Environmental Research 148 (2016) 411–420

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Assessment of air and water contamination by disinfection by-products at 41 indoor swimming pools

Robert Tardif [a,*], Cyril Catto [a], Sami Haddad [a], Sabrina Simard [b], Manuel Rodriguez [b]

[a] Department of Environmental and Occupational Health, School of Public Health, Université de Montréal, Canada
[b] Research Chair on Drinking Water, Université Laval, Québec City, Canada

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
7 April 2016
Accepted 9 April 2016
Available online 28 April 2016

Keywords:
Disinfection
By-products
Swimming pools
Chlorine
Trihalomethanes
Haloacetic acids
Chloramines

ABSTRACT

This study was aimed at assessing the profiles (occurrence and speciation) of disinfection by-product (DBP) contamination in air and water of a group of 41 public indoor swimming pools in Québec (Canada). The contaminants measured in the water included the traditional DBPs [i.e., four trihalomethanes (THMs), six haloacetic acids (HAAs)] but also several emergent DBPs [i.e., halonitriles, halonitromethanes, haloketones and nitrosodimethylamine (NDMA)]. Those measured in the air comprised THMs and chloramines (CAMs). Overall, extremely variable DBP levels were found from one pool to another (both quantitatively and in terms of speciation). For instance, in water, among the four THMs, chloroform was usually the most abundant compound (37.9 ± 25.7 μg/L). Nevertheless, the sum of the three other brominated THMs represented more than 25% of total THMs at almost half the facilities visited (19 cases). In 13 of them, the levels of brominated THMs (66 ± 24.2 μg/L) even greatly outweighed the levels of chloroform (15.2 ± 6.31 μg/L). Much higher levels of HAAs (294.8 ± 157.6 μg/L) were observed, with a consistent preponderance of brominated HAAs in the swimming pools with more brominated THMs. NDMA levels which were measured in a subset of 8 pools ranged between 2.8 ng/L and 105 ng/L. With respect to air, chloroform was still the most abundant THM globally (119.4 ± 74.2 μg/m^3) but significant levels of brominated THMs were also observed in various cases, particularly in the previously evoked group of 13 swimming pools with preponderant levels of brominated THMs in water. CAM levels (0.23 ± 0.15 mg/m^3) varied highly, ranging from not detected to 0.56 mg/m^3. Overall, the levels were generally relatively high compared to current guidelines or reference values from several countries, and they point to a relatively atypical presence of brominated compounds, and to significant levels of emergent DBPs for which health risk is less documented.

1. Introduction

Exposure to disinfection by-products (DBPs) through chlorination swimming pool waters raises questions about the safety for health of both users and employees, given the suspected harmful effects of these contaminants. The international scientific community is mobilizing around this topic which has been the subject of recent reviews and reports (Jacobs et al., 2007; Teo et al., 2015; Chowdhury et al., 2014; Silva et al., 2012; ANSES, 2010, 2013; Zwiener et al., 2007). Interest has not waned over the past five years, especially regarding the suspected impacts on respiratory health (e.g., asthma) and mutagenic and genotoxic potentials of DBPs (Bougault et al., 2009; Cantor et al., 2010; Fernandez-Luna et al., 2011; Font-Ribera et al., 2010; Kogevinas et al., 2010; LaKind et al., 2010; Liviac et al., 2010; Parrat et al., 2012; Richardson et al., 2014; Weisel et al., 2009). In Europe, the subject, which has been dealt with since the 1980s, is the focus of an increasing number of studies (Silva et al., 2012; Bessonneau et al., 2011; Aggazzotti et al., 1990; Aggazzotti et al., 1993; Aggazzotti et al., 1995, 1998; Fantuzzi et al., 2001). Only few studies documented the matter of exposure to DBPs at swimming pools in Québec (Lévesque et al., 1994, 2000).

Usually, three classes of "traditional" compounds are identified: Trihalomethanes (THMs), including chloroform (TCM), dichlorobromomethane (DCBM), chlorodibromomethane (CDBM), and bromoform (TBM); haloacetic acids (HAAs), including, in particular, monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), and dibromoacetic acid (DBAA); and chloramines (CAMs), which include monochloramine (MCAM), dichloramine (DCAM) and trichloramine (TCAM). THMs, which are very volatile compounds, can disperse in the air, while HAAs are mainly concentrated in the water. In the CAM group, we

* Correspondence to: DSEST, School of Public Health, University of Montreal, P.O. Box 6128 Branch A, Montreal, Canada H3C 3J7.
E-mail address: Robert.Tardif@umontreal.ca (R. Tardif).

http://dx.doi.org/10.1016/j.envres.2016.04.011
0013-9351/

find mainly MCAM in water and TCAM in the air.

In addition, "traditional" DBPs have to be distinguished with other compounds referred to as "emerging" DBPs (eDBPs), which have been discovered more recently through advances made in analytical procedures (Mercier Shanks et al., 2013; Richardson et al., 2007; Richardson et al., 2014; Weaver et al., 2009; Zwiener et al., 2007). In the long list of these eDBPs, we find, in particular: haloacetonitriles (HANs), including trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN) and bromochloroacetonitrile (BCAN); halonitromethanes (HNMs), including chloropicrin (CPK) or trichloronitromethane, as well as the haloketones (HKs), including 1,1-Dichloro-2-propanone (11DCPone) or 1,1,1-trichloro-2-propanone (111TCPone); and, finally, *N*-nitrosodimethylamine (NDMA).

