate, such as urine, hair, saliva and body care products originating from the swimmers (Lahl et al., 1981; Thacker and Nitnaware, 2003; Kanan and Karenfil, 2011). The results presented in Fig. 1 lead us to surmise that a large proportion of the TOC observed in pools may originate primarily from the swimmers. Indeed, depending on the characteristics of the OM, TOC could contribute differently to DBP formation. According to Kanan and Karenfil (2011), body fluid analogs (BFAs) introduced by the swimmer were more reactive than the OM from the filling water. These authors also demonstrated that BFAs produce more HAAs than THMs.

3.3. Comparison of DBPs between indoor and outdoor pools

Measured DBP concentrations in water varied according to the type of pool (indoor versus outdoor) (Table 1). The levels of tTHM, HAA9 and CAMi observed for indoor and outdoor pools during the summer are presented in Table 2 and the various water quality parameters measured during the same period are summarized in Table 3. According to these results, the water of outdoor pools contained on average two times more tTHM and HAA9 than water of indoor pools (Table 2). These differences are statistically significant according to the Kolmogorov–Smirnov test (SPSS 13.0, p < 0.05). In their recent study, Cardador and Gallego (2011) also observed higher concentrations of HAAs in the water of outdoor pools than water in indoor pools. These results might be explained by the fact that outdoor pool water contains more and different types of DBP precursors than indoor pool water. Given that outdoor...
pools are exposed to the external environment, other additional factors such as wind (airborne particles), grass, soil, leaves, insects, rain and temperature may increase the level of contamination of water in this type of pool. In fact, values for turbidity, conductivity and TOC (water contamination indicators) are also higher in outdoor pools (Table 3). The average concentration of TOC in outdoor pool water was approximately two times higher than the concentration found in indoor pool water (Table 3). Such levels of TOC could be associated with the relatively high number of swimmers in outdoor pools during the summer, especially children, and a larger quantity of urine in the water, which then adds to other precursors of DBPs. Indeed, citric acid and hydroxybenzoic acids could be a precursor of chloroform (the main THM) in urine (Chambon et al., 1983). Likewise, certain nitrogenic organic compounds found in urine and sweat (Ueno et al., 1996) and other organic substances (microorganisms, blossoms, leaves and dirt) and those from sun cream (Sakkas et al., 2003) could also play a role in the formation of DBPs in the water of outdoor pools.

For outdoor pools, it is possible that relatively high levels of TOC provoke higher chlorine demand and, thus, higher chlorine doses in order to maintain higher residual chlorine levels, consequently favoring further DBP formation. However, no significant statistical correlation (Pearson test with significance level of 0.01) was observed for this type of pool between the concentrations of TOC and the concentrations of THM or CAMi (r = 0.111 and r = 0.038, respectively). However, a positive and a statistically significant correlation was observed between TOC and HAA9 (r = 0.182, Pearson test with significance level of 0.05). These results suggest that TOC is not necessarily a good indicator of DBP precursors in the water of outdoor pools. Nevertheless, for indoor pools, correlations between TOC and each of the three groups of DBPs were all significant (Pearson test with significance level of 0.01; r = 0.359 for THM, r = 0.288 for HAA9 and r = 0.302 for CAMi). The relationship between levels of TOC and THMs in the water of indoor pools was also observed by Clauser et al. (2005).

The exposure of water in outdoor pools to the sun’s UV rays could also contribute to the difference between the levels of DBPs in these pools versus indoor pools. Indeed, studies carried out by Liu et al. (2006) on surface water have shown that prolonged exposure to UV (medium-pressure lamp) can increase their HAA and THM content. For chloramines, exposure to UV rays may also contribute to explain the differences between the two types of pools (Table 2). Unlike tTHM and HAA9, the average concentration of CAMi observed in outdoor pools was far lower (approximately five times less) than that of indoor pools (this was also the case for combined chloramines, as shown in Table 3, which is an indicator of total chloramines). These differences are statistically significant according to the Kolmogorov–Smirnov test (SPSS 13.0, p < 0.05). This result may seem surprising, since very comparable average concentrations of ammonia (precursor to chloramines) and free available residual chlorine were observed in the water of both types of pools (Table 3). One possible explanation could be that the formation of trichloramine in pool water is associated with the reaction of urea (introduced by swimmers) with chlorine to form chloramines (Schmalz et al., 2011). More specifically, urea could react with chlorine to form chlorurea (1,1,3,3-tetrachlorourea) and then produce DBPs in these pools versus indoor pools. Indeed, studies carried out by Liu et al. (2006) on surface water have shown that prolonged exposure to UV (medium-pressure lamp) can increase their HAA and THM content. For chloramines, exposure to UV rays may also contribute to explain the differences between the two types of pools (Table 2). Unlike tTHM and HAA9, the average concentration of CAMi observed in outdoor pools was far lower (approximately five times less) than that of indoor pools (this was also the case for combined chloramines, as shown in Table 3, which is an indicator of total chloramines). These differences are statistically significant according to the Kolmogorov–Smirnov test (SPSS 13.0, p < 0.05).

