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Effect of chloride on the formation of volatile disinfection byproducts in chlorinated swimming pools

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ABSTRACT

Chloride can accumulate in chlorinated swimming pool water. Although substantial efforts have been made to examine the effects of halide ions on the formation of volatile disinfection byproducts (DBPs), most have focused on bromide. The effects of chloride ion concentration on the formation of volatile DBPs in swimming pools remain largely unstudied. In this study, chlorination of typical precursors and body fluid analogue (BFA) were investigated with variable chloride concentration and pH. The formation of three volatile DBPs (NCl_3, $CHCl_3$ and $CNCHCl_2$) was observed to be linearly correlated with chloride concentration, both in bench experiments and in actual swimming pool water samples. Free chlorine consumption was also observed to increase with chloride concentration. These behaviors appear to be attributable to shifts in speciation of free chlorine, with higher chloride resulting in higher concentration of molecular chlorine (Cl_2), which is much more reactive than HOCl. The results of this work suggest that changes in pool management strategies to promote low chloride concentration could be important for control of volatile DBPs in pools and to economize free chlorine usage.

1. Introduction

Swimming pool water must be treated to minimize the risk of infection caused by microbial pathogens. Chlorine has been widely used for this purpose, usually by addition in the solid form (e.g., $Ca(OCl)_2$) or liquid form (e.g., NaOCl), or through a salt water chlorinating system. An important drawback of chlorination is the formation of disinfection byproducts (DBPs), some of which represent threats to human health (Barrett et al., 2000; Richardson et al., 2002; Woo et al., 2002; Zwiener et al., 2007). Among them, volatile DBPs have attracted attention because they may promote respiratory ailments and other adverse health effects among swimmers and pool patrons. As a result, considerable effort has been devoted to understanding the kinetics of volatile DBP formation, their toxicity, and fate in swimming pool water and air.

Volatile DBPs, including trichloramine (NCl_3), chloroform ($CHCl_3$), dichloroacetonitrile ($CNCHCl_2$), cyanogen chloride (CNCl) and dichloromethlyamine (CH_3NCl_2) are generated from chlorination of organic precursors that are present in swimming pool water (Li and Blatchley, 2007). Uric acid has been demonstrated to be an effective precursor for the formation of CNCl and NCl_3 (Lian et al., 2014); urea is an important precursor for the formation of NCl_3 (Blatchley and Cheng, 2010; Li and Blatchley, 2007); and chlorination of creatinine will generate CH_3NCl_2 (Li and Blatchley, 2007; Weng et al., 2013). Each these volatile DBPs has been identified as regularly occurring in chlorinated pools (Weaver et al., 2009; Zare Afifi and Blatchley, 2015).

It is not uncommon for pool water to remain essentially unchanged for periods of several years or longer, with the exception of water that is replaced as a result of evaporation or splashing by swimmers. This pool management approach is motivated by a number of factors, including simplicity and the costs of water replacement, heating, and treatment. However, this practice also offers the potential for constituents that are stable, both in terms of degradation by reaction and gas/liquid transfer, to accumulate in pools. Chloride (Cl^-) represents a constituent that displays these characteristics, and as such has the potential to accumulate in pools. As an illustration, the chloride concentration in chlorinated pools in Poland was observed to range from 213 to 396 mg/L (Michalski and Mathews, 2007).

As a further illustration, consider the conditions that are applied

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with so-called "salt water" pools, in which molecular chlorine (Cl_2) is generated *in-situ* by electrochemical oxidation of Cl^-. For these systems, the concentration of NaCl should be maintained in the range of 2000–6000 mg/L.

The broad ranges of the concentration of chloride ion that are observed in pools motivated the central question of this study: could such high concentrations of chloride affect the formation of volatile DBPs?

Previous research has demonstrated that the presence of chloride in ppm can increase trihalomethanes (THMs) formation resulting from chlorination of carbohydrates (Navalon et al., 2008). Chloride has also been demonstrated to play an important role in chlorine substitution reactions due to its influence on the speciation of free chlorine (Sivey et al., 2010; Sivey and Roberts, 2012), which are governed by the following reactions (25 °C, 0.0 M ionic strength), all of which can be assumed to be in equilibrium in pool settings: (Beach and Margerum, 1990), (Sivey et al., 2010)

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-,$$
$$K_h = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} = 4.3 \times 10^{-4}\ M^2 \quad (1)$$

$$HOCl \rightleftharpoons H^+ + OCl^-,$$
$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 4.0 \times 10^{-8}\ M \quad (2)$$

$$2HOCl \rightleftharpoons Cl_2O + H_2O,$$
$$K = \frac{[Cl_2O]}{[HOCl]^2} = 8.7 \times 10^{-3}\ M^{-1} \quad (3)$$

In general, reactions between free chlorine and DBP precursors involve a combination of oxidation and chlorine substitution. The most abundant forms of free available chlorine (FAC) are hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-); HOCl is often assumed to be the primary chlorinating agent. The concentrations of Cl_2 and Cl_2O are always low relative to HOCl in swimming pools, as well as in common drinking water applications. However, Cl_2O and Cl_2 have been demonstrated to be far more effective chlorinating agents than HOCl for some precursors, and are capable of influencing rates of DBP precursor chlorination in solutions of FAC (Georgi et al., 2007; Voudrias and Reinhard, 1988).

