



Trihalomethanes in chlorine and bromine disinfected swimming pools: Air-water distributions and human exposure

Carolina Lourencetti^a, Joan O. Grimalt^{a,*}, Esther Marco^a, Pilar Fernandez^a, Laia Font-Ribera^b, Cristina M. Villanueva^b, Manolis Kogevinas^b

^a Department of Environmental Chemistry (I.D.E.A.-C.S.I.C.), Jordi Girona, 18, 08034-Barcelona, Catalonia, Spain

^b Centre for Research in Environmental Epidemiology (C.R.E.A.L.), Dr. Aiguader, 88, 08003-Barcelona, Catalonia, Spain

ARTICLE INFO

Article history:

Received 15 August 2010

Accepted 22 March 2012

Available online xxxx

Keywords:

Water disinfection

In-door swimming pools

Trihalomethanes

Bromoform

Exhaled air pollutants

Volatile organic compounds

ABSTRACT

This first study of trihalomethanes (THMs) in swimming pools using bromine agents for water disinfection under real conditions shows that the mixtures of these compounds are largely dominated by bromoform in a similar process as chloroform becomes the dominant THM in pools disinfected with chlorine agents. Bromoform largely predominates in air and water of the pool installations whose concentration changes are linearly correlated. However, the air concentrations of bromoform account for about 6–11% of the expected concentrations according to theoretical partitioning defined by the Henry law. Bromoform in exhaled air of swimmers is correlated with the air concentrations of this disinfectant by-product in the pool building. Comparison of the THM exhaled air concentrations between swimmers and volunteers bathing in the water without swimming or standing in the building outside the water suggest that physical activity enhance exposure to these disinfectant by-products. They also indicate that in swimming pools, besides inhalation, dermal absorption is a relevant route for the incorporation of THMs, particularly those with lower degree of bromination.

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1. Introduction

Many disinfection treatments are used to eliminate viruses and bacteria in swimming pool waters. Chlorine-based chemicals are the most common products in use due to the versatility, effectiveness, low cost and retentive power of chlorine (Judd and Black, 2000). However, chlorination has some disadvantages such as formation of undesired disinfection by products (DBPs) by reaction with organic matter (Chu and Nieuwenhuijsen, 2002; Zwiener et al., 2007). Among these, trihalomethanes (THMs), e.g. chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3), are the most abundant (Rook, 1977).

Deleterious effects such as bladder cancer (Hamidin et al., 2008; IARC, 2004; Villanueva et al., 2006), colon cancer (Hamidin et al., 2008), adverse outcomes on respiratory function and asthma (Nickmilder and Bernard, 2007) and reproductive function (Aggazzotti et al., 2004; Nieuwenhuijsen et al., 2002) have been associated to THMs ingestion. Human exposure to THMs as consequence of domestic activities (Gordon et al., 1998, 2006; Miles et al., 2002; Weisel et al., 1999) and swimming pool attendance (Aggazzotti et al., 1995, 1998; Caro and Gallego, 2007, 2008a; Fantuzzi et al., 2001; Lévesque et al., 1994; Villanueva et al., 2007) has been investigated to assess the main intake routes and processes leading to higher increase of these compounds in

body burden. Studies of alveolar air (Caro and Gallego, 2007) and volatile compounds in urine (Caro and Gallego, 2008a; Caro et al., 2007) have been used for this purpose.

In swimming pools, alternative disinfectant treatments such as ozonation (Glauner et al., 2005; Lee et al., 2009; Richardson et al., 1999), electrolysis (Glauner et al., 2005; Landeen et al., 1989; Lee et al., 2009; Richardson et al., 1999) and bromination (Gordon et al., 1997) have been used for elimination of the irritating chlorine effects on swimmers and for reduction of DBP formation (Zwiener et al., 2007). Among these, the use of bromine compounds is becoming increasingly popular. However, HBrO is more reactive than HClO and has strong potential for the formation of THMs containing more bromine than chlorine atoms (Acero et al., 2005) which are generally more cytotoxic and mutagenic (Plewa et al., 2002). The occurrence of dermatitis in users of swimming pools undergoing bromination has been reported (Pardo et al., 2007).

Model waters with elevated organic matter concentrations have been used to study THM formation by oxidation with HClO and HBrO under different agitation conditions (Judd and Jeffrey, 1995). However, the formation and air-water distribution of THMs in swimming pools as well as human intake as consequence of bromination remains to be described. The present study is devoted to compare the concentrations of THMs in air and water of in-door swimming pools using chlorination and bromination for disinfection as well as to assess human exposure as consequence of bathing and swimming. Human THM intake during these activities is evaluated

* Corresponding author. Tel.: +34 934006118; fax: +34 932045904.

E-mail address: joan.grimalt@idaea.csic.es (J.O. Grimalt).

from measurement of exhaled breath using a recently reported method (Lourencetti et al., 2010) that has been adapted for this purpose.

2. Material and methods

2.1. Chemicals

CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3 , 4-bromofluorobenzene, fluorobenzene and Tenax TA (60/80 mesh) were purchased from Supelco, Inc. (Bellefonte, PA, USA). Sodium thiosulfate (analysis grade) was from Panreac (Barcelona, Catalonia, Spain). Deionized water was obtained from Merck (KGaA, Darmstadt, Germany).

2.2. Swimming pools

Two swimming pools from Barcelona, Catalonia, Spain, using chlorination or bromination agents for water disinfection were selected for study. The former (33 m long, 25 m wide, 2.1–2.2 m deep) is located inside a building of 40 m length, 34 width and 10 m height and the latter (20 m long, 10 m wide, 1.8 m deep) is located inside a building of 27 m length, 14 m width, 4 m height. Both swimming pools are situated in the same area of the city and receive tap water from the same supply. Both pools operate in a close loop system by which either chlorine or bromine agents are supplied as disinfectants following a standardized protocol. The bromination process uses 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) which is available under commercial names such as DiHalo®, Halobrome®, Aquabrome® and others. In aqueous solution this compound generates HBrO and HClO , the latter rapidly combines with NaBr (one end product of BCDMH disinfection) and produces more HBrO .