The ability of nitrogenous compounds to react quickly with chlorine to form chloramines (Hailin et al., 1990) or other DBPs could explain the low levels of ammonia in both types of pools (where the pH levels are favorable to monochloramine formation) (see Table 3). Given the higher volatility of chloramines in outdoor pools (where the atmosphere is less

![Fig. 1 – Average concentrations of total organic carbon (TOC) in drinking water and water of the swimming pools under study for the five municipal distribution systems (bars represent standard deviations).](image-url)
confined than for indoor pools) and the possibility of photodegradation by UV rays (World Health Organization, 2006; Li and Blatchley III, 2009), it is probable that the levels of chloramines that may form during the chlorination of the water in these pools was underestimated.

Differences in the proportions of HAA9 species between both types of pools were also observed. Indeed, for outdoor pools, the average concentrations of DCAA and TCAA were practically equivalent (375 \( \mu \text{g/L} \) and 374 \( \mu \text{g/L} \), respectively). In the case of indoor pools, the average concentration of TCAA (158 \( \mu \text{g/L} \)) was slightly lower than DCAA (186 \( \mu \text{g/L} \)). These results are difficult to explain because of the number of site-specific factors associated with each pool that may contribute to the formation and variability of DBPs.

### 3.4. Impact of water temperature on DBPs

Pool water temperatures may also have an effect on the presence of DBPs, as temperature affects the kinetics of reactions between chlorine and OM as well as DBP volatility. A detailed analysis of outdoor pools\(^1\) (heated and unheated) was carried out to show the effect of temperature on DBP levels (Fig. 2a and b). In these figures, it is possible to note that for both groups of pools (heated and unheated), the average concentrations of free available residual chlorine and TOC were comparable. Higher average levels of tTHM, HAA9 and CAMi were observed in heated pools. Significant differences (based on the Kolmogorov–Smirnov test, SPSS 13.0, \( p < 0.05 \)) between the two types of pools were observed for tTHM and DCAA concentrations (not for TCAA and CAMi). The fact that differences in average concentrations of CAMi between heated and unheated pools were not statistically significant might be explained by the relatively high volatility of these substances in warmer water. In fact, the behavior of CAMi or others volatile compounds dissolved in water can be estimated using the air/water partition coefficient based on Henry’s law constant (\( H \)). Furthermore, according to Stottmeister and Voigt (2006), Henry’s law constant values show that trichloramine (\( H = 435 \)) escapes from indoor pool

### Table 3 – Average values of water quality parameters measured in water of indoor and outdoor pools during (summer period).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Indoor pools(^a)</th>
<th>Outdoor pools(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>Average value</td>
<td>Minimum value</td>
</tr>
<tr>
<td>Ammonia nitrogen (mg/L)</td>
<td>4.53</td>
<td>2.16</td>
</tr>
<tr>
<td>Free residual chlorine (mg/L)</td>
<td>0.173</td>
<td>0.100</td>
</tr>
<tr>
<td>Total chlorine (mg/L)</td>
<td>1.55</td>
<td>0.77</td>
</tr>
<tr>
<td>Combined chlorine (mg/L)</td>
<td>2.70</td>
<td>1.43</td>
</tr>
<tr>
<td>pH</td>
<td>0.714</td>
<td>0.360</td>
</tr>
<tr>
<td>Water temperature</td>
<td>7.47</td>
<td>6.92</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>29.0</td>
<td>27.3</td>
</tr>
<tr>
<td>UV absorbance at 254 nm (cm(^{-1}))</td>
<td>0.020</td>
<td>0.102</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>1391</td>
<td>659</td>
</tr>
</tbody>
</table>

\(^{a}\) Average values calculated from monthly samples collected in summer.

