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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 halides (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 was 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.

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## 1. 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., 2014; Hansen et al., 2012a,b; 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). A significant increase in the mutagenicity of swimmers' urine was detected after swimming (Kogevinas et al., 2010). Exposure to DBPs in swimming pools may take place via dermal absorption, inhalation, and ingestion (Zwiener et al., 2007). 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., 2007). The occurrence of DBPs in swimming pools has

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been investigated in numerous studies (Chowdhury et al., 2014). Among DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) have been studied extensively in swimming pools around the world (Aggazzotti and Predieri, 1986; Aggazzotti et al., 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 (Manasfi et al., 2017b). 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., 2012a,b; 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 Chainieux, 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., 2017a; Plewa et al., 2010; Richardson et al., 2007; Yang et al., 2014). Kogevinas et al. (2010) found that the change in the frequency of micronucleated lymphocytes after swimming increased in association with higher concentrations of the brominated THMs in the breath of swimmers. In this latter study, authors also showed that urine mutagenicity increased significantly after swimming, in association with the higher concentration of exhaled bromoform. 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 total organic halides 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. Determining the occurrence of DBPs in water and air of seawater pools generates data that is helpful for risk assessment studies. The study also aimed at determining the extractable organic halides (EOX) contents in the pools and evaluating the contribution of the traditionally measured and some emerging DBP chemical classes to the EOX concentrations. EOX is one of the parameters that evaluate the overall contents of halogenated organic compounds in water (Wegman and Greve, 1977). By determining the fraction of EOX accounted for by the main chemical classes of known DBPs, the fraction of EOX representing unknown DBPs could be estimated. Since there are complex mixtures of organic compounds that react

with chlorine in swimming pools quantifying only specific families of DBPs such as THMs and HAAs does not necessarily reflect the occurrence levels of other compounds that could occur at higher concentrations and possess higher toxicities (Lakind et al., 2010). Thus, it is important to assess the overall organic halides content and determine the contribution of the chemical classes known to occur in pools to the overall organic halides content.

## 2. Materials and methods

### 2.1. Study site and sample collection

Three indoor swimming pools located in wellbeing and touristic resorts in Southern France were included in the study. All the pools were filled using seawater and treated with chlorine. In all the pools, seawater was obtained from the Mediterranean. A detailed description of the studied pools including pool area, depth, volume, filtration type, and mean daily frequentation is presented in Table S1 (Supplementary information). 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 ( $\text{Br}^-$ ) 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-L 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.

### 2.2. 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). Sodium sulfate (ACS reagent), 2,4,6-tribromophenol (99%), and tribromoacetaldehyde (97%) were purchased from Sigma-Aldrich. Tribromoacetaldehyde was used to generate its hydrated form, bromal hydrate (BH), in ultrapure water (Millipore, resistivity >18 M $\Omega$  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).

### 2.3. 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 ascorbic acid, which was also used as a quenching agent. Samples were then extracted by liquid–liquid extraction (LLE) by adding MTBE (5 mL) and shaking manually during 2 min. Sodium sulfate (10 g) was added to enhance separation of the two liquid phases. 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

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