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Occurrence of brominated disinfection byproducts in the air and water of chlorinated seawater swimming pools

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Abstract

An undesirable consequence of disinfection is the formation of chemical contaminants known as disinfection byproducts (DBPs). Chronic exposure to DBPs has been linked to adverse health effects. The occurrence of DBPs in chlorinated pools filled with seawater (such as thalassotherapy pools and pools in spas) has received little attention so far. The present study evaluated the speciation and levels of disinfection byproducts in indoor swimming pools filled with seawater and treated with chlorine. Water and air samples were collected from three indoor swimming pools located in Southern France. Several classes of DBPs including trihalomethanes, haloacetic acids, haloacetonitriles, and trihaloacetaldehydes were analyzed in water. Halogenated volatile organic compounds were analyzed in air. Extractable organic halide (EOX) contents were determined using combustion micro-coulometry system. The speciation of DBPs identified in the three pools was predominantly brominated. The mean (arithmetic) concentration of bromoform, dibromoacetic acid, tribromoacetic acid, dibromoacetonitrile and bromal hydrate in the three pools were 79.2, 72.9, 59.9, 26.9 and 10.0 $\mu\text{g/L}$, respectively. By weight, HAAs represented the most abundant chemical class followed by THMs. In air, bromoform was the most abundant THM occurring at a mean concentration of 133.2 $\mu\text{g/m}^3$ in the three pools. The mean EOX level was 706 $\mu\text{gCl}^-/\text{L}$ for the three pools. In average, the quantified DBPs accounted for only 14% of EOX, thus 86% of EOX remained unknown. Further research is warranted to identify the unknown DBPs.

Keywords

Disinfection byproducts; seawater swimming pools; brominated compounds; chlorination; total organic halide

Introduction

Disinfection is a critical process in which pathogenic microorganisms are eliminated from water. During this process, undesirable byproducts known as disinfection byproducts (DBPs) are formed because of reactions between disinfectants and organic compounds present in water. Swimming pool water constitutes a medium in which complex loads of organic compounds are brought into water by swimmers (Lakind et al., 2010). Discharges of saliva, sweat, hair particles, or personal care products are sources of organic compounds that react with disinfectants and ultimately lead to the formation of DBPs (Chowdhury et al., 2014b; Hansen et al., 2012; Kim et al., 2002; Teo et al., 2015). The occurrence of DBPs in swimming pools constitutes a health concern since

exposure to these compounds has been linked to a range of adverse health effects (Hrudey, 2009; Villanueva et al., 2015). Chronic exposure to DBPs has been associated with an increased risk of bladder cancer (Villanueva et al., 2004). Some epidemiological studies have suggested an increased risk of asthma among professional swimmers and child swimmers (Font-Ribera et al., 2010; Weisel et al., 2009). Some studies have demonstrated that DBPs could induce adverse reproductive health outcomes (Klinefelter et al., 1995; Nieuwenhuijsen et al., 2000). Furthermore, extensive evidence exists about the genotoxicity and carcinogenicity of several DBPs (Richardson et al., 2007). Exposure to DBPs in swimming pools may take place via dermal absorption, inhalation, and ingestion (Zwiener et al., 2007a). Inhalation and dermal exposure have been considered to be the main routes of human exposure to DBPs in swimming pools, while ingestion from accidental water swallowing has been classified as a minor route (Xu and Weisel, 2005; Zwiener et al., 2007a). The occurrence of DBPs in swimming pools has been investigated in numerous studies (Chowdhury et al., 2014b). Among DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) have been studied extensively in swimming pools around the world (Aggazzotti and Predieri, 1986; Aggazzotti, G., Fantuzzi, G., Tartoni, P.L. and Predieri, 1990; Chu and Nieuwenhuijsen, 2002; Daiber et al., 2016; Dyck et al., 2011; Judd and Black, 2000; Kim et al., 2002; Manasfi et al., 2016; Parinet et al., 2012; Simard et al., 2013). Richardson et al., 2010 identified more than 100 DBPs and measured the concentrations of chloramines and THMs in chlorinated and brominated swimming pools. Recently, Daiber et al., (2016) evaluated the occurrence of DBPs and the associated mutagenicity of water in swimming pools and spas. However, the overwhelming majority of these studies investigated the levels and speciation of DBPs in chlorinated swimming pools filled with municipal (tap) water. Very little data has been documented regarding the speciation and levels of DBPs in chlorinated pools filled with seawater. In the latter, the high salt content particularly in bromide and the slightly basic pH (~8) could affect the formation reactions of DBPs leading to DBP profiles and distributions distinct from those typically found in tap water pools (Hansen et al., 2012; Hua et al., 2006; Le Roux et al., 2012). Since the early 1900s, the use of seawater in swimming pools has been widely practiced in thalassotherapy centers in Europe for presumed health benefits (Parinet et al., 2012). Furthermore, seawater pools can now be found in water parks around the Mediterranean and on cruise ships and ferries (World Health Organization, 2006). Seawater pools are also found in hotels and spas over the world, especially those offering wellness programs (Smith and Puczko, 2009). In France, there are around fifty thalassotherapy centers distributed along the coasts (Charlier and Chainoux, 2009). According to some estimates, French thalassotherapy centers welcome more than one million users annually (Schwartz, 2005). For adverse health outcome considerations, the formation of DBPs in seawater is an issue of concern since the few studies conducted in seawater pool setting showed a predominance of brominated DBPs. Several studies have provided evidence regarding the far higher toxicities of brominated DBPs compared to their chlorinated analogues (Jeong et al., 2015; Manasfi et al., 2017; Plewa et al., 2010; Richardson et al., 2007; Yang et al., 2014). In previous investigations, Parinet et al. (2012) studied the levels of two chemical classes of DBPs namely trihalomethanes (THMs) and haloacetic acids (HAAs) in chlorinated seawater pools. In a recent study, Manasfi et al. (2016) reported the levels of several classes of DBPs including THMs, HAAs, haloacetonitriles (HANs), and trihaloacetaldehydes (THAs) in seawater pools in Southeastern France. However, no data has been provided so far regarding the occurrence of DBPs in the air of seawater pools and the organic halide contents of water in these pools. The present study was conducted in order to investigate the speciation and levels of DBPs in the air and water of indoor seawater pools in Southern France. The study also aimed at determining the extractable organic halide (EOX) contents of these pools and evaluating