The physical and chemical parameters of the waters in these swimming pools, such as water temperature, pH, free and combined chlorine and total bromine are given in Table 1. Free and combined chlorine and bromine were determined with the N,N-diethyl-p-phenylenediamine method with a portable photometer (DINKO Instruments). Both pools were attended by general population, mainly children during swimming classes and adults. Numbers of individuals attending the pools while sampling were recorded.

2.3. Air sampling

Samples were obtained by pulling air through 0.5 cm diameter and 9 cm long stainless steel tubes containing 0.18 g of Tenax TA (60/80 mesh, Supelco Inc., Bellefonte, PA, USA). After packing, the tubes were conditioned by helium purging and four heating cycles from 60 °C to 325 °C holding this temperature for 30 min. This packing was activated for 10 min at 325 °C before use. The tubes were connected to a constant flow sampling pump (Universal Pump Model 224-PCXR8; 5–5000 mL min^{-1} , SKC Inc., Eighty Four, PA, USA) (EPA Method TO-17) (Woolfenden and McClenny, 1997). An adjustable low flow tube holder dual set at an average flow rate of 7 mL min^{-1} was used to collect indoor air samples during 20 min. Samples were

collected every 20 min during the whole day of human exposure testing. The tubes were situated at distances of 0.60 m from the ground and 1.5 m from the swimming pool edge. The sampling pump was calibrated *in situ* with a Dry-Cal DC-Lite (BIOS, Butler, NJ, USA) prior to sampling and at the end of the sampling day.

2.4. Water sampling

Composite water samples (250 mL) were collected at the four swimming pool corners, resulting in combined samples of 1 L. At least 3 composite samples were collected during each sampling day. After gently mixture, water was transferred to headspace-free 40 mL glass vials with Teflon-faced rubber septa and open-top screw plugs, avoiding bubble formation. The vials contained 3 mg of sodium thiosulfate (Panreac, Catalonia, Spain) for quenching residual chlorine and bromine. All samples were stored at 4 °C until analysis and were analyzed no later than 14 days after sampling as recommended by EPA Method 524.2 (US EPA, 1992).

2.5. Exhaled air

A detailed description of the portable system employed for collection of exhaled air is given elsewhere (Lourencetti et al., 2010). Participants ($n=50$ swimmers, $n=8$ for people bathing in the pools without exercise and $n=10$ standing besides the pool outside the water in the chlorine disinfection pool and $n=12$ for people swimming in the bromine disinfection pool) were requested to provide two exhaled breath samples, one just before exposure, and another within 5 min after exposure for 40 min in the swimming pool. THMs in exhaled breath were concentrated in the same tubes described for air sampling.

2.6. Analyses

THMs in indoor air and exhaled air samples were determined by an Automatic Thermal Desorption System (ATD400, Perkin Elmer, Waltham, MA, USA) coupled to an Autosystem gas chromatograph with electron capture detection (GC-ECD; Perkin Elmer). The sampling tubes were thermally desorbed at 300 °C for 5 min with a flow rate of 50 mL min^{-1} of ultra-pure helium and the target compounds were swept from the tube to a preconcentration cold trap (−25 °C) made of quartz (16 cm length, 0.4 cm i.d. tube and packed with 0.04 g of Tenax TA between two layers of silanized wool). The cold trap was rapidly heated to 300 °C and kept at this temperature for 10 min to transfer the target compounds to the GC-ECD system through a transfer line heated to 225 °C. Flow desorption and the flows of inlet split and outlet split were 50, 210 and 8 mL min^{-1} , respectively. In these conditions about 8% of the sample was transferred to the GC column and detector. Chromatographic separation was performed on a DB-624 capillary column (0.53 mm i.d., 75 m long, 3 μm film thickness; J&W Scientific, Folsom, CA, USA). The initial GC oven temperature was set to 40 °C for 5 min, then ramped at 5 °C min^{-1} to 160 °C held at this temperature for 1 min, and ramped again to the final temperature of 210 °C at 10 °C min^{-1} , where it was held for 5 min. Detector temperature was 290 °C. Helium (8 mL min^{-1}) and nitrogen (34 mL min^{-1}) were used as carrier and make up gasses, respectively.

Water samples were analyzed using a SOLATek 72 Multi-Matrix Vial Autosampler coupled to a Purge-and-Trap Concentrator Tekmar 3100 (Tekmar-Dohrmann, Mason, OH, USA) which automatically dispensed aliquots of water samples and internal standards into a 25 mL purging device. These compounds were purged from water samples with helium at 36.5 mL min^{-1} during 11 min and adsorbed onto a Tenax® silica gel-charcoal trap (Supelco) at room temperature. After desorption at 225 °C for 4 min, the target compounds were transferred directly to a Trace GC coupled to a Voyager MS

Table 1

Physical and chemicals parameters in the studied chlorinated and brominated swimming pools.

Parameters	Cl disinfection Mean $\pm$ SD (range)	Br disinfection Mean $\pm$ SD (range)
pH	7.3 $\pm$ 0.1 (7.02–7.54)	7.2 $\pm$ 0.07 (7.08–7.2)
Water T (°C)	27.3 $\pm$ 0.4 (26.5–28)	27.9 $\pm$ 0.2 (27.8–28.1)
Free chlorine ($\text{mg} \cdot \text{L}^{-1}$)	1.1 $\pm$ 0.3 (0.6–1.8)	–
Combined chlorine ($\text{mg} \cdot \text{L}^{-1}$)	0.38 $\pm$ 0.09 (0.22–0.58)	–
Total bromine ($\text{mg} \cdot \text{L}^{-1}$)	–	1.5 $\pm$ 0.06 (1.4–1.5)

– Not controlled.

