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Monitoring and factors affecting levels of airborne and water bromoform in chlorinated seawater swimming pools

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ABSTRACT

Water and air quality of eight seawater swimming pools using chlorine disinfection was measured during four sampling campaigns, spread on one full-year, and in four thalassotherapy centers located in Southeast of France. Concentrations of trihalomethanes (THMs) in air and in water as well as concentrations of parameters, including nonpurgeable organic carbon (NPOC), free residual chlorine (Cl_f), pH, Kjeldhal Nitrogen (KN), salinity, conductivity, bromide ions and, water and air temperature, were measured. Water and air samples were collected in triplicates morning — at the opening of the pools —, noon and night — at the closing of the pools —, in summer and winter. Data analysis was performed by Principal Component Analysis (PCA) and rotated component matrix, from both data quality and other parameters such as TOC, aromaticity (UV_{254}), pH, hygrometry, and free residual chlorine (Cl_f). This statistical analysis demonstrates a high correlation between TOC, Cl_f and UV_{254} and THM levels found in air and water, particularly for the major ones ($CHBr_3$ in water: 300.0 μg/L mean, 1029.0 μg/L maximum; $CHBr_3$ in air: 266.1 μg/m^3 mean, 1600.0 μg/m^3 maximum, and $CHClBr_2$ in water: 18.9 μg/L mean, 81.0 μg/L maximum; $CHClBr_2$ in air: 13.6 μg/m^3 mean, 150.0 μg/m^3 maximum). These high levels of bromoform ($CHBr_3$) are particularly worrisome in such health institutions, even these levels do not exceed the Permissible Exposure Limit (PEL) of 5 mg/m^3 as an 8 hour time-weighted average currently fixed by various administrations, such as Occupational Safety and Health Administration (OSHA).

Introduction

Thalassotherapy (term coined by the French doctor de la Bonnardière in 1869) has begun establishing health therapy centers for early 1920s, at first in France and then in Great Britain and Germany (Schwartz, 2005). This practice has been defined by the French Medical Academy in 1960 as being *the use of seawater, seaweed, sea mud or other sea resources and/or the marine climate for the purpose of medical treatment with a medicinal effect* (Crecente et al., 2012). Till 1998, thalassotherapy was covered by French medical insurance as a standard treatment for sore throats, digestive problems, rheumatic arthritis, musculoskeletal injury, development disorders in children, respiratory problems (asthma and bronchitis), endocrine imbalances and skin diseases (*e.g.*, psoriasis) (Roullier, 1991; Shani et al., 1995; Charlier and Chaineux, 2009). The decision

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to stop reimbursing these cures was not linked to the questioning of the healing properties of this practice, but rather because it has turned into tourism and leisure activities at the end of 1990s. Thalassotherapy is indeed now included in health or spa tourism, which already represents a $156 billion global industry but is still an emerging and rapidly growing sector (Johnston et al., 2011; Cockerell, 1996). Furthermore, health or spa tourism is currently one of the tourism products with the highest rates of growth (Farnos, 2003).

Whereas some researchers question the healing properties of seawater cures (Robiner, 1990; Lotti and Ghersetich, 1996; Tsuchiya et al., 2003a, 2003b; Boulet, 2006), another area of concern is about the impact of chemical treatment on the physical–chemical content of seawater. Indeed, supposed healthy benefits of seawater are partially connected to their mineral salt contents that are believed to be absorbed through the skin during immersion of users (Kazandjieva et al., 2008; Moss, 2010). However, as there is no specific legislation concerning pools and other medical therapy equipment relating to hygiene and security rules, in France and in most of European countries, the thalassotherapy pools use the public swimming pool legislation (Chapuis et al., 2004; ANSES, 2013). This lack of specific legislation on seawater swimming pools thus implies the use of chlorine-based compounds (in France, only these compounds are authorized as chemical disinfectants since November 2011) to prevent outbreak diseases caused by feces-associated microbes, such as viruses and bacteria (WHO, 2006; Papadopoulou et al., 2008; Schets et al., 2011). Users represent not only a major source of micro-organisms but also inputs of organic compounds (human body fluids coming from urine, sweat, hair, mucus, skin and/or personal-care products) (Seredyńska-Sobecka et al., 2011; Weng and Blatchley, 2011; Keuten et al., 2012; Duirk et al., 2013; Santos et al., 2012). The combination of a residual disinfectant need (residual of free chlorine higher or equal to 2 mg/L Cl_2 in France) with continuous inputs of organic compounds from users leads to the formation of disinfection by-products (Judd and Bullock, 2003; Weaver et al., 2009; Kanan and Karanfil, 2011; Manasfi et al., 2017a).