the contribution of the traditionally measured and some emerging DBP chemical classes to the EOX concentrations. Determining the occurrence of DBPs in air and water of seawater pools will help document data that is necessary for risk assessment studies.

Materials and Methods

Study Site and Sample collection

Three indoor swimming pools located in Southern France were included in the study. All the pools were filled using seawater and treated with chlorine. A detailed description of the studied pools including type of activity, pool volume, pool area, water filtration type, and average daily frequentation is presented in Table S1.

Table S1. Characteristics of the studied indoor chlorinated seawater pools

Pool	Surface (m ²)	Depth (m)	Volume (m ³)	Type of filtration	Type of use	Age Category	Mean Daily Frequentation
F	143	1.5	215	Sand	Swimming/ relaxing	Adult	40
H	91	0.8-2.2	160	Sand	Swimming/ relaxing	Adult	65
J	24	1.3	32	Sand	Swimming/ sport activity*	Adult	45

*e.g. aerobic exercises in water

In all the pools, seawater was obtained from the Mediterranean and was sand filtered before filling the pools. The sampling campaign was conducted in spring 2016. Free residual chlorine and total chlorine were determined on-site during sampling. Other physicochemical parameters including temperature, pH, and conductivity were also determined on-site using specific electrodes (WTW Multiline P4 multimeter, Weilheim, Germany). Samples were collected in triplicates for laboratory analysis. To determine total organic carbon (TOC), total nitrogen (TN), and bromide (Br⁻) levels, samples were collected in amber glass bottles (1 L) with PTFE-lined screw caps. In addition, samples were collected in 65-mL vials with PTFE-lined screw caps for the analysis of DBPs and EOX in water. In these samples, ascorbic acid was added as a quenching agent in the vials before sampling, and the vials were filled without any remaining headspace to avoid any loss of volatile DBPs. All samples were transported at 4 °C and treated within 48 h. For the analysis of DBPs in air, canisters (Entech) of 6-liter capacity were used to sample air in the indoor pools. Sampling was performed by filling canisters from the air above the water level (1 m) in less than one minute. A blank canister was obtained by collecting air samples from the ambient air outside swimming pool facilities.

Chemicals

Analytical standards including THM calibration mix, halogenated volatile mix (containing HANs), HAA esters calibration mix, 2,3-dibromopropionic acid solution, and chloral hydrate solution were purchased from Supelco (USA). Tribromoacetaldehyde (97%) was purchased from Aldrich (United Kingdom) and was used to generate its hydrated form bromal hydrate (BH) in

ultrapure water (Millipore, resistivity >18 M Ω cm). A standard stock solution of each compound was prepared in Methyl *tert*-butyl ether (MTBE, purity 99.8%) which was purchased from Merck (Germany). L-ascorbic acid, crystalline, reagent grade was purchased from Sigma (China). Sulfuric acid, analytical grade reagent, was purchased from Fisher Scientific (UK).

Water sample preparation

For the analysis of EOX, THMs, HANs, THAs sample aliquots (50 mL) were first adjusted to a pH value ranging between 4.5 and 5.5 by adding sulfuric acid. Samples were then extracted by liquid-liquid extraction (LLE) by adding MTBE (5 mL) and shaking manually during 2 min. Then, the organic phase was separated. For the analysis of HAAs, U.S.EPA method 552.3 (Domino et al., 2003) was used with slight modifications. In brief, sample aliquots (40 mL) were acidified to a pH < 1 by adding concentrated sulfuric acid and were then extracted with MTBE (4 mL). 2,3-dibromopropionic acid was added to the extracts as a surrogate. Subsequently, the resulting organic phase was transferred into 15 mL vials to which acidified methanol was added and placed in a water bath at 50 °C for 2 h to transform the HAAs into their methyl ester derivatives. After cooling, 4 mL of saturated sodium bicarbonate solution were added before collecting the organic phase containing the HAA esters in chromatographic vials.