\(^{b}\) Average values calculated from samples collected every two weeks in summer.

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Fig. 2 – a–b. Average concentrations of the measured DBPs in the water of outdoor heated and non-heated swimming pools during the summer period; a) tTHM and CAMi; b) DCAA, TCAA et HAA9 (bars represent standard deviations).

\(^1\) For this analysis, only outdoor pools were included, since all indoor pools are heated.
water 966 times faster than monochloramine ($H = 0.45$), 286 times faster than dichloramine ($H = 1.52$) and three time faster than chloroform (the more prevalent THM). Likewise, even if HAA are, a priori, non-volatile compounds, water temperature seems to favor chemical transformation or the destruction of these compounds (Wu et al., 2001). Moreover, Lifongo et al. (2004) observed an increase in the degradation speed of TCAA in surface water with an increase of temperature and the presence of radiation similar to UV. Also, Zhang and Minear (2002) observed that water temperature can have an effect on HAAs, especially trihaloacetic acids (BDCAA, DBCAA and TBAA), promoting the decomposition of these acids into corresponding trihalomethanes. This phenomenon might also explain higher measured levels of tTHM in the heated pools (as presented in Fig. 2a).

3.5. Inter- and intra-pool variations of DBPs

In order to consider in greater detail the variability of DBPs between pools (inter-pool variations), three indoor and three outdoor pools supplied by the same municipal distribution network (Quebec) were selected for illustrative purposes. As observed in Fig. 3a and b, considerable differences in DBPs were observed between the two groups of pools (indoor and outdoor), demonstrating that inter-pool variations of DBPs are very much related to specific local characteristics (e.g., external contribution of organic contaminants) and management operations (e.g., pool chlorination practices). Moreover, major differences were noted in the presence of DBPs between the three indoor pools (significant differences for tTHM and HAA9 based on the Kruskal–Wallis test, SPSS 13.0, $p < 0.01$), but also between the three outdoor pools (significant differences for tTHM and CAMi based on the Kruskal–Wallis test, SPSS 13.0, $p < 0.05$). This inter-pool variability between the same type of pool (indoor or outdoor) might possibly be explained by the variability of organic contaminants present in the water (external contribution of OM), but also by compounds introduced by swimmers. Indeed, indoor pools with higher TOC concentrations appear to be the most inclined to form DBPs (Fig. 3a). This same trend was observed in outdoor pools (Fig. 3b). DBP variability between the pools of same type (indoor or outdoor) was also observed in pools supplied by other distribution systems (results not shown).

Intra-pool variations of DBPs were also observed in both types of pools. Indeed, high standard deviations (represented by error bars) for tTHM, HAA9 and CAMi (Fig. 3a–b) led us to believe that these are attributable primarily to seasonal/temporal variations within the same pool. These results confirm observations made by Chu and Nieuwenhuijsen (2002). These variations could be the result of the temporal variability of DBP precursors in water (e.g., in accordance with the variability of number of swimmers) and operational practices (temporal changes in disinfectant with online chlorine control). For example, in one outdoor pool where various samples were collected daily (for various days during the week), we observed considerable variations of DBPs and precursor indicators from the morning to the afternoon. Indeed in this pool, average levels of TOC were 7.3 and 9.9 mg/L in the morning and the afternoon, respectively; average concentrations of tTHMs were 141 and 169 µg/L in the morning and the afternoon, respectively; and average levels of HAA9 were 1105 and 1248 µg/L in the morning and the afternoon, respectively. These data suggest that contaminants associated with swimmers accumulate during the day. However, intra- and inter-pools DBP variations are difficult to interpret. Several factors that can contribute to the formation and variability of DBPs, such as pool attendance, management strategy, water renewal rates and chlorine doses are site-specific.

