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Occurrence and health risk assessment of halogenated disinfection byproducts in indoor swimming pool water

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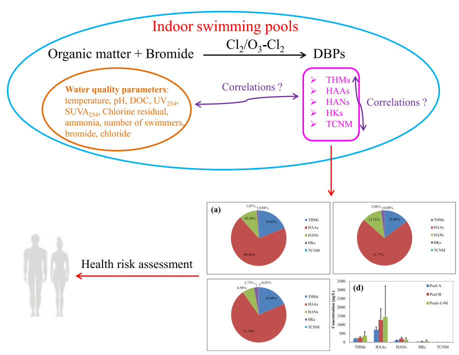
HIGHLIGHTS

- The concentrations of several categories of DBPs in indoor pools were determined.
- The correlations between DBPs and water quality parameters were evaluated.
- The correlations between different DBP categories were evaluated.
- The health risks of the DBPs to human were examined.

GRAPHICAL ABSTRACT



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ABSTRACT

Swimming pool disinfection byproducts (DBPs) have become a concern in many countries all over the world. In this study, the concentrations of several categories of DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs) and trichloronitromethane (TCNM), in 13 public indoor swimming pools in Nanjing, China were determined, the correlations between DBPs and water quality parameters as well as between different DBP categories were evaluated, and the health risks of the DBPs to human were examined. The results indicate that the DBP levels in the swimming pools in Nanjing were relatively high, with HAAs as the most dominant category, followed by THMs, HANs, HKs and TCNM sequentially. Bromochloroacetic acid (BCAA), trichloromethane (TCM), dichloroacetonitrile (DCAN), and 1,1,1-trichloropropanone (1,1,1-TCP) were the most dominant species among HAAs, THMs, HANs, and HKs, respectively. For all the different categories of DBPs, the concentrations in the pool disinfected with ozonation/chlorination were lower than those in the pool disinfected with chlorination. The DBP levels were generally not affected by the number of swimmers and the DBP levels on different dates were relatively stable. Besides, the chlorine residual seemed to be a critical concern in most of the swimming pools in this study. Moreover, there were some correlations between DBPs and water quality parameters as well as between different DBP categories. It is to be noted that the predicted cancer and health risks of the DBPs in these swimming pools were generally higher than the regulatory limits by USEPA, and thus DBPs in these swimming pools should be concerned.

1. Introduction

Swimming is beneficial for human health and has some advantages over other activities for people of all ages and physical conditions, and

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thus it has become a widely enjoyed sport for leisure as well as exercise all over the world. Swimming pools can be found in public areas, hotels, spas and private homes, mainly including indoor and outdoor swimming pools. To inactivate microbial pathogens and prevent waterborne diseases in swimming pools, swimming pool water is subjected to disinfection with various disinfectants, such as chlorine, chloramine, chlorine dioxide, and ozone, while chlorine is most commonly used (Chowdhury et al., 2014). However, while disinfection effectively prevents the infection by microbes in swimming pools, it also leads to the formation of disinfection byproducts (DBPs) due to the unintended reactions between disinfectants, bromide/iodide ions, and natural organic matter (NOM) as well as human inputs (e.g., constituents of sweat and urine, skin particles, hair, and personal care products) in swimming pools (Weisel et al., 2009).

DBPs were first reported in drinking water (Rook, 1974), and later a large number of studies have been carried out to investigate drinking water DBPs, including their occurrence and toxicity (Richardson et al., 2007). Up to now, more than 600 DBPs have been identified in drinking water, and many of them are mutagenic and carcinogenic (Richardson et al., 2007; Zhang et al., 2008; Zhai et al., 2014). In most recent years, several aromatic halogenated DBPs in drinking water have been newly identified, which have been demonstrated to be even more toxic than the previous aliphatic halogenated DBPs (Zhang et al., 2008; Zhai et al., 2014; Yang and Zhang, 2013; Liu and Zhang, 2014). In 1980, Weil et al. (1980) and Beech et al. (1980) reported the presence of trihalomethanes (THMs) in swimming pool water for the first time. Later, various categories of DBPs have been reported in swimming pool water in different countries all over the world (Chowdhury et al., 2014). To date, the DBPs identified in swimming pools include THMs and other haloalkanes, haloacetic acids (HAAs) and other haloacids, halodiacids, haloaldehydes, haloacetonitriles (HANs), haloketones (HKs), halonitromethanes (HNMs), haloamides, haloalcohols, and some aromatic halogenated DBPs (Zwiener et al., 2007; Richardson et al., 2010; Xiao et al., 2012; Wang et al., 2013). Compared with drinking water DBPs, swimming pool DBPs have their own distinct characteristics: (1) organic precursors: for drinking water DBPs, the main organic precursor is NOM; but for swimming pool DBPs, the organic precursors can be NOM and many other human inputs, such as sweat, urine, lotions, sun screams, cosmetics and soap residual (Kim et al., 2002; WHO, 2006), which are much more complex than that of drinking water; (2) temperature: swimming pool water generally has a higher temperature than drinking water; (3) disinfectant dose: the higher temperature of swimming pool water leads to the higher rates of chlorine decay, and thus swimming pools use higher doses of chlorine to ensure free chlorine residuals in the pool water (Richardson et al., 2010; Weisel et al., 2009); (4) organic loads: swimming pool water obtain continuous loading of dissolved organic carbon and dissolved organic nitrogen from swimmers while the organic loads of drinking water are just from source water without any further loading; and (5) exposure routes: for drinking water DBPs, the major exposure route is oral ingestion, but for swimming pool DBPs, the main exposure routes are inhalation and dermal permeation, with ingestion from accidental swallowing of swimming pool water being a minor route (Zwiener et al., 2007).