Analytical methods for water analysis

Free residual chlorine and total chlorine were measured on-site by the colorimetric DPD method using a portable spectrophotometer (AQUALYTIC-AL 800, Germany). Bromide levels in water were measured using an ICS-3000 Dionex ion chromatography system, 30 mM NaOH eluent with a flow rate of 1.5 ml/min at 30 °C. A Dionex IonPac AS11-HC (4 × 250 mm) analytical column and a Dionex Ionpac AG11-HC (4 × 50 mm) guard column were used (Thermo Scientific, USA). Total Organic Carbon (TOC) and Total Nitrogen (TN) were measured using high temperature catalytic oxidation technique (Multi N/C 2100, Analytik Jena, Germany). The pretreated sample was injected (50 μ l) into the furnace filled with a Pt preconditioned catalyst. The combustion was realized at 800 °C and the combustion products were carried by high purity oxygen (Linde Gas) allowing detection of CO₂ by non-dispersive infrared (NDIR) and detection of NO by chemiluminescence (CLD). Organic extracts containing DBPs were analyzed using a gas chromatograph coupled to a ⁶³Ni electron-capture detector (GC-ECD model Clarus 580, Perkin Elmer, Norwalk, CT, USA). An Elite 5MS capillary column was used for the separation. Helium 5.0 was used as a carrier gas at 1 mL/min. Nitrogen was used as a make-up gas at 30 mL/min. For the analysis of THMs, HPs, HANs and HKs, the temperature program was as follows: initially 35 °C increasing to 145 °C at a rate of 10°C/min, then at a rate of 20 °C/min up to 225 °C and finally at 10 °C/min to 260 °C, held for 2 min. For the analysis of HAAs, the temperature was initially set to 40 °C, then increased to 75 °C at a rate of 15 °C/min, then increased to 100 °C at 5 °C/min, and finally temperature reached 135 °C at 10 °C/min and held for 2 min. External calibration was performed using a set of 7 standard solutions. The solutions were prepared by adding aliquots of the standard stock solution in reconstituted seawater and later conducting the same treatment as pool water samples. Reconstituted seawater was prepared according to ASTM International standard practice for the preparation of substitute ocean water (method D1141-98, 2013). Analysis of organic halides was performed using a combustion/micro-coulometer system. Coulometric titration with silver ions was performed using organic halide analyzer (TOX-300, Mitsubishi, A1-Envirosciences, France). The analyzer was coupled to an automatic boat controller (ABC-210, Mitsubishi, A1-Envirosciences, France). An aliquot of 50

μL of the MTBE extracts obtained using LLE was injected using an autosampler (ASC-250L, Mitsubishi, A1-Envirosiences, France) equipped with a syringe of 100- μL capacity. Samples were introduced into the combustion tube under a flow of O_2 and Ar adjusted at 200 mL/min. The combustion of the extracted organohalides was followed by pyrolysis at 900 °C resulting in the formation of hydrogen halides (HX) which were then determined with micro-coulometric titration. Calibration was performed by spiking reconstituted seawater with bromoform. Precision and recovery were determined by injecting 50 μL of MTBE extracts obtained from seawater spiked with bromoform at 376 $\mu\text{gCl/L}$. Average percent recovery was 91.5% and relative standard deviation was 4.4% based on 4 replicates of the 376 $\mu\text{gCl/L}$ solution. Data processing was performed using the software TOX-300 (version 1.0.0, A1-Envirosiences, France). For quality control, reconstituted seawater was extracted and used as a blank to demonstrate absence of contamination from the high chloride concentrations typically present in seawater. Seawater and water reagent blanks were included with each sequence. Analysis of samples was conducted in triplicate. Limits of detection (DL) and the limits of quantification (QL) for the analyzed chemicals and parameters are presented in Table S2.

Table S2. Method detection limits (DL) and quantification limits (QL) for the analyzed chemicals/parameters

Chemical/Parameter (Unit)	DL	QL
Chloroform ($\mu\text{g/L}$)	0.8	2.4
Bromodichloromethane ($\mu\text{g/L}$)	0.3	0.9
Dibromochloromethane ($\mu\text{g/L}$)	0.2	0.6
Bromoform ($\mu\text{g/L}$)	0.2	0.6
Dichloroacetonitrile (DCAN) ($\mu\text{g/L}$)	0.2	0.6
Trichloroacetonitrile (TCAN) ($\mu\text{g/L}$)	0.3	1.2
Bromochloroacetonitrile (BCAN) ($\mu\text{g/L}$)	0.3	0.9
Dibromoacetonitrile (DBAN) ($\mu\text{g/L}$)	0.2	0.6
Monochloroacetic acid (MCAA) ($\mu\text{g/L}$)	1.2	3.4
Monobromoacetic acid (MBAA) ($\mu\text{g/L}$)	0.9	2.7
Dichloroacetic acid (DCAA) ($\mu\text{g/L}$)	0.7	2.1
Trichloroacetic acid (TCAA) ($\mu\text{g/L}$)	0.5	1.5
Bromochloroacetic acid (BCAA) ($\mu\text{g/L}$)	0.5	1.5
Dibromoacetic acid (DBAA) ($\mu\text{g/L}$)	0.4	1.2
Bromodichloroacetic acid (BDCAA) ($\mu\text{g/L}$)	0.6	1.8
Chlorodibromoacetic acid (CDBAA) ($\mu\text{g/L}$)	0.5	1.5