Nitrate (NO_3^-) is another stable anion that has characteristics that allow its accumulation in pools. Lee et al. (2010) reported modest, positive linear correlations between nitrate concentration and the concentrations of THMs and other DBPs ($r = 0.49–0.58$) in pools treated with chlorine; however, they did not report a relationship with chloride. Nitrate is a stable product resulting from oxidation of organic-N precursors, and it will accumulate in pools as a result of excretion of N-containing compounds in chlorinated water when combined with extended operation with little or no dilution or water replacement (Judd and Bullock, 2003). As such, conservative ions such as nitrate function as an indicator of the age and extent of use of water in pools.

-Chloride, resulting largely from reduction of FAC, can also serve as an indicator of the age and extent of use of water in pools. Moreover, nitrate concentrations tend to be positively correlated with chloride concentration. Given these facts, it is reasonable to hypothesize that chloride ion concentration could be correlated with the concentrations of THMs and other chlorinated DBPs. However, unlike nitrate, it is possible to develop mechanistic explanations to link chloride concentration to the concentrations of some chlorinated DBPs.

Although the role of chloride in chlorination has been largely overlooked to date, the effects of other halide ions, especially bromide, have been extensively studied in drinking water (Heller-Grossman et al., 1999; Navalon et al., 2008; Pan and Zhang, 2013a, 2013b; Richardson et al., 2010). The presence of bromide has been observed to increase the concentrations of brominated DBPs, including THMs, as a result of HOBr formation from oxidation of Br^- by free chlorine. Brominated DBPs tend to be more toxic than their chlorinated analogs (Liviac et al., 2010), but they also tend to be present in swimming pool water at concentrations far below the concentrations of their chlorinated analogs (Weaver et al., 2009) Also by comparison, the concentration of chloride tends to be much higher than the concentration of bromide in pool water. Given these facts, it was hypothesized that changes in chloride ion concentration could affect DBP dynamics in pools. Therefore, the objectives of this study were to examine reactions of several organic precursors that are common in swimming pools with chlorine using independent variables of chloride concentration and pH. Volatile DBPs including NCl_3, $CHCl_3$, $CNCHCl_2$, NH_2Cl, CNCl and CH_3NCl_2 were monitored to explore the effects of chloride on their formation. NCl_3, $CHCl_3$ and $CNCHCl_2$ are among the most frequently detected DBPs in swimming pool water (Chowdhury et al., 2014; Li and Blatchley, 2007). NCl_3 is a highly volatile DBP that enters the body largely through inhalation. It has been linked to increases in asthma and respiratory illnesses due to both occupational and recreational exposure in indoor swimming pools (Bernard et al., 2003; Thickett et al., 2002). THMs, especially $CHCl_3$, are often the most prevalent chlorination byproducts, and exposure to these compounds has been associated with increased risks of bladder and colon cancer, as well as other diseases (Liang and Singer, 2003; Nieuwenhuijsen et al., 2000; Villanueva et al., 2007). $CNCHCl_2$ has been reported to be an irritant of the respiratory system and skin; it has also been identified as a possible mutagen in humans (Osgood and Sterling, 1991).

2. Experimental section

2.1. Materials and methods

All reactants used in this study, unless otherwise noted, were purchased as reagent-grade chemicals from Sigma-Aldrich and used without further purification. Dilution to target aqueous-phase concentrations was accomplished with distilled, deionized water. Standard solutions of chloroform and dichloroacetonitrile were prepared gravimetrically from pure compounds. Standard solutions of trichloramine, monochloramine and dichloromethylamine were prepared by chlorination of urea at chlorine/urea molar ratio of 5.0:1.0 at pH 7.0 (Lian et al., 2014), chlorination of ammonium chloride at a chlorine/ammonia molar ratio of 1.00:1.03 at pH 10.0 (Shang and Blatchley, 1999), and chlorination of methylamine at a Cl/N molar ratio of 2.0 (Li and Blatchley, 2007), respectively. Cyanogen chloride was prepared as needed from the 1:1 stoichiometric reaction of potassium cyanide and sodium hypochlorite according to the method used by Wu et al. (1998). Chloride used in this study was developed by pretreatment of 99.5% NaCl by ozone and free chlorine to oxidize bromide to bromate to limit the role of bromide. Free chlorine stock solutions were standardized in terms of their UV absorbance at 292 nm ($\varepsilon_{OCl,\ max} = 350\ M^{-1}cm^{-1}$, 25 °C, and pH > 9.5). BFA stock solutions were prepared by diluting known constituents of human body fluids, including urea, uric acid, creatinine, L-histidine and citric acid. The composition of the BFA solution used in this work is listed in Table S1.

In considering the chloride concentration in each of the solutions, it is important to recognize the process by which the source of chlorine used in these experiments is manufactured. Specifically,