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Influence of physical activity in the intake of trihalomethanes in indoor swimming pools



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ABSTRACT

This study describes the relationship between physical activity and intake of trihalomethanes (THMs), namely chloroform (CHCl₃), bromodichloromethane (CHCl₂Br), dibromochloromethane (CHClBr₂) and bromoform (CHBr₃), in individuals exposed in two indoor swimming pools which used different disinfection agents, chlorine (Cl-SP) and bromine (Br-SP). CHCl₃ and CHBr₃ were the dominant compounds in air and water of the Cl-SP and Br-SP, respectively. Physical exercise was assessed from distance swum and energy expenditure. The changes in exhaled breath concentrations of these compounds were measured from the differences after and before physical activity.

A clear dependence between distance swum or energy expenditure and exhaled breath THM concentrations was observed. The statistically significant relationships involved higher THM concentrations at higher distances swum. However, air concentration was the major factor determining the CHCl₃ and CHCl₂Br intake in swimmers whereas distance swum was the main factor for CHBr₃ intake. These two causes of THM incorporation into swimmers concurrently intensify the concentrations of these compounds into exhaled breath and pointed to inhalation as primary mechanism for THM uptake. Furthermore, the rates of THM incorporation were proportionally higher as higher was the degree of bromination of the THM species. This trend suggested that air–water partition mechanisms in the pulmonary system determined higher retention of the THM compounds with lower Henry's Law volatility constants than those of higher constant values. Inhalation is therefore the primary mechanisms for THM exposure of swimmers in indoor buildings.

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1. Introduction

Swimmers, staff personnel and visitors are exposed to trihalomethanes (THMs), e.g. chloroform (CHCl₃), bromodichloromethane (CHCl₂Br), dibromochloromethane (CHClBr₂) and bromoform (CHBr₃), in indoor swimming pools (Aggazzotti et al., 1990, 1993, 1995, 1998; Erdinger et al., 2004; Font-Ribera et al., 2010; Kozłowska et al., 2006; Lévesque et al., 1994, 2000; Lindstrom et al., 1997; Lourencetti et al., 2012). They are formed by water chlorination/bromination and reaction with organic matter (Rook, 1974). In addition to these compounds other disinfection by-products have been identified in indoor swimming pool waters (Richardson et al., 2010) but THMs are the most studied. Long term exposure to these compounds is associated with bladder cancer risk increase (Hamidin et al., 2008; Villanueva et al., 2007, 2015).

* Corresponding author. Fax: + 34 932045904. *E-mail address:* joan.grimat@idaea.csic.es (J.O. Grimalt). In a previous study we showed that there are important differences in THM uptake between people swimming, simply bathing (no physical activity) or standing (outside the water) in indoor swimming pools (Lourencetti et al., 2012). In all cases, THM intake was measured from the exhaled breath concentrations. The end-exhaled (alveolar) air gives representative estimates of the concentration of the organic constituents in blood due to the gas exchange in the blood/breath interface of the lungs (Pleil and Lindstrom, 1997). The differences observed between these three groups of swimming pool users were consistent with previous studies showing that besides ingestion, inhalation and dermal absorption may also be significant THM uptake pathways (Backer et al., 2000; Xu and Weisel, 2005; Gordon et al., 2006).

In the present study, we investigate whether the physical activity developed in the pools can be related to THM intake. This is an important aspect for improving the understanding of the processes of THM incorporation in swimmers and for assessment of the possible deleterious effects of THM exposure in these sport practitioners. CHCl₃ is usually the dominant compound in swimming pools using chlorination. Studies involving THM analysis of exhaled breath-alveolar air, blood or urine in these pools often observe the concentrations of CHCl₂Br, CHClBr₂ or CHBr₃ below limit of quantification (Aggazzotti et al., 1998; Fantuzzi et al., 2001; Caro and Gallego, 2008; Cammann and Hubner, 1995). However, the more brominated THMs are important since they are those showing higher cytotoxic and mutagenic potential (Plewa et al., 2002; Kogevinas et al., 2010) or those involving higher deleterious effects in the respiratory system upon swimming (Font-Ribera et al., 2010).