Tribromoacetic acid (TBAA) ($\mu\text{g/L}$)	1.0	3.0
Chloral hydrate ($\mu\text{g/L}$)	0.2	0.6
Bromal hydrate (BH) ($\mu\text{g/L}$)	0.1	0.3
Free Residual Chlorine (mg/L)	0.02	0.1
Total Chlorine (mg/L)	0.02	0.1
Total Organic Carbon (TOC) (mg C/L)	0.2	0.5
Total Nitrogen (TN) (mg N/L)	0.1	0.4
Total Organic Halide (TOX) ($\mu\text{g Cl/L}$)	50	100

Analytical methods for air analysis

Analysis of air samples collected in canisters was carried out with a proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS 8000, Ionicon Analytik GmbH, Innsbruck, Austria) equipped with a switchable reagent ion module. O_2^+ mode was used to investigate the presence of halogenated volatile organic compounds (VOCs). O_2^+ can be used as reagent ion to increase the detection ability of the PTR-ToF-MS, since VOCs with proton affinities lower than water can then be ionisable. Mass spectra up to an m/z ratio of 500 were recorded, with a resolution $m/\Delta m$ of 3500. Parameters of the PTR-ToF-MS during the experiments were as follows: $T_{\text{drift}} = 50\text{ }^\circ\text{C}$, $P_{\text{drift}} = 2.04\text{ mbar}$, $E/N = 95\text{ Td}$, $U_{\text{drift}} = 400\text{ V}$. U_{drift} is the electric potential applied to the drift tube; T_{drift} and P_{drift} are the temperature and the pressure in the drift tube, respectively. E is the strength of the electrical field in V/cm and N is the gas number density in cm^3 . The ratio E/N in Townsend ($1\text{ Townsend} = 10^{-27}\text{ cm}^2/\text{V}$) is a defining characteristic of the drift tube. Data from PTR-ToF-MS were analyzed with the software Tofware (version 2.5.7, Tofwerk). The air concentrations were calculated using the following equation:

$$[\text{VOC}^+] = [\text{O}_2^+]_0 \cdot [\text{VOC}] \cdot k \cdot t$$

Where $[\text{O}_2^+]_0$ and $[\text{VOC}^+]$ are the transmission corrected densities of the primary ion O_2^+ and of the VOC^+ ions respectively, expressed in counts per second (cps). k is the reaction rate constant between the VOC and O_2^+ (cm^3/s) and t is the residence time of the ions in the drift tube ($t = 100\text{ }\mu\text{s}$). Concentrations were calculated based on O_2^+ reaction collisional rate of $2 \cdot 10^{-9}\text{ cm}^3/\text{s}$.

Results and Discussion

Physicochemical parameters

Physicochemical parameters including air temperature, water temperature, pH, conductivity, TOC, TN, bromide content, levels of free residual chlorine, and total chlorine were determined. Table 1 presents the values of the physicochemical parameters measured in the studied pools.

Table 1. Physicochemical parameters of the studied pools

Pool	Air Temperature (°C)	Water Temperature (°C)	pH	Conductivity at 25°C (mS/cm)	[Br-] (mg/L)	Free Chlorine (mg/L)	Total chlorine (mg/L)	TOC (mg/L)	TN (mg/L)
F	22.7	32.2	8.5	75.0	88.5	1.6	1.75	2.7	1.4
H	21.5	30.9	8.4	65.6	75.0	1.3	1.50	3.1	1.8
J	24.2	33.1	8.3	73.2	78.3	1.0	1.10	3.9	2.3

The measured pH values ranged between 8.3 and 8.5. These pH values do not conform to the French recommendations for swimming pools, according to which pH should be maintained between 6.9 and 7.7 for pools treated with chlorine. This recommendation has been established to avoid decrease in the disinfecting ability, which takes place at higher pH due to the formation of the less potent hypochlorite ions (OCl^-) (ANSES, 2010). The latter recommendation targets swimming pools without considering the type of pool filling water and a recommendation regarding pH that is specific to seawater pools or pools disinfected with bromine does not exist so far. However, in chlorinated seawater pools bromine is the disinfectant that is formed from the reaction of chlorine with bromide present in seawater. Thus, equilibrium between HOBr/BrO^- ($\text{pK}_a = 8.63$) should be considered instead of equilibrium between HOCl/ClO^- ($\text{pK}_a = 7.54$). In this way, the pH between 8.3 – 8.5 should not compromise disinfection. Pool temperatures ranged from 30.9 to 33.1 °C and 21.5 to 24.2 °C in water and air, respectively. Bromide levels were relatively high ranging from 75.0 to 88.5 mg/L. Typically, seawater contains around 65 mg/L bromide (Magazinovic et al., 2004). Conductivity of water ranged from 65.6 to 73.2 mS/cm. This high conductivity is in agreement with the high salt content expected in seawater. However, the higher conductivity and bromide concentrations measured in the pools compared to those typically measured in seawater could be due to evaporation especially that waters of these pools were heated. TOC levels ranged between 2.7 and 3.9 mg/L. Previously, heterogeneous TOC levels varying from as low as 1.5 mg/L to as high as 39.3 mg/L have been reported in swimming pools (Chu and Nieuwenhuijsen, 2002; Hang et al., 2016). In seawater pools, Parinet et al. (2012) reported levels ranging between 2.8 and 8.6 mg/L. More recently, TOC levels reaching 11.88 mg/L were detected in seawater swimming pools in Southeastern France during summer period (Manasfi et al., 2016). This variability in TOC levels is related to characteristics of the filling water as well as to swimmers behavior and activities since the latter are main contributors to TOC observed in pools (Simard et al., 2013). The lower levels of TOC measured in this study compared to other studies could be related to lower frequentation rates in the investigated pools. In addition, the type of activity of pools was mainly soft which could reduce the discharge of sweat in comparison to other pools where swimmers' activities could be more vigorous. TN levels ranged between 1.4 and 2.3 mg/L. Human body fluid discharges in swimming pools are believed to be a major source of nitrogen in swimming pools (Chowdhury et al., 2014b). Keuten et al. (2012) studied the release of anthropogenic pollutants in swimming pools and estimated that TN released per person is 46 mg within the first minute of showering. During a 30-min exercise, it was estimated that TN release reaches 77.3 mg/bather (Keuten et al., 2014). Free residual chlorine levels ranged between 1.0 and 1.6 mg/L. The latter level is slightly