The concentrations (annual means) of THMs and HAAs measured during a period of one year in 15 indoor swimming pool waters in Québec City were shown to fluctuate between 18 and 217 μg/L and between 34 and 1536 μg/L, respectively. In the same study, on another sample of 39 outdoor swimming pools, the concentrations could exceed 300 μg/L for THMs and 2100 μg/L for HAAs (Simard et al., 2013). Following this work, a new study was set up at two indoor swimming pools to analyze the levels of DBPs in both the water and the air, and the associated short-term variations (hourly and daily) (Catto et al., 2012b). However these investigations only were restricted to "traditional" DBPs.

In this context, the objective of this study was to assess the profile of environmental contamination by both traditional and emergent DBPs of a large group of indoor public swimming pools. This assessment is based on spot field sampling campaigns where DBPs were measured simultaneously in the air and the water.

2. Methodology

The study is based on an intensive sampling program that measured the environmental levels of various DBPs in forty-one swimming pools and on the analysis of the extensive database that resulted. The program was designed to put the differences and variations observed into perspective and draw up as representative and as complete a portrait as possible of the DBP contamination in swimming pool water and air in the province of Québec (Canada), in terms of occurrence and speciation of the compounds under study.

2.1. Selection of swimming pools

Indoor swimming pools of Montréal city were invited to participate in the study on a voluntary basis. A similar invitation was also addressed to all of the indoor public pools of Québec City, as well as to two university swimming pools. We eventually selected n=41 swimming pools and stopped the recruitment for logistical constraints.

2.2. Parameters measured

2.2.1. Water and air DBPs

The contaminants measured in the water included all the traditional and emergent DBPs previously mentioned, i.e., TCM, DCBM, CDBM and TBM among THMs; MCAA, MBAA, DCAA, TCAA, BCAA, and DBAA among HAAs; TCAN, DCAN, BCAN and DBAN among HANs; CPK among HNMs; and, 11DCPone and 111TCPone among HKs. The levels of the four THMs and CAMs were also measured in the air.

2.2.2. Physiochemical parameters

In addition, the following physicochemical parameters were measured in the water: conductivity, turbidity, UV 254 nm absorbance and dissolved organic carbon (the two latter, indicators of the presence of organic matter, precursors of DBPs), as well as pH, temperature and, of course, free residual chlorine, total residual chlorine and monochloramine (MCAM).

2.2.3. Other information

The number of bathers were counted during the visit by the staff responsible for sampling. A questionnaire (see Appendix C in Tardif et al. (2015)) was submitted online afterward to each of the participating facilities to collect information about the age of the pool, its bather load and capacity, the practices/recommendations issued to bathers with respect to hygiene, the configuration of the site and the swimming pool basin, the ventilation conditions and the treatment devices used.

2.3. Sampling plan

Participating swimming pools were visited either during October and November 2012. Each visit lasted approximately two and a half to three hours. The visits took place during the week days, with the objective of covering at least one hour of activities in the pool (free swims or classes), to ensure that there was a minimum bather load and subsequently that the water was being agitated enough to produce a usual diffusion of the volatile contaminants into the air.

Water samples were taken at the beginning and again at the end of the visit to measure traditional DBPs (i.e., THMs, HAAs), in addition to MCAM, free residual chlorine, total residual chlorine and pH. The water temperature was also recorded. For eDBPs and physicochemical parameters other than those cited previously, a single sample was taken in the middle of the visit. Water samples were taken at a depth of 30 cm, generally at the foot of the most centrally located lifeguard chair beside the pool.

Air measurements were carried out by collecting samples continuously for 95 minutes (for THMs) and 120 minutes (for CAMs) during the visit. The pumps were systematically positioned at the height of the most centrally located lifeguard chair to capture the air in the respiratory zone of a person standing at the edge of the swimming pool (approximately 150 cm above the water's surface). For THMs, a pump was installed at the foot of the same chair to capture the air at approximately 30 cm above the water's surface. For CAMs, another pump set at a low position was used, but only in one-third of the swimming pools investigated, depending on the availability of the pumps.

2.4. Measurements in water

2.4.1. Analysis of THMs

To measure the levels of THMs in water, samples were collected in 40 mL borosilicate vials. Ammonium chloride (NH_4Cl) had previously been added to the vials [166 μL of NH_4Cl (30 g/L)] to neutralize the free chlorine and to block the formation of the compounds under study. The samples were kept refrigerated at 4 °C. For the analysis, an aliquot of 0.8 mL was taken and transferred into a 2 mL chromatography micro-vial. A volume of 20 μL of the internal standard (EPA fortification solution, cat. no. 47,358-U) at a concentration of 0.8 μg/mL, containing a mixture of fluorobenzene, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4, was added to the samples. The compounds were extracted from the water using solid-phase microextraction (SPME), which consists of adsorption of THMs with an extraction fibre as a solid support (PDMS 100 μm Supelco, cat. no. 57,341 – U), in headspace mode using an automatic autosampler (CTC-Combipal) and analyzed with an ion trap mass spectrometry. The method detection limits (MDL) for TCM, DCBM, CDBM and TBM are 1.1 μg/L, 0.6 μg/L,