(ThermoQuest Finnigan, Waltham, MA, USA) equipped with a DB-624 capillary column (0.53 mm i.d., 75 m long, 3 μ m film thickness; J&W Scientific). The column was held at 35 °C during 4 min, ramped to 150 °C at 4 °C min⁻¹ and then to 210 °C at 11 °C min⁻¹ with a final holding time of 4 min. The injection was operated in splitless mode for 2 min. Helium was used as carrier gas. Its flow was held at 5 mL min⁻¹ during the first minute and then it was decreased to 3.5 mL min⁻¹ in 45 s. The mass spectrometer was operated in EI mode at 70 eV. The ion source and GC interface temperatures were kept at 200 °C and 270 °C, respectively. The emission current was 150 μ A and the detector voltage was set at 400 V. Calibration, standards and samples were injected following the time scheduled selected ion monitoring (SIM) mode reported in (Lourencetti et al., 2010).

Quantification was performed with the internal standard method using fluorobenzene and 4-bromofluorobenzene. Standards of these compounds and THMs were obtained from Supelco (Bellefonte, PA, USA).

2.7. Quality control and quality assurance

Calibration curves were prepared with external standards to determine the THM concentrations in air samples. Seven standard dilutions of a THM mix were prepared between 0.01 and 1 μ g ml⁻¹ in n-pentane. One microliter of this dilution was injected directly onto different Tenax TA tubes. Good linearity was obtained for CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃ with the following correlation coefficients (r^2): 0.999, 0.999, 0.998 and 0.997, respectively.

Calibration curves for water samples were prepared using the internal standards, fluorobenzene and 4-bromofluorobenzene. Nine standard dilution of a THMs mix were prepared between 0.01 and 10 ng ml⁻¹ in water. Good linearity was obtained with $r^2 > 0.999$ for all THMs. When the quantitative response differed more than $\pm 15\%$ from the calibration curve for air or water, a new calibration curve was obtained.

Limits of detection (LOD) and quantification (LOQ) were calculated from blanks by averaging the signal of all blanks plus 3 or 10 times the standard deviation, respectively. In indoor air samples, LOD were 1.7, 0.28, 0.076 and 0.076 ng for CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃, respectively. In water samples they were 0.015, 0.004, 0.005 and 0.011 μ g L⁻¹, respectively.

Sampling pump flow errors were in the order of 5%. The flow errors in the calibrator were 1%. Tenax TA tubes were tested in series to determine breakthrough. Examination of back-up tubes showed no breakthrough for the collected sample volumes.

Analytical precision was calculated from replicate analysis of indoor air and water samples. Air measurements ($n=6$) showed mean relative differences between sample pairs of 3.2%, 5%, 4.8% and 4.9% for CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃, respectively, and the mean relative differences for water measurements ($n=12$) were 4.5%, 3.5%, 3.7% and 1.4%, respectively. Representativeness and reproducibility are described in detail elsewhere (Lourencetti et al., 2010). The coefficients of variation (%) were 4.5–5.6, 3.4–3.7, 2.9–4.5 and 0.98–1.9% for representativeness of CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃, respectively, and 5.4, 3.8, 4.1 and 1.6 for reproducibility, respectively. These values resulted in calculated uncertainties (Caro and Gallego, 2008b) of 9.9%, 6.7%, 7.8% and 2.8% for CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃, respectively.

2.8. Statistical analyses

Statistical analyses were performed using a SPSS (Statistical Package for the Social Sciences) version 14.0. The Shapiro–Wilk Test was used to verify if THM concentrations in indoor air and water samples followed normal distributions. Spearman rank correlation was used to estimate correlations between variables. The Mann–

Whitney test, a non-parametric version of an unpaired samples t -test, was used for comparison between time-series of water concentrations.

3. Results and discussion

3.1. THMs in water

The average THM concentrations in the waters of the chlorinated and brominated swimming pools are shown in Table 2. CHCl₃ is the dominant compound in the former (Fig. 1), as commonly observed in the THM distributions of other pools using chlorination for disinfection (Table 2). In quantitative terms, average total THM concentrations in the chlorinated pool of the present study, 50 μ g L⁻¹, are similar to those observed in other pools (Aggazzotti et al., 1995, 1998; Fantuzzi et al., 2001; Lee et al., 2009) but lower than those observed in other studies (Caro and Gallego, 2007, 2008a). One distinct feature of the chlorinated pool from the present study is the high relative composition of chloro-brominated THMs (Fig. 1). The higher abundance of these compounds reflects the higher proportion of bromide in the supply waters (7 mg L⁻¹; Ventura and Rivera, 1985). THM distributions in tap waters from Barcelona are dominated by CHBrCl₂, 23 μ g L⁻¹, due to the high bromide content in the waters used for chlorination and CHCl₃ is the second major constituent, 20 μ g L⁻¹ (Villanueva et al., 2003). CHBr₂Cl and CHBr₃ are present in similar concentrations, ca 10 μ g L⁻¹ (Villanueva et al., 2003). The formation of brominated THM in the presence of bromide is due to the formation of HBrO by reaction with HClO and to the preferential reaction of this disinfectant vs HClO with organic matter (Nieuwenhuijsen et al., 2002; Noke et al., 1999; Symons et al., 1993). In swimming pool waters, repeated chlorination in closed-loop systems, in which water is not changed but repeatedly disinfected, tend to increase the proportion of the more chlorinated THM due to the lack of bromine renewal compensating for the THM volatilization losses. The whole process results in a CHCl₃ enrichment in comparison to the THM composition of the tap water supply.

Besides the presence of bromide in the supply waters, several other factors can influence the THMs formation in water, such as disinfection processes and chemicals, water source, pH, temperature, concentration of residual chlorine, residence time, reaction time, total or organic carbon and disturbance (Kristensen et al., 2010; Lee et al., 2009; Panyakapo et al., 2008; Thacker and Nitnaware, 2003; Wang et al., 2010). Lee et al. (2009) observed higher values for the brominated THM in a swimming pool in Korea which uses an electrochemically generated mixed oxidants (EGMO) process for water disinfection when compared with others employing chlorine and ozone/chlorine. The results were mainly attributed to the presence of bromide ions from salt used in the EGMO process.

