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Quality Aspects of the
Man-made Recreational
Water Environment

**FOURTH
INTERNATIONAL
CONFERENCE
SWIMMING
POOL & SPA**

EFFECT OF SELECTION OF pH IN SWIMMING POOLS ON FORMATION OF CHLORINATION BY – PRODUCTS

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ABSTRACT

Chlorine is used as disinfection agent in public swimming pools, but also reacts with organic matter in the water forming chlorinated disinfection by-products. In order to evaluate the effect of choice of pH-setpoint in the pool we investigated the effect of chlorination of artificial body fluid analogue at different pH-values between 6 and 8. The formation of trihalomethans, haloacetic acids and haloacetonitriles was measured. It was found that the formation of trihalomethans decreased with decreased pH. Haloacetic acid formation remained almost constant over the pH-range and haloacetonitrile formation increased with decreasing pH. As haloacetonitriles contributes the most to the genotoxicity of the water the predicted genotoxicity of the water was highest at the lowest pH value in the range tested.

Adding bromine in the experiments resulted in decreased haloacetic acids formation and increased formation of haloacetonitriles and trihalomethans. Addition of bromide in the experiments resulted in a shift in the formation of DBP to more brominated DBPs which contributed to that the predicted genotoxicity of the water increased significantly regardless of the pH-level.

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| Keywords | disinfection by-products, pH, bromide, haloacetonitriles, trihalomethans |
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INTRODUCTION

Chlorine is the main disinfectant used to prevent infections in public swimming pools, but chlorine also reacts with organic matter in the water and forms disinfection by-products (DBPs). The organic matter stems from the humic substances in the filling water and from sweat, urine, hair, skin cells and residues of personal care products added by the swimmers. The DBPs can be measured as a sum of all the halogenated compounds (TOX). In an American survey of DBPs occurrence in chlorinated drinking water it was found that approximately 30 % of the TOX comprise known compounds (Krasner et al., 2006). Some DBPs increase the risk of asthma, are carcinogens, or irritate the eyes and skin (WHO, 2006).

Chlorine is the common name for hypochlorous acid, which is formed by gaseous chlorine reacting with water. The hypochlorous acid dissociates in water to hypochlorite (eq. 1) and has a pKa value of 7.5.

$$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+ \quad (1)$$

The hypochlorous acid is much more effective than hypochlorite to kill bacteria, cysts and spores and to inactivate virus (White, 1992). Thus if the pH in a swimming pool is in the lower end of the regulated range, a lower amount of chlorine is necessary to obtain the same disinfection ability.

The legislation is on a national level and is generally similar between countries. A guideline is often given as to pH, chlorine and combined chlorine level together with a limit for the total amount of trihalomethans (THMs) as an indicator of the total DBP level. In Denmark the chlorine level must be within 0.5–3 mg/L at pH 7.0–8.0. In Germany the recommended chlorine dose is lower (0.3–0.6 mg/L at a pH 6.5–7.6) whereas in the USA, in the UK and Australia the chlorine level is 1–3 mg/L (Zwiener et al., 2007) with pH at 7.2–7.8. The guideline from WHO (2006) is that the pH of swimming pools should be between 7.2 and 7.8 and the chlorine level at 1 mg/L, not exceeding 1.2 mg/L.

The regulation of DBPs in swimming pools has focused on trihalomethanes and chloramines only, which are groups of DBPs which are easy to measure. However, recent research has shown that other chlorinated molecules such as cyanogen halides, haloacetates (HAAs) and haloacetonitriles (HANs) (Zwiener et al., 2007; Glauner et al., 2005) are much more relevant DBPs since they are directly linked to cancer risk and generally more toxic. Plewa et al., (2008) compared the cyto- and genotoxicity of a broad range of DBPs and found that the toxic potency of HANs is higher than the HAAs which were more toxic than the THMs. In a recent paper, seven public pools of different types with different disinfection and water treatment were all found to have higher genotoxic potency than their supply water (Liviatic et al., 2010). The higher genotoxic potency may be due to longer disinfectant contact time and different precursors, e.g. carbon-rich humic substance in drinking water compared to nitrogen-rich substances from the swimmers (Liviatic et al., 2010).

Inspired by the German standards use of lower chlorine concentrations combined with lower pH a Danish full scale study experimentally operated a public indoor swimming pool at pH 6.7 and 0.4 mg chlorine/L compared to the traditional pH 7.3 and 1.5 mg/L of chlorine: the study showed a decrease in THM, adsorbable organic halides (AOX) and combined chlorine while microbiological quality was retained (Kristensen et al., 2007). Based on this study it has been suggested to change the regulations for swimming pools to promote running of the pools at lower pH, specifically changing the lower limit for the pH from 7.0 to 6.8, while lowering pH even to 6.0 has been discussed.