higher than the maximal level recommended in France for free residual chlorine (between 0.4 and 1.4 mg/L) (ANSES, 2010).

Occurrence of DBPs

Table 2 provides an overview of the concentrations of DBPs measured in water and air of the studied pools.

Table 2. Concentrations of the identified DBPs in the water (in $\mu\text{g/L}$) and air (in $\mu\text{g/m}^3$) of the three indoor seawater pools

Chemical	Pool F	Pool H	Pool J	Mean	SD
In Water ($\mu\text{g/L}$)					
Chloroform	N.D	N.D	N.D	-	-
Bromodichloromethane	N.D	N.D	N.D	-	-
Dibromochloromethane	2.1	4.5	5.5	4.0	1.7
Bromoform	49.7	101.3	86.5	79.2	26.6
TTHM	51.8	105.8	92.0	83.2	28.1
MCAA	N.D	N.D	N.D	-	-
MBAA	N.D	N.D	N.D	-	-
DCAA	N.D	N.D	N.D	-	-
TCAA	N.D	N.D	N.D	-	-
BCAA	3.4	6.2	8.7	6.1	2.7
DBAA	30.5	84.4	103.7	72.9	37.9
BDCAA	1.1	1.6	3.3	2.0	1.2
CDBAA	4.5	10.1	15.5	10.0	5.5
TBAA	28.5	67.8	83.4	59.9	28.3
HAA-9	68.0	170.1	214.6	150.9	75.2
CH	N.D	N.D	N.D	-	-
BH	8.5	9.2	12.4	10.0	2.1
DCAN	N.D	N.D	N.D	-	-
BCAN	N.D	N.D	N.D	-	-
DBAN	18.3	28	34.5	26.9	8.2
In air ($\mu\text{g/m}^3$)					
Chloroform	N.D	N.D	N.D	-	-
Bromodichloromethane	N.D	N.D	N.D	-	-
Bromoform	240.1	137.7	21.7	133.2	109.3
Dibromochloromethane	20.7	13.0	3.6	12.4	8.6

TTHM: sum of four trihalomethane concentrations (or THM-4); MCA: monochloroacetic acid; MBAA: monobromoacetic acid; DCAA: dichloroacetic acid; TCAA: trichloroacetic acid; BCAA: bromochloroacetic acid; DBAA: dibromoacetic acid; BDCAA: bromodichloroacetic acid; CDBAA: chlorodibromoacetic acid; TBAA:

tribromoacetic acid; HAA-9: sum of the nine haloacetic acid concentrations; N.D: Not Determined, for compounds which were not detected or at detected at levels below quantification limits

DBPs in pool water

In all the pools, the speciation of the occurring DBPs was predominantly brominated (Table 2). This speciation is linked to the relatively high levels of bromide present in the filling seawater, since bromide ions react with the added chlorine resulting in the formation of bromine (Deborde and von Gunten, 2008). Consequently bromine reacts with organic compounds leading to the formation of brominated DBPs (Heeb et al., 2014; Hua et al., 2006). Bromine is even more potent than chlorine in halogenating organic compounds (Gallard et al., 2003). Brominated DBPs detected in the pools included HAAs, THMs, HANs and THAs. Figure 1 shows the distribution of THMs in water. Among THMs, bromoform was the most abundant compound with concentrations that ranged from 49.7 to 101.3 $\mu\text{g/L}$. Dibromochloromethane was also detected at lower levels (ranged from 2.1 to 5.5 $\mu\text{g/L}$). In average, TTHM level in the three pools was 83.2 ± 28.1 $\mu\text{g/L}$. Data reported in the literature about levels of TTHMs in seawater pools is limited. Beech et al. (1980) reported high levels of TTHM (657 ± 354 $\mu\text{g/L}$) in seawater pools in USA. Recently, Parinet et al. (2012) reported an important variability in TTHM levels in seawater pools in France with levels ranging from as low as 32.2 $\mu\text{g/L}$ to as high as 995.6 $\mu\text{g/L}$. In a previous report, Manasfi et al. (2016) reported levels ranging from 50.4 to 91.8 $\mu\text{g/L}$ in seawater pools during summer period. Unlike in seawater pools, the occurrence of THMs in swimming pools filled with tap water has been well documented (Chu and Nieuwenhuijsen, 2002; Fantuzzi et al., 2001; Guilherme and Rodriguez, 2014; Lourencetti et al., 2012; Richardson et al., 2010; Righi et al., 2014; Simard et al., 2013; Zwiener et al., 2007b). In these pools, chloroform has been determined as the predominant THM. Chu and Nieuwenhuijsen (2002) reported average concentration of 125.2 $\mu\text{g/L}$ in 8 indoor swimming pools in England. Richardson et al. (2010) reported a TTHM average levels of 49.6 $\mu\text{g/L}$ and 60.2 $\mu\text{g/L}$ in chlorinated and brominated tap water pools in Spain, respectively. Simard et al. (2013) reported an average TTHM level of 64 $\mu\text{g/L}$ in indoor swimming pools in Canada. Figure 2 shows the distribution of HAAs in water. Among HAAs, dibromoacetic acid (DBAA) was the most abundant compound followed by tribromoacetic acid (TBAA).