In contrast, the THM composition in the brominated swimming pool waters exhibits a strong CHBr₃ predominance. In this case, repeated closed-loop bromination leads to chlorine exhaustion by THM volatilization and strong CHBr₃ enrichment. The results from this real indoor swimming pool were similar to those observed in a model pool using hypobromous acid as disinfectant and an analogue of human urine as organic loading (Judd and Jeffrey, 1995). CHBr₃ was the principal product using HBrO (CHCl₃ in the case of HClO), and more THMs products were formed employing the bromide-based disinfectant under the same controlled conditions.

3.2. THMs in air

The THM distributions in the in-door air of the two swimming pools show a strong parallelism with the distribution observed in the waters (Table 2). In quantitative terms, average total THM concentrations in the chlorinated pool, 72 μ g m⁻³, are higher than in some other studies, e.g. 58 μ g m⁻³ (Fantuzzi et al., 2001), but lower than in

Table 2Mean and ranges of THM concentrations in water ($\mu\text{g L}^{-1}$) and in-door air ($\mu\text{g m}^{-3}$) in various swimming pools considered in the present and previous studies.

Disinfection	Sample	n	CHCl ₃		CHBrCl ₂		CHBr ₂ Cl		CHBr ₃		Reference
			Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	
Cl	Air	18	213	66–650	nd	–	nd	–	nd	–	Aggazzotti et al. (1995) ^a
	Water	18	33	17–47	–	–	–	–	–	–	
Cl	Air	4	170 $\pm$ 27	140–200	20 $\pm$ 4.1	16–24	11 $\pm$ 2.1	9.0–14	0.2	0.2	Aggazzotti et al. (1998) ^a
	Water	4	34 $\pm$ 9.6	25–43	2.3 $\pm$ 0.6	1.8–2.8	0.8 $\pm$ 0.2	0.5–10	0.1	0.1	
Cl	Air	5	46 $\pm$ 19	–	8.7 $\pm$ 5.1	–	3.1 $\pm$ 2.3	–	0.8	–	Fantuzzi et al. (2001) ^a
	Water	5	33 $\pm$ 25	–	4.2 $\pm$ 1.3	–	1.9 $\pm$ 2.0	–	0.4 $\pm$ 0.5	–	
Cl	Water	24	121	45–212	8.3	2.5–23	2.7	0.67–7	0.9	0.67–2	Chu and Nieuwenhuijsen (2002)
Cl	Air	3	–	85–235	nd	–	nd	–	nd	–	Erdinger et al. (2004) ^a
	Water	3	–	7.0–24.8	nd	–	nd	–	nd	–	
Cl	Air	5	220	92–340	8.0	4.3–12.1	1.0	–	nd	–	Caro and Gallego (2007, 2008a) ^a
	Water	18	120 $\pm$ 7.4	85–155	2.0 $\pm$ 0.14	1.8–2.2	nd	–	nd	–	
Cl	Water	72	40.7	0.2–102	3.0	nd – 10.5	0.5	nd–5.6	nd	nd	Lee et al. (2009)
Cl	Air	82	32 $\pm$ 12	18–61	15 $\pm$ 4.3	8.2–23	14 $\pm$ 4.0	6.4–22	11 $\pm$ 4.3	5.9–22	This study ^a
	Water	70	15 $\pm$ 3.5	8.5–20	14 $\pm$ 4.3	9.4–25	13 $\pm$ 4.5	6.7–23	7.2 $\pm$ 3.2	3.1–16	
Br	Air	10	4.5 $\pm$ 2.5	1.8–6.9	3.0 $\pm$ 1.1	1.9–4.2	7.3 $\pm$ 1.2	6.4–8.7	75 $\pm$ 19	55–92	This study ^a
	Water	9	0.21 $\pm$ 0.11	0.08–0.29	0.41 $\pm$ 0.19	0.23–0.6	2.4 $\pm$ 0.22	2.1–2.6	60 $\pm$ 4.9	52–61	

SD—standard deviation. Cl—chlorination. Br—bromination. nd: non detectable. –: not determined.

^a Samples collected during human exposure studies.

other cases, e.g. 200–230 $\mu\text{g m}^{-3}$ (Aggazzotti et al., 1995, 1998; Caro and Gallego, 2007, 2008a). In our study, CHBr₃ largely dominates in the brominated pool whereas CHCl₃ is the major compound in the air of the chlorinated pool (Fig. 1). The CHCl₃ abundance in the last case is consistent with previous reports from other chlorinated pools (Aggazzotti et al., 1995, 1998; Erdinger et al., 2004; Fantuzzi et al., 2001). Consistently with the THM composition in the waters, the close-loop disinfection system tends to selectively increase either CHCl₃ or CHBr₃ in the chlorinated or brominated swimming pools, respectively. Thus, THMs in air and water exhibit parallel distributions. However, comparison of the air/water THM compositions of the chlorinated pool shows higher relative abundance of CHCl₃ in air which may be explained by the higher vapor pressure of this compound vs. other THM.

On the other hand, the absolute THM air and water concentrations included in the present study are generally similar or lower than those reported in other pools using chlorination for disinfection (Table 2). Conversely, the in-door air and water concentrations of CHBr₃ in the brominated pool are very high in comparison with these previous studies. These high values are due to the strong dominance of this compound in the THM mixture but in terms of total THM concentrations the levels are similar to those reported in other pools (Table 2).

Calculation of the Spearman's rank correlation coefficients of the in-door air and water THM concentrations in each pool shows significant linear correlations at $p < 0.01$ or less (Table 3) involving higher air concentrations at higher water levels. A positive correlation was also found for CHCl₃ in a previous study (Aggazzotti et al., 1995). These linear correlations indicate a direct dependence of the in-door air concentrations from the water concentrations which is consistent with a continued transfer of water borne THM into air.