Though beneficial for formation of THM, AOX and chloramines it was not considered how the lowering of pH would influence the more toxicological relevant DBPs. Literature on chlorination of drinking water indicates that this is highly relevant since lowering pH has resulted in a decrease in THM concentration but an increase in formation of HAAs (Liang and Singer, 2003). However such effects may depend on the water type since chlorination of two geographically different water types resulted in increased THM formation with increasing pH in both cases while HAA concentration decreased in the first case with increasing pH but increased in the second case (Bougeard et al., 2008).

The primary objective of this study was to assess the impact of pH on THM, HAN, and HAA formation under controlled chlorination conditions. The studies were conducted as batch experiments with an artificial sweat and urine analogue (Judd and Bullock, 2003) added to deionized water allowing us to simulate the load from bathers. The chlorine was added as initial constant free chlorine concentration at pH 6.0, 6.5, 7.0, 7.5 or 8.0 to investigate the effect of changing pH. Bromide was added to examine the effect on the formation of DBPs. To investigate the significance of the change in the formation of THM, HAN and HAA the toxic potency of each compound is used to estimate the toxicity of the water at the different pH levels.

EXPERIMENTAL PROCEDURES

REAGENTS AND MATERIALS

All chemicals were analytical grade purchased from Sigma-Aldrich. The standards used in the analytical procedures were purchased from Sigma-Aldrich as well.

BATCH EXPERIMENTS

The chlorination experiments were carried out as batch experiments. Deionized water was buffered with phosphate buffer at pH 6.0, 6.5, 7.0, 7.5, and 8.0. The water was added body-fluid analogue (BFA) prepared as suggested by Judd and Bullock (2003) corresponding to 1 mg TOC/L in the experiments. Chlorination was conducted at the pHs 6.0, 6.5, 7.0, 7.5 and 8.0. A constant start concentration of free chlorine, i.e. HOCl + OCl⁻, was set to 35 mg/L. The experiment was performed headspace-free in blue-cap bottles sealed by red caps with PTFE seal (SCHOTT DURAN ®) to avoid stripping of the volatile compounds. The bottles were kept at 25°C for 48 hours. Afterwards samples were taken to analyse THM, HAN and HAA and the chlorine residues and pH were measured. The experiments were repeated with 1 mg Br⁻/L added.

ANALYSIS OF TRIHALOMETHANS AND HALOACETONITRILES

Free chlorine in THM and HAN samples was quenched by adding ammonium chloride solution to the Purge & Trap-Vials before it was filled head-space-free with the sample. The samples were analyzed at the same day by purge and trap (AQUATEk 70, Teledyne Tekmar) coupled to a gas chromatograph (HP 6890 Series GC System, Hewlett Packard) with mass spectrometer (5973 Mass selective detector, Hewlett Packard).

ANALYSIS OF HALOACETIC ACIDS

The analysis of the haloacetic acids is a modified version of EPA 552.2. Sulfuric acid, sodium sulfate, surrogate standard and methyl-tertbutyl ether (MtBE) were added to the samples and extracted on a shaking table. The MtBE phase was transferred to a test tube and acidified methanol was added. The samples were placed in an oven to methylize the acids. Afterwards the samples were neutralized by adding saturated sodium bicarbonate solution. The MtBE phase was transferred to a GC vial and analyzed on a gas chromatograph (7890A GC System, Agilent Technologies) coupled to a mass spectrometer (5975C, Agilent Technologies).

ANALYSIS OF CHLORINE AND COMBINED CHLORINE

The residual chlorine and the pH of the water sample were measured. The hypochlorite stock solution and the free and total chlorine in the samples were measured with a photometer (DR 2800, Hach Lange) using the diethyl-p-phenyldiamine method from a cell test kit (LCK 310, Lange).

RESULTS AND DISCUSSION

EFFECT OF PH ON THM, HAN AND HAA FORMATION

Reaction of chlorine with BFA resulted in formation of the chlorinated species of THMs, HANs and HAAs (Figure 1). Increasing the pH resulted in increased THM formation, while HAN formation decreased (Figure 1). The change in THM formation is consistent with the findings when chlorinating drinking water (Liang and Singer, 2003, Bougeard et al., 2008). Chlorination of drinking water has demonstrated that the HAA formation can either increase or decrease depending on the nature of the organic matter (Bougeard et al., 2008). As seen in Figure 1 the formation of HAA almost remained constant when the pH varied.