Several previous studies have investigated the occurrence of DBPs in swimming pool water in different countries all over the world, and the results are summarized in Table S1 in the supporting information (SI). Most of these studies were focused on the measurements of THMs and HAAs. It is to be noted that few studies reported the occurrence of swimming pool DBPs in China. Therefore, the occurrence of swimming pool DBPs in China is still an important topic that calls for investigation.

DBPs in water and air of swimming pools may pose adverse effects to human. Honer et al. (1980) reported that swimming pool water caused mutagenic responses in strain TA100 of Salmonella typhimurium. Another study revealed that swimming pool water resulted in higher mutagenicity than drinking water (Saito et al., 1996). It has also been reported that recreational pool waters showed higher toxicity than their tap water sources (Plewa et al., 2011). However, Richardson et al. (2010) found that the mutagenicity of swimming pool water was similar to typical drinking water. Previous researchers have also conducted some health risk assessments for swimming pool DBPs. Panyakapo et al. (2008) calculated the lifetime cancer risk from swimming pool DBPs to be 7.53×10^{-4} in a study in Thailand. Lee et al. (2009) examined the lifetime cancer risk through inhalation of THMs in the range of $7.77 \times 10^{-4} - 1.36 \times 10^{-3}$ in a study in Korea. In another study in Taiwan, cancer risks for male and female swimmers were predicted to be 6.87×10^{-5} and 5.46×10^{-5}, respectively, and inhalation was the major route, which contributed more than 99% of the risks (Chen et al., 2011). According to the previous studies, in most cases, the predicted health risks were higher than the regulatory limit of 10^{-6} (USEPA, 2006), and thus the health risks of swimming pool DBPs should be a critical concern. However, few studies reported the health risks of swimming pool DBPs in China.

The purposes of this study were to investigate the concentrations of several categories of DBPs, including THMs, HAAs, HANs, HKs and trichloronitromethane (TCNM), in public indoor swimming pool water in Nanjing, China, to evaluate the correlations between DBPs and water quality parameters as well as between different DBP categories, and to predict the health risks of the swimming pool DBPs to human.

2. Materials and methods

2.1. Chemicals and reagents

Methyl tert-butyl ether (MtBE) and methanol (HPLC grade) were purchased from Tedia. Standard solutions of 4 THMs (chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM)), 9 HAAs (bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDBAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid (TBAA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA)), 4 HANs (trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN)), 2 HKs (1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP)), and TCNM in MtBE (2000 mg/L) were purchased from Supelco (USA). All other chemicals used in this study were purchased at the highest purities available from Nanjing Chemical Reagent Co. Ltd. Ultrapure water (18.2 MΩ·cm) was supplied by a Merck Millipore simplicity purifier system.

2.2. Collection, characterization and storage of the swimming pool water samples

Swimming pool water samples were collected from 13 public indoor swimming pools (A–M), which were distributed in 5 different districts in Nanjing, Jiangsu Province, China. Pool A was a representative of the pools disinfected with ozonation/chlorination, and Pool B was a representative of the pools disinfected with chlorination, and they were investigated and compared in detail in this study. While Pools C–M were treated as a whole to calculate an average value to represent a typical pool with chlorination, for which the investigation was less detailed. For Pool A (ozonation/chlorination: disinfected with ozone followed by chlorine) and Pool B (chlorination: disinfected with sodium dichloroisocyanurate), the samples were collected on three different dates in March, April and May, 2014, respectively. On each day, 5 swimming pool water samples at 12:00 pm, 14:00 pm, 16:00 pm, 18:00 pm and 20:00 pm were collected. Therefore, for these two pools, 15 samples were collected for each. Besides, on each day, one tap water sample corresponding to each swimming pool was collected for comparison. For the other 11 pools (chlorination), one sample was collected on a day in March, April or May for each pool. Free chlorine residual was measured with the DPD (*N, N-diethyl-p-phenylenediamine*) method using a