The observed air and water THM concentrations (Table 2) can also be compared in terms of the Henry constants. Thus, the adimensional form of these constants (H/RT) has been calculated for 27 °C and has been used to estimate the air concentrations in equilibrium with the water concentrations. Comparison of these theoretical air concentrations with the measured values shows observed/theoretical ratios of 0.6–5.6% and 2.9–11% in the pools using chlorination and bromination for disinfection, respectively (Table 3). In both cases the measured air concentrations are significantly lower than those expected from equilibrium with water concentrations. The difference is probably due to the ventilation systems in the buildings containing the pools which are continuously driving the system away from its equilibrium. In these conditions, air–water exchange is kinetically controlled by the mass transfer from the bulk water to the air–water interface, which can be described by the water–air mass transfer

velocity $K_{i,a-w}$ (cm/s). Using the stagnant two-film model, $K_{i,a-w}$ can be calculated from the equation

$$\frac{1}{K_{i,a-w}} = \frac{1}{k_{i,w}} + \frac{1}{k'_{i,a}}$$

where $k_{i,w}$ is the water-phase transfer velocity and $k'_{i,a}$ is the air-phase transfer velocity ($k_{i,a}$) multiplied by the dimensionless Henry law constant corrected by water temperature.

$k_{i,a}$ is determined by using water vapour as the test substance. The mass transfer velocity of water vapour across the air $k_{water,a}$ depends on wind speed u_{10} . For wind speeds < 10 m/s this relation can be taken as approximately linear following the expression $k_{water,a} = 0.2 \cdot u_{10} + 0.3$. Thus, $k_{i,a}$ can be determined from the equation

$$k_{i,a} = k_{water,a} \cdot \left(\frac{D_{i,a}}{D_{water,a}} \right)^{0.67}$$

where $D_{i,a}$ and $D_{water,a}$ are the molecular diffusivities of the THM and water vapour in air, respectively, that can be estimated from the molecular weight following the expression

$$\frac{D_{i,a}}{D_{water,a}} = \left(\frac{PM_i}{PM_{water}} \right)^{-0.5}$$

To calculate the water phase transfer velocity $k_{i,w}$ the Schmidt number of the selected compound, $S_{i,w}$, must be known. This parameter is the ratio between the molecular diffusivity of each compound, $D_{i,w}$, which controls compound transport, and the kinematic viscosity, ν , which is related to turbulence. CO₂ is used as reference substance:

$$k_{i,w} = k_{CO_2,w} \cdot \left(\frac{S_{i,w}}{600} \right)^{-0.5}$$

where $S_{i,w}$ is the Schmidt number of each THM corrected by water temperature and $k_{CO_2,w}$ is the water phase transfer velocity of CO₂ equal to 0.65×10^{-3} at wind speeds < 4.2 m/s, $S_{i,w} = 600$, and 20 °C (Livingstone and Imboden, 1993). To transform this value to other compounds and temperatures we first calculate $D_{i,w}$ and $S_{i,w}$ at 25 °C. $D_{i,w}$ can be estimated from the regression between molar mass and the molecular diffusion coefficient in water (Schwarzenbach et al., 2003).

$D_{i,w} = \frac{2.7 \times 10^{-4}}{PM_i^{0.71}}$ and then $S_{i,w} = \frac{\nu_{water}}{D_{i,w}}$ where $\nu_{water} = 8.93 \times 10^{-3}$ cm²/s at 25 °C.