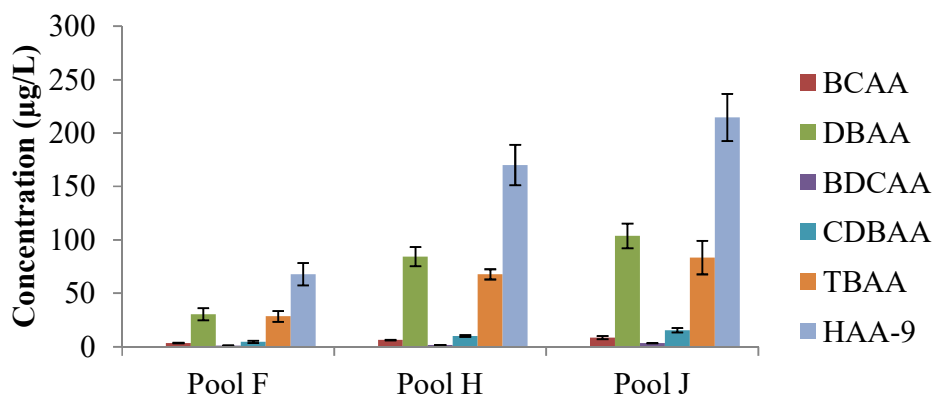


Figure 2. Distribution of the detected HAAs in the water of the studied pools. Error bars represent replicate standard deviation.

These two compounds alone represented about 88% of the total HAA (HAA-9) content by weight.

Chlorodibromoacetic (CDBAA), bromochloroacetic acid (BCAA), and bromodichloroacetic acid (BDCAA) were also detected at levels far lower than those of DBAA and TBAA. In total, HAA-9 ranged between 68.0 and 214.6 $\mu\text{g/L}$ with an average concentration of $150.9 \pm 75.2 \mu\text{g/L}$. These levels tend to be situated in the lower range of HAA-9 levels that have been reported in swimming pools previously. Parinet et al. (2012) reported HAA-9 levels ranging between 84.01 and 2232.89 $\mu\text{g/L}$ in seawater pools. Simard et al. (2013) reported an average level of 412.9 $\mu\text{g/L}$ in indoor tap water pools. Tardif et al. (2016) reported levels ranging from 109.2 to 886.2 $\mu\text{g/L}$ in indoor tap water pools. In tap water pools, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA acid), the chlorinated analogues of DBAA and TBAA respectively, represent the most abundant HAAs (Lee et al., 2010; Tardif et al., 2016).

In the present study, HAAs represented the most abundant chemical class (by weight) among the determined DBPs. The occurrence of HAAs at highest concentrations by weight has been observed for HAAs in tap water swimming pools also (Chowdhury et al., 2014b). This abundance of HAAs in chlorinated swimming pool water is distinct than that typically identified in drinking water. In the latter, THMs are the most abundant class of DBPs rather than HAAs. In swimming pools, the high abundance of HAAs is favored by anthropogenic organic inputs brought into water by swimmers (Kanan and Karanfil, 2011). In addition, HAAs exist in the ionic form at pH relevant to swimming pools and thus tend to accumulate in water without suffering from outgassing due to high volatility as in the case of THMs (Chowdhury et al., 2014a). Among HANs, dibromoacetonitrile (DBAN) was detected in the three pools at levels that ranged from 18.3 to 34.5 $\mu\text{g/L}$ and an average concentration of $26.9 \pm 8.2 \mu\text{g/L}$. Interestingly, the highest concentration of HANs occurred in pool J where TN was the highest (2.3 mg/L). The contribution of N-containing compounds to the formation of HANs has been previously demonstrated (Shah and Mitch, 2012). Kim et al. (2002) observed that the presence of compounds such as urea and proteins of human origin promote the formation of HANs in chlorinated pool water. The N-containing amine precursors are present extensively in body fluids released by swimmers (Teo et al., 2015). Furthermore, the formation of HANs from precursors such as body fluid analogs was shown to increase in the presence of bromide ions (Hansen et al. 2011, Chowdhury et al., 2014b). Occurrence of HANs in seawater pools has been very scarcely documented. Levels comparable to those detected in this study were reported by Manasfi et al. (2016) in seawater pools where DBAN levels ranged between 14.0 and 28.6 $\mu\text{g/L}$. Recently, Daiber et al. (2016) reported levels of DBAN ranging between 35.3 and 1102 $\mu\text{g/L}$ in brominated pools and spas. HANs occurrence in tap water swimming pools has been investigated by fewer studies compared to the occurrence of THMs and HAAs (Chowdhury et al., 2014b). Lee et al. (2010) reported dichloroacetonitrile (DCAN) as the predominant HAN in tap water pools with an average level of 3.9 $\mu\text{g/L}$. Hang et al. (2016) reported levels of DCAN varying from less than 0.5 up to 205.5 $\mu\text{g/L}$ in chlorinated tap water swimming pools. Among THAs, bromal hydrate (BH), which is the hydrated form of tribromoacetaldehyde, was detected in the three pools at levels that ranged from 8.5 to 12.4 $\mu\text{g/L}$ with a mean concentration of $10.0 \pm 2.1 \mu\text{g/L}$. The occurrence of BH in seawater pools has been very poorly documented. However, recent evidence about its mutagenic and genotoxic potential warrants further investigations concerning the occurrence of this compound in swimming pools (Manasfi et al., 2017). In tap water pools, chloral hydrate, the chlorinated analogue of BH, has been frequently detected. Lee et al. (2010) reported an average level of 10.2 $\mu\text{g/L}$ in swimming pools in Korea. Daiber et al. (2016) reported levels as high as 556 $\mu\text{g/L}$ in chlorinated public pools in USA.