Adding of chlorine in rich-bromide waters leads to the rapid oxidation of bromide ions (Br^-) into hypobromous acid (HOBr), that is readily more reactive with organic matter than hypochlorous acid (HClO) (Kampioti and Stephanou, 2002; Fabbricino and Korshin, 2009; Tian et al., 2013). The occurrence of brominated compounds in seawater swimming pools is poorly documented whereas the toxicity of brominated compounds is known to be greater than their chlorinated analogs (Erdinger et al., 2004; Richardson et al., 2007; Kogevinas et al., 2010; Plewa et al., 2010). In a previous paper (Parinet et al., 2012), occurrence of brominated compounds was investigated in water of seawater swimming pools: bromoform ($CHBr_3$) was the most abundant trihalomethane (THM) compound found with levels ranging from 28.7 to 930.7 mg/L (272.1 mg/L median) followed by dibromochloromethane ($CHCl_2Br$) with a median level of 14.85 mg/L (63.58 mg/L maximum). Bromoform has been classified as a group B2 (probable human carcinogen) by US-EPA (ATSDR, 1990). Because bromoform can be absorbed into the body through the skin but also by inhalation (Beech et al., 1980; Xu et al., 2002), it seems thus important to determine the exposure levels of seawater pools' users to bromoform (and to the other THM) not only in water but also in air. This study thus has been carried out to determine the THM-4 (Total THM, TTHM) levels of exposure in air and water of four thalassotherapy centers located in Southeast of France during four sampling campaigns, spread on two days in summer and two days in winter.

1. Materials and methods

1.1. Thalassotherapy centers

Four seawater establishments (called after E1, E2, E3 and E4) from Southeast of France, using chlorination agents (bleach or dichloroisocyanuric acid) for water disinfection were selected for this study. E1 and E2 possess 2 pools (E1.A, E1.B and E2.A and E2.B); E3 possesses only one pool (E3.A) and E4 possesses 3 pools (E3.A, E3.B and E3.C). Pools E1.A, E2A, E4.A and E4.B are used only for relaxing or swimming activities (notice that E4.A is not connected to other basins — E4.B and E4.C — in this establishment and is not heated), whereas E1.B, E2.B and E4.C are used only for sport activities. E3.A is used equally for relaxing or sport activities. Globally, water temperature of pools devoted to swimming or relaxing are lower (29–32°C) than those used for sport activities (33–34°C). These temperatures are preset and kept constant, whatever the season, in the range measured. All the swimming pools are disinfected continuously by bleach except E4.A and E4.C, which are disinfected once a week by dichloroisocyanuric acid. The hydraulic characteristics and mean daily frequentation of the whole pools are presented in the Supplementary section (Appendix A Table S1).

These indoor-swimming pools received seawater from the Mediterranean Sea. Physical–chemical and chemical quality of raw seawaters feeding these pools are reported in the Supplementary section (Appendix A Table S2).

Physico-chemical parameters (conductivity, pH, turbidity, water and air temperature, hygrometry, total residual chlorine) were recorded on-site at the time of sampling. Total residual chlorine was measured (Urbansky et al., 2000) and the other physico-chemical parameters were determined with specific electrodes. Free and combined bromines were determined by the *N*-*N*-diethyl-p-phenylenediamine (DPD) colorimetric method (Lourencetti et al., 2012). Bromide and chloride were measured with an ICS-3000 Dionex ion chromatography system using a 30 mM NaOH eluent at 1.5 mL/min and 30°C.

Water and air were sampled in triplicate at the opening and, at the closing of the basins, during two consecutive days in winter (February 2016) and two consecutive days in summer (August 2016), to study the potential influences of basin frequentation (higher frequentation leading to higher organic load in the pools), and of potential supplementary organic inputs from bathers in summer (*e.g.*, sweat, sunscreens). Indeed, as observed during previous campaigns, thalassotherapy user behavior pattern in summer, alternatively consists in self-tanning outside the pools and in cooling himself down inside the pools, thus bringing in the pools a cocktail of organic compounds ready to react with HOBr (Manasfi et al., 2016, 2017b). Moreover, people who attend thalassotherapy centers to be older in winter ("curist" period) than in summer ("non-curist" period, including mainly families accompanied with children).

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