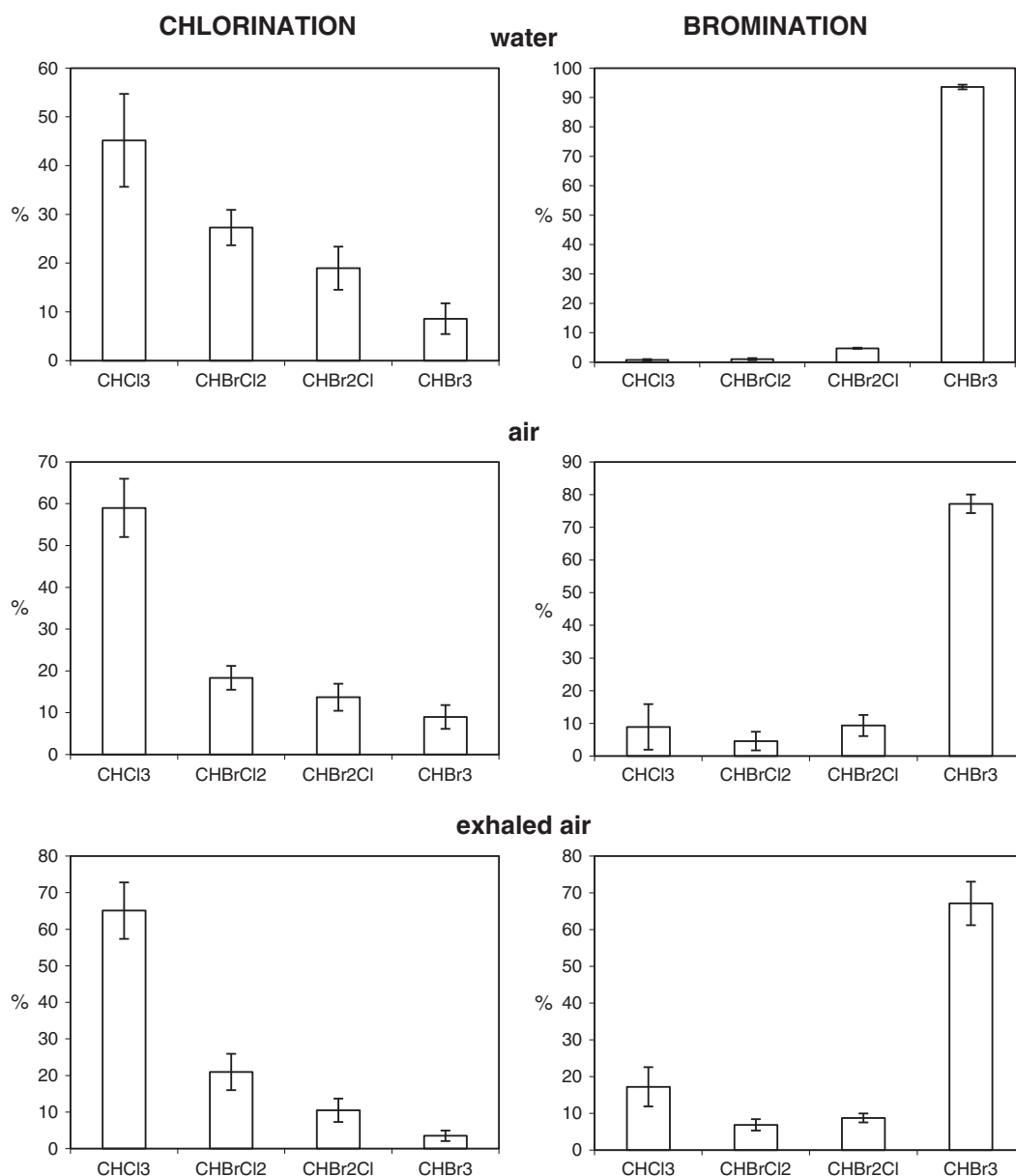


Fig. 1. Histograms representing the average molar THM relative composition in water and in-door air of the swimming pools using Cl and Br for disinfection and exhaled air of volunteers present in the swimming pools. Error bars indicate standard deviation.

Table 3

Comparison of the THM concentrations in in-door air and water in the swimming pools using Cl and Br for disinfection.

Compound	H/RT ^a	Cl disinfection				Br disinfection			
		Air–water correlation ^b (n = 68)		K _{a-w} ^c	M/T ^d %	Air–water correlation ^b (n = 12)		K _{a-w} ^c	M/T ^d %
		r	p			r	p		
CHCl ₃	0.12	0.569	0.000	0.00052 ± 0.00021 ^e	0.9–1.4	0.867	0.000	0.00054 ± 0.00022 ^e	10–11
CHBrCl ₂	0.065	0.326	0.007	0.00046 ± 0.00018 ^e	0.6–0.7	0.930	0.000	0.00048 ± 0.00019 ^e	5–5.9
CHBr ₂ Cl	0.035	0.448	0.000	0.00041 ± 0.00016 ^e	1.9	0.937	0.000	0.00042 ± 0.00017 ^e	6–6.6
CHBr ₃	0.017	0.387	0.001	0.00037 ± 0.00015 ^e	3.8–5.3	0.727	0.007	0.00037 ± 0.00015 ^e	2.9–4.2

n = number of samples. r, determination coefficient of the regression analysis; p, level of significance.

^a Adimensional Henry constants ($R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$, $T = 300 \text{ °K}$; H values at 20 °C are reported in Batterman et al. (2000).

^b Linear correlations between air and water concentrations (r, Spearman's rank correlation coefficients).

^c Overall air–water mass transfer velocity.

^d Air concentration ratios (measured/theoretical in %), theoretical values were calculated from the Henry law using the observed THM water concentration ranges in each pool.

^e The uncertainty ranges were calculated from a sensitivity analysis and the uncertainties in the air and water mass transfer coefficients (Bramford et al., 2002; Hoff et al., 1996).

Finally, $S_{i,w}$ values at 25 °C can be transformed to values at 27 °C using the Stokes–Einstein relation which derives in the expression

$$S_{i,w}(T_2) = S_{i,w}(T_1) \cdot \left(\frac{\nu_{\text{water}}(T_2)}{\nu_{\text{water}}(T_1)} \right)^2 \cdot \frac{T_1}{T_2}$$

More details on these calculations can be found in Batterman et al. (2000), Livingstone and Imboden (1993) and Schwarzenbach et al. (2003).

The calculated water-air mass transfer velocities of these THMs in both pools (Table 3) show distributions that are consistent with the observed respective air compositions (Fig. 2), either as such or after calculation of pool emission flows by multiplication by THM concentrations. The general agreement between these distributions and the linear correlations between in-door air and water THM concentrations support a dependence of the THMs air concentrations from the continued emission generated by the aquatic pool processes. The measured low in-door air concentrations in comparison to the equilibrium values indicate that the pool ventilation systems successfully decreased the air concentrations of these compounds from the pool buildings. Efficient ventilation is useful to decrease people exposure to THM in these installations.

3.3. Exhaled air

THM were measured in exhaled air of volunteer people present in the swimming pool during sampling. Volunteers were requested not to drink tap water and not to shower in the exposure day prior to swimming pool measurements. They were also requested not to swim for one week prior to the experiment. About 15% of the volunteers attend indoor swimming pools at least once per week and approximately 50% of them consume municipal tap water at home. Study participants were requested to swim, to bath in the water

without physical activity or to stand besides the pool outside the water for 40 min in all cases. Exhaled breath was measured before and after this period and the reported results correspond to the THM concentration differences of these two analyses (final–initial time). The observed distributions parallel those found in air and water (Fig. 1). The occurrence of CHCl_3 in alveolar air of swimmers (Aggazzotti et al., 1995; Caro and Gallego, 2008a; Lévesque et al., 1994) and workers (Caro and Gallego, 2008b) has been reported in previous studies on chlorinated swimming pools. In one of these studies, the occurrence of other THMs such as CHBrCl_2 and CHBr_2Cl but not CHBr_3 was also reported in workers. The present study extends this previous knowledge showing that all four THMs, including CHBr_3 , are found in the alveolar air of swimmers from chlorinated swimming pools and that this compound and all the other THMs are also present in swimmers of brominated pools.

These exhaled air THM concentrations in swimmers both the chlorinated and brominated swimming pools show statistically significant linear correlations with the concentrations of these compounds in the indoor air of the facilities (Fig. 3). Correlation coefficients (r^2) between 0.46 and 0.83 are observed when plotting all pooled data from both swimming pools. Representation of the data corresponding to each pool shows r^2 values of 0.31–0.62 and 0.67–0.94 for the chlorinated and brominated pools, respectively (Fig. 3). Accordingly, the THMs found in higher concentration in exhaled breath of swimmers in the chlorinated and brominated pools are CHCl_3 and CHBr_3 , respectively, involving concentration maxima of $8 \mu\text{g m}^{-3}$ in both cases. Both examples show that the measured concentrations in exhaled breath constitute about one eighth of the ambient indoor THM concentrations.