DBPs in pool air

Bromoform and dibromochloromethane were detected and quantified in the ambient air of the three pools. The main halogenated species detected were assigned their formulae based on the measured exact mass and the isotopic peak patterns: CHBr_2^+ (m/z 170.844), and CHClBr^+ (m/z 126.894). Reactions between halogenated VOCs and O_2^+ as reagent ion have been reported to proceed via a dissociative charge transfer reaction, generally resulting in the loss of a halogenated atom (Spanel and Smith, 1999). In the case of THM containing both bromine and chlorine atoms, the loss of a bromine atom is favoured (Mayhew et al., 2003). Accordingly, CHBr_2^+ and CHBrCl^+ represented the ions obtained from bromoform (CHBr_3) and dibromochloromethane (CHBr_2Cl) after bromine loss, respectively. Other halogenated species namely BrO^+ (m/z 94.913) and BrCO^+ (m/z 106.913) were also detected but their origin has not been elucidated yet.

As shown in Table 2, bromoform was the predominant DBP in air in the three pools at concentrations ranging from 21.7 to 240.1 $\mu\text{g}/\text{L}$ and a mean concentration of $133.2 \pm 109.3 \mu\text{g}/\text{m}^3$. Dibromochloromethane was detected at levels ranging between 3.6 and 20.7 $\mu\text{g}/\text{m}^3$ with a mean concentration of $12.4 \pm 8.6 \mu\text{g}/\text{m}^3$. In total, TTHM level in air ranged between 25.3 and 260.8 $\mu\text{g}/\text{m}^3$ with a mean concentration of $145.6 \pm 117.8 \mu\text{g}/\text{m}^3$.

Figure 3 shows the distribution of TTHM levels in the air and water of the pools. While water in pool H had two-fold higher TTHM concentration than in pool F (105.8 and 51.8 $\mu\text{g}/\text{L}$, respectively), air in pool H contained lower TTHM concentration than in pool F (150.7 and 260.8 $\mu\text{g}/\text{m}^3$, respectively).

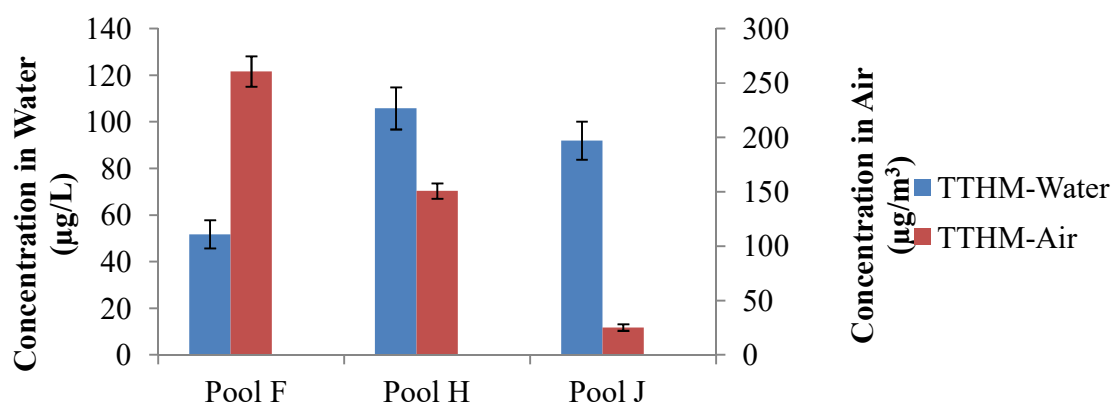


Figure 3. Distribution of total trihalomethanes (TTHM) in the air and water of the studied pools. Error bars represent replicate standard deviation