The results do not support the possible impact of pH and free chlorine on the formation of DBPs in swimming pools, as observed by Kanan (2010), Schmalz et al. (2011) and Hansen et al. (2012) in laboratory-based studies. In fact, the pH of pool water is regulated in Quebec and must be maintained between 7.2 and 7.8. Thus, it is not unusual to obtain very low variations between the pools (for indoor pools, annual average pH of 7.52 ± 0.28 and for outdoor pools, summer average pH value of 7.85 ± 0.19). Such is also the case for free chlorine (annual average value of 1.55 ± 0.45 mg/L for indoor pools, and summer average value of 1.66 ± 0.46 mg/L for outdoor pools).

To better illustrate the intra-pool variations of DBPs according to the management strategy, the impact of water renewal on DBPs was analyzed for a given pool. According to

![Fig. 3](image-url)
Lahl et al. (1981) and Erdinger et al. (2004), a complete renewal or the regular circulation of water in a pool would reduce the quantity of OM, and thus the potential formation of DBPs. Results of the variability of HAA9 in the selected pool closed for two months (July and August) are presented in Fig. 4. During the closure period, the pool water was chlorinated, but not renewed with fresh water (the same water during the entire closure period), no additional OM was added (as there were no swimmers) and water filtration was maintained sufficiently. Results in Fig. 4 show that maintaining chlorination without the presence of swimmers and without renewing water would promote the accumulation of HAAs over time. The accumulation of HAAs was possibly sustained by the fact they are not volatile compounds compared to chloramines and THMs for which variations were very low during the same period (from 0.71 to 1.17 mg/L and from 51.3 to 97.2 µg/L), respectively. HAAs are soluble compounds with low volatility. They are stable in the presence of high doses of chlorine and THMs for which variations were very low during the same period (from 0.71 to 1.17 mg/L and from 51.3 to 97.2 µg/L), respectively. HAAs are soluble compounds with low volatility. These conditions combined with the recirculation of water (without the addition of fresh water) could result in an accumulation of HAAs in the pool water and in an increase in their concentrations, as shown in Fig. 4.

Some management strategies for pools should be reviewed or considered to reduce the formation of DBPs. Regular maintenance of filters or treatment by filtration using granulated activated carbon (Kim and Kang, 2008) can be effective means to reduce DBPs already present in water. The reduction of DBP precursors at the source is an effective way of preventing the formation of DBPs. Reducing precursor levels (e.g. urea) by dilution (by frequently adding fresh water), or by using improved water treatment technologies such as ozone-activated carbon or photo-oxidation (Stottmeister and Voigt, 2006) can help to minimize DBP occurrence in pool water. Closer attention to hygiene measures paid by swimmers before swimming (Stottmeister and Voigt, 2006; Keuten et al., 2012) can also contribute to reducing DBP precursors.

4. Conclusions

The analysis and interpretation of the results of this study that included 54 municipal public pools served to establish the following conclusions:

- DBP levels in swimming pools are greater than those found in drinking water, especially for HAAs. This phenomenon is probably associated primarily with the chlorination of water in the pool and the presence of a relatively high organic load and higher water temperature found in pools than in drinking water.
- The type of pool appears to have an impact on the levels of DBPs formed. The measured concentrations of THMs and HAAs are greater in outdoor pools, whereas the measured concentrations of CAMi are higher in indoor pools. Moreover, outdoor pools with heated water contain more DBPs than unheated pools.
- There is great variability in tTHM, HAA9 and CAMi levels in pools supplied by the same municipal drinking water network, suggesting than individual pool characteristics and management strategies play a major role in DBP formation. For example, lower water renewal in pools may promote the accumulation of HAAs over time.
- The results suggest that swimming in indoor and outdoor public pools can be an important route of human exposure to THMs, HAAs and chloramines. As is the case with showers, water in pools may promote routes of exposure different than those for drinking water (primarily through contact with the skin and inhalation). Although ingestion is the main route of exposure to HAAs and this route is not significant in pools (Cardador and Gallego, 2011), the presence of this DBP group could prove to be an indicator of behavior for other non-volatile compounds for which data is not yet available.

Lastly, the results of this study will be useful to estimate DBP levels in the air of swimming pools in a seasonal basis (Dyck et al., 2011; Catto et al., 2012) and for evaluating the actual exposure of swimmers to DBPs in municipal pools for epidemiological studies. In future studies, other DBPs and their variability must be documented in swimming pools. Also, the occurrence of DBPs in other types of recreational waters (e.g. private and residential pools, spas) disinfected by chlorine or other disinfectants should be investigated in future work.

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