The close correspondence between exhaled air in people present in the pools and ambient air is related to physical activity. Thus, the eight individuals that were requested to only bath in the chlorinated pool without swimming and those which stood besides the pool outside the water had THM concentrations in exhaled air with no correlation to those in ambient air. Furthermore, their THM concentrations in exhaled air were about 3.5 and 7 times lower, respectively, than in the swimmers (Figs. 3 and 4). Erdinger et al. (2004) also found higher CHCl_3 intake in swimmers than in swimmers breathing compressed air and subjects walking around the pool with no contact with the water. The results of our exposure experiments are also consistent with another study in which THM intake was measured by analysis of urine and blood (Cammann and Hubner, 1995). These differences may respond to different causes. Physical activity during swimming may enhance exposure by increasing the pulmonary ventilation and blood pressure and surface capillary perfusion. These aspects are also relevant for dermal absorption since they decrease the transdermal path length for THM diffusion and increase the blood flow under the skin. Additionally, the rate of dermal absorption increases when the skin is fully hydrated and at higher degree of body surface immersion (Brown et al., 1984).

The higher THM concentrations in exhaled breath from people bathing in the pool without physical exercise than in people standing besides the pool outside the water (Fig. 4) are also relevant. These differences involve a factor of about two and suggest that dermal absorption is also an important route for the rapid ingestion of THM in water since bathing individuals may incorporate these compounds by respiration and through skin whereas standing people outside the water only have the inhalation pathway. Higher differences between the exhaled breath THM concentrations of these two groups are found for the compounds with lower degree of bromination (Fig. 4) which may reflect higher skin absorption rates due to their higher molecular diffusivity.

Comparison of the average exhaled air THM distributions in the three groups of volunteers shows a predominance of CHCl_3 in all cases (Fig. 4) which likely reflect the dominance of this compound in air and water of the chlorinated swimming pool. However, there is a

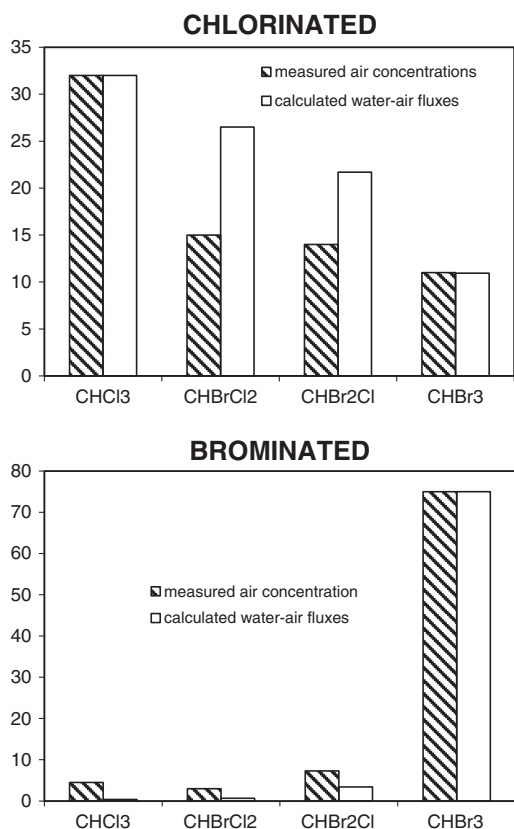


Fig. 2. Measured in-door air concentrations ($\mu\text{g}/\text{m}^3$) and water-to-air fluxes calculated from fugacities $\mu\text{g}/(\text{m}^2 \text{ s})$ in the chlorinated and brominated swimming pools.