In the present study, we are using a previously developed method for THM analysis in exhaled breath-alveolar air (Lourencetti et al., 2010) that provides low detection limits. Furthermore, two swimming pools using different systems, chlorination and bromination (Gordon et al., 1997) have been chosen for study. With this approach, the exposure of swimmers to all THM species has been assessed and the relationship between intake of these compounds and extent of physical exercise has been investigated.

2. Materials and methods

2.1. Study design

The two indoor swimming pools selected for study were located in Barcelona, in the same area of the city and received tap water from the same supply. Different disinfections agents, chlorine (chlorinated swimming pool, Cl-SP) and bromine (brominated swimming pool, Br-SP) were used. The bromination process uses 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), that is available under the commercial names DiHalo[®], Halobrome[®] and others. In aqueous solution this compound generates HOBr and HOCl, and the latter rapidly combines with NaBr (one end product of BCDMH disinfection) to produce more HOBr (Judd and Jeffrey, 1995). The sizes of the Cl-SP and Br-SP were 33 m × 25 m × 2 m and 20.9 m × 13.5 m × 1.3 m, respectively. The floor ceiling heights in the two buildings were 10 m and 5 m, respectively.

All participants (*n*=47) were not professional swimmers, nonsmokers and within an age range of 23–51, average 31 years. The characteristics of the population including these participants have been described elsewhere (Kogevinas et al., 2010). The influence of physical activity was investigated comparing the THM concentrations in exhaled breath of all subjects. Thirty-nine of them swam during 40 min at their capacity (32 in the Cl-SP and 7 in the Br-SP). In the Cl-SP, 8 subjects were asked to bathe during 40 min without physical activity. Distance of swimming, and number of laps were self-reported for each individual in both pools. The exposure time, 40 min, was selected based on an estimative of the usual swimming time of non-competitive swimmers.

THM intake was assessed from the difference between exhaled breath concentrations after and before swimming or bathing. A portable system collecting the end-exhaled breath (Lourencetti et al., 2010) was employed for this purpose. THM concentrations in swimming pool water and indoor air were monitored during all exposure experiments.

2.2. Sampling

Water, indoor air and exhaled breath samples were collected following the protocol described elsewhere (Lourencetti et al., 2010). Briefly, composite water samples (250 mL) were collected at the four swimming pool corners, and combined in 1 L samples. At least 3 composite samples were collected during each swimming day. After gently mixing, 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 for quenching residual chlorine and bromine. All samples were stored at 4 °C until analysis which was performed no later than 14 days after sampling as recommended by EPA Method 524.2 (US EPA, 1986).

Indoor air samples were obtained by pulling air through 0.5 cm diameter and 9 cm long stainless steel tubes containing 0.18 g of Tenax[®]. 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; Woolfenden and McClenny, 1997). An adjustable low flow tube holder dual set was used to collect indoor air samples during 20 min at an average flow rate of 7 mL min⁻¹. 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.

THMs in exhaled breath were concentrated in the same tubes described for air sampling using the portable system described by Lourencetti et al. (2010). Participants were requested to provide two exhaled breath samples (1 L each sample), one just before swimming or bathing, and another within 5 min after these activities.

2.3. Chemicals

THMs standards and internal standards for water analysis, 4-bromofluorobenzene and fluorobenzene and Tenax[®] (60/80 mesh) were purchased from Supelco, Inc. (Bellefonte, PA, USA). Sodium thiosulfate (analysis grade) was from Panreac (Barcelona, Catalonia, Spain), while deionized water was obtained from Merck (KGaA, Darmstadt, Germany).

2.4. THM analysis

THMs in indoor air and exhaled air samples were determined by an Automatic Thermal Desorption System (ATD400, PerkinElmer, Waltham, MA, USA) coupled to an Autosystem gas chromatograph with electron capture detection (GC-ECD; PerkinElmer). 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 inlet and outlet split flows were 50, 210 and 8 mL min⁻¹, respectively. In these conditions about 10% 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, were it was held for 5 min. Detector temperature was 290 °C. Helium (8 mL min⁻¹) and nitrogen $(34 \text{ mL} \text{min}^{-1})$ were used as carrier and make up gases, respectively. Good correlation coefficients (r > 0.997) were obtained employing calibration curves with external standards $(0.01-1 \ \mu g \ mL^{-1})$ for all compounds.

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