Furthermore, while pools H and J had comparable TTHM concentrations in water (105.8 and 92.0 $\mu\text{g}/\text{L}$, respectively), they had considerably different TTHM concentrations in air (150.7 and 25.3 $\mu\text{g}/\text{m}^3$, respectively). Previously, THM concentrations in pool water and air have not been strongly correlated (Aggazzotti et al., 1995). Several factors could affect the outgassing of volatile compounds into the air including water temperature, air temperature, concentration in water, intensity of air circulation (ventilation), and the turbulence in water caused by vigorous activity of pool users (Chowdhury et al., 2014b). In this study, the high TTHM level in the air in pool F seems related to poor ventilation in this facility (partially defective ventilation system as

described by the pool operator). To our knowledge, this is the first paper reporting the levels of THMs in the ambient air of chlorinated indoor seawater pools. The air concentrations of bromoform reported here are comparable to levels reported for chloroform in the air of tap water pools. Chloroform concentrations ranging from 36 to 241 $\mu\text{g}/\text{m}^3$ has been reported in the ambient air of indoor swimming pools in Germany (Lahl et al., 1981). Aggazzotti et al. (1995) reported chloroform levels ranging from 48.0 to 459.5 $\mu\text{g}/\text{m}^3$ in indoor swimming pools in Italy. More recently, Richardson et al. (2010) reported mean TTHM levels of 72.1 and 89.5 $\mu\text{g}/\text{m}^3$ in the air of chlorinated and brominated pools in Spain, respectively.

Extractable Organic Halides (EOX) contents

Table 3 shows the measured EOX contents in pool waters. EOX ranged between 510 and 920 $\mu\text{gCl}/\text{L}$ with a mean level of $706 \pm 205 \mu\text{gCl}/\text{L}$. The highest EOX was detected in pool J that also had the highest DBP content (by weight). The contribution of DBPs quantified in water to the total EOX ranged between 11 and 17% approximately.

Table 3. Extractable organic halides (EOX) levels and the percentage contribution of the identified chemical classes of DBPs to the measured EOX in pool waters

	Pool F	Pool H	Pool J	Mean	SD
EOX ($\mu\text{gCl}/\text{L}$)	510	690	920	706	205
Identified DBPs (by weight) ($\mu\text{g}/\text{L}$)	146.6	313.1	353.5	271.1	109.7
% TTHM in EOX	4.31	6.51	4.26	5.03	1.28
% HAA in EOX	4.70	8.60	8.19	7.16	2.14
% HAN in EOX	1.27	1.44	1.33	1.35	0.09
% THA in EOX	0.59	0.47	0.48	0.52	0.07
% All identified DBPs in EOX	10.87	17.02	14.26	14.05	3.08

As a result, unknown halogenated species represented between 89 and 83% of the EOX contents of the pool waters. Figure 4 presents the mean contribution of the identified chemical classes of DBPs to the mean EOX in the three pools. HAAs represented the highest EOX fraction among the identified DBPs (7.2%) followed by THMs (5.3% of TOX). HANs (DBAN) and THAs (BH) represented 1.3% and 0.5% of EOX, respectively.

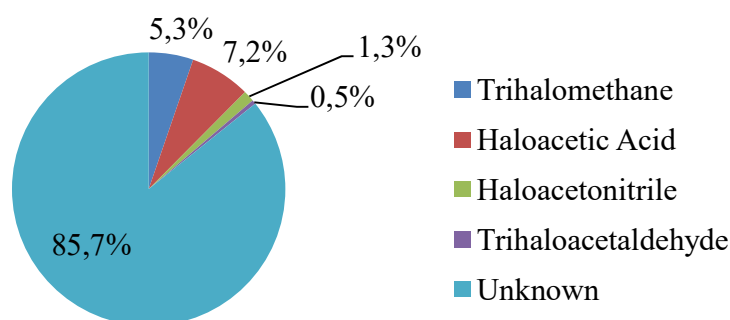


Figure 4. Mean contribution of the identified DBP chemical classes to the measured extractable organic halides (EOX)

Consequently, an average 85.7% of EOX is still unaccounted for by the quantified DBPs in the indoor seawater pools. In drinking water, it has been estimated that around 70% of the EOX is still unknown (Richardson and Postigo, 2011). A higher unknown fraction of EOX in swimming pools is not surprising knowing that complex cocktails of organic precursors are introduced into pool waters (Lakind et al., 2010). The introduced organic loads react with disinfectants generating complex profiles of halogenated byproducts beyond those which are classically quantified (Daiber et al., 2016; Richardson et al., 2010). Precursors such as personal care products worn by swimmers can also react with disinfectants leading to the production of halogenated transformation products (Teo et al., 2015). Previous reports have shed the light on the implication of emerging precursors such as UV filters in the generation of DBPs in swimming pools (Manasfi et al., 2015; Santos et al., 2012; Zwiener et al., 2007a). Recently, halobenzoquinones were detected in swimming pool waters resulting from chlorination reactions of some personal care products (Wang et al., 2013).

Conclusions

This study shows that in chlorinated seawater pools the speciation of DBPs in the water and air is predominantly brominated. Bromoform, DBAA and TBAA, DBAN, and BH were the main THMs, HAAs, HANs and THAs detected in the three indoor pool waters, respectively. In the air, brominated THMs were detected with bromoform being the most abundant species. The occurrence of brominated DBPs at relatively high levels is of health concern since several investigations have demonstrated higher toxicities for brominated species (Jeong et al., 2015; Manasfi et al., 2017; Richardson et al., 2007; Yang et al., 2014). The quantified DBPs represented only a small fraction (an average of 14%) of EOX content measured in the pools. Therefore, most of EOX (86% fraction) was not accounted for by the quantified DBPs and remains unknown. These findings emphasize the need for further research to identify the halogenated DBPs with unknown nature and toxicity and for which users could be exposed to while swimming or in the context of an occupational exposure.

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