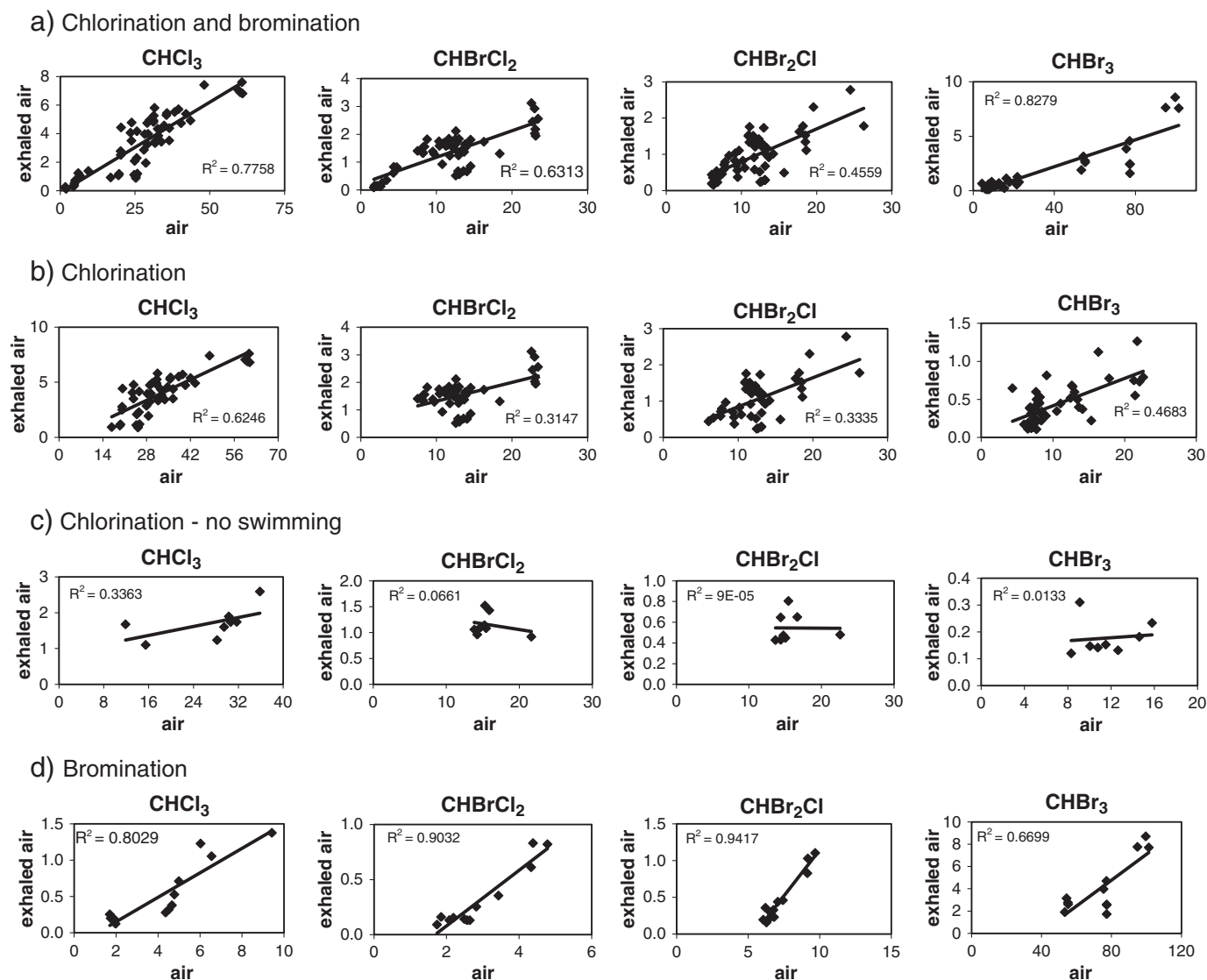


Fig. 3. Representation of the THM concentrations ($\mu\text{g m}^{-3}$) in exhaled air of volunteers vs in-door air in swimming pools: (a) aggregated data of swimmers in pools using Cl and Br for disinfection; (b) swimmers in the chlorinated swimming pool; (c) volunteers bathing in the chlorinated swimming pool without exercise; (d) swimmers in the brominated swimming pool.

higher proportion of CHCl_3 in the swimmers than in the non swimmers, 60 and 50%, respectively (Fig. 4). The difference is balanced by the higher proportion of CHBrCl_2 in non-swimmers (35–37%) than in swimmers (20%). These differences are not consequence of a specific route for CHBrCl_2 intake, e.g. dermal absorption vs inhalation, since the group of non-swimmers also includes those volunteers standing besides the pool outside the water who are exposed to THM only by inhalation. Maybe the difference is related to a lower degree of diffusion of the THM mixtures through all tissues by the non-swimmers, who have incorporated lower amounts of these compounds in the same period than swimmers. It will be more pronounced for CHCl_3 since this one is the THM with highest molecular diffusivity.

4. Conclusions

The THM concentrations in ambient air of the swimming pools reflect the THM distributions in the pool waters which are predominated by CHCl_3 or CHBr_3 according to the use of chlorination or bromination for disinfection. Since these studied pools operate in

close-loop, the system tends to selectively increase either CHCl_3 or CHBr_3 in the chlorinated or brominated swimming pools, respectively.

Comparison of the THMs air and water distributions shows that CHCl_3 has a higher relative proportion in air than in water of the chlorinated pool which can be explained by the higher vapor pressure of this compound vs the other THMs. In the brominated pool, the air THM distribution also shows a relative enrichment in CHCl_3 and the other chlorinated THMs but CHBr_3 largely predominates. In any case, the measured THM air concentrations are about 0.6–5.6% and 2.9–11% of the theoretical equilibrium THM water values in the chlorinated and the brominated pools, respectively. These low rates probably reflect the efficiency of the ventilation systems in the pool buildings.

The THM composition in the exhaled air of the participants strongly correlates with that of the ambient air in the pool building and shows a diverse THM intake pattern according to the disinfection method chosen. The measured concentrations in exhaled breath constitute about one eighth of the ambient indoor concentrations. However, the observed correlations are related to physical activity. Thus, people only staying in the pool without physical activity showed no correlation between their THM concentrations in their exhaled air vs ambient air. Comparison of the two groups of non-

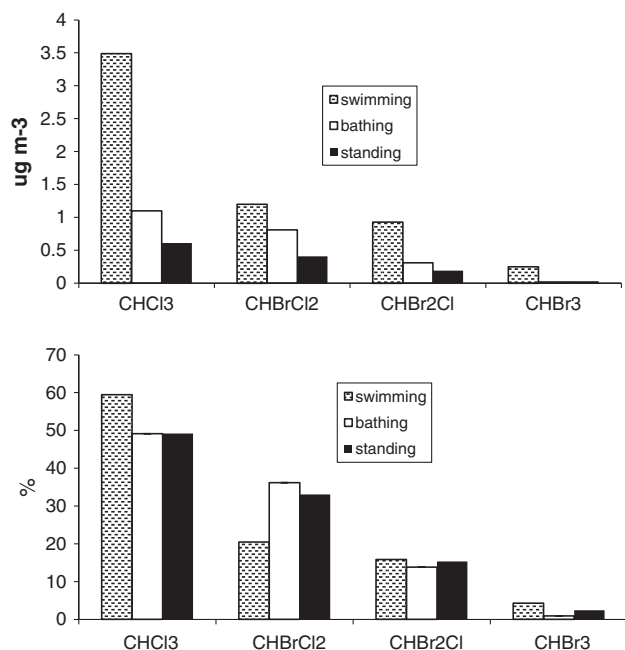


Fig. 4. Absolute (top) and relative (bottom) THM distributions in exhaled air in people swimming, only bathing in the water without exercise and standing besides the pool outside the water in the chlorinated swimming pool.

swimmers shows that dermal absorption is a very relevant route for incorporation of THM (up to about 40% of inhalation). THM with lower degree of bromination are incorporated in higher proportion through this pathway.

Acknowledgements

Financial support to GRACCIE Consolider Ingenio Network (CSD2007-00067) and PISCINA Project (SAF2005-07643-CO3-02) from the Spanish Ministry of Science and Innovation is acknowledged. CL thanks the CSIC-Banco de Santander agreement for a PhD fellowship. This paper was also sponsored by research group 2009SGR1178 from Generalitat de Catalunya.

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