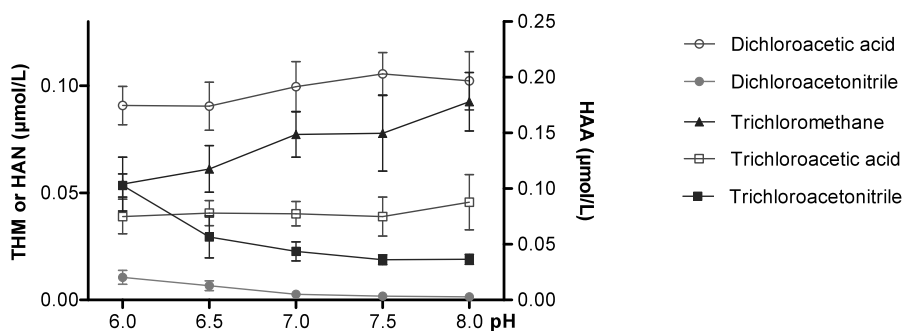


Figure 1 Effect of pH on the molar yields of THMs, HANs and HAAs when body fluid analogue reacted with chlorine at same initial free chlorine concentration. Bromide was not added to this experiment and therefore bromine containing byproducts were not detected. The error bars represent the standard deviation of six replicates. (Reaction time = 48 h, temperature = 25 °C and BFA addition = 1 mg TOC/L).

EFFECT OF BROMIDE

The experiments were performed with addition of bromide as well. That caused formation of brominated DBPs (Figure 2). The hypochlorous acid oxidizes the bromide and forms hypobromous acid (HOBr) (White, 1992), which can react with the organic matter and form bromated DBPs. The pKa of HOBr is 8.7 (White, 1992) and therefore hypobromous acid (HOBr) is the prevailing species at all pH levels used in these experiments. The tendency for change in the formation of the DBPs at different pH-levels was the same as in the experiments with only chlorine for HANs, while the formation of the HAAs and the THMs differed. The presence of bromide influences the amount of DBPs produced. The formation of HAA at pH 7 is decreased with presence of bromide from 0.27 $\mu\text{mol/l}$ to 0.11 $\mu\text{mol/l}$, whereas the formation of THM and HAN increased (THM from 0.077 $\mu\text{mol/l}$ to 0.11 $\mu\text{mol/l}$ and HAN from 0.025 $\mu\text{mol/l}$ to 0.056 $\mu\text{mol/l}$). The increase in the molar concentration of THM resulting from addition of bromide was also observed by Hua et al., (2006). A decrease in the HAA5 (sum of chloroacetic acid, bromoacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid) with increasing bromide level was found as well. However, Hua et al., (2006) found that HAA9 molar concentration increased with increasing bromide concentration especially at higher bromide levels. In a later work of Hua and Reckhow (2008) it was found that dihalogenated acetonitriles (dHANs) increased with increasing bromide level, which was also found in this work (dHANs increased from 0.003 $\mu\text{mol/l}$ to 0.03 $\mu\text{mol/l}$). The effect of bromide on the DBP formation and speciation seems to be the same as when chlorinating drinking water even though the precursors are different.

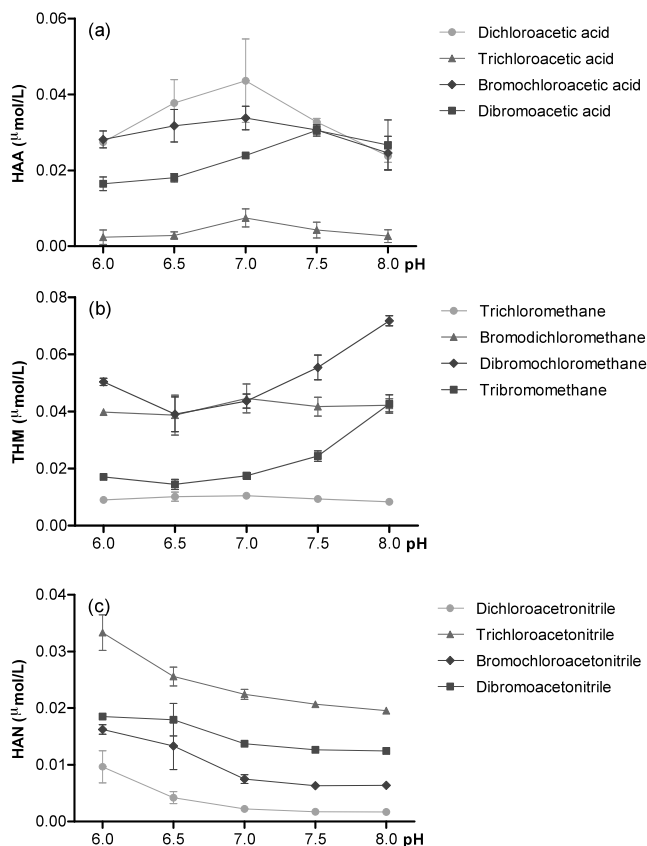


Figure 2 Effect of bromide on the formation of HAAs (a), THMs (b) and HANs (c) when body fluid analogue reacted with chlorine at the same initial free chlorine concentration. The error bars represent the standard deviation of three replicates. (Reaction time = 48 h, temperature = 25°C, bromide concentration = 1 mg/L and BFA addition = 1 mg TOC/L).

GENOTOXICITY

The genotoxic potency of the water at each experiment is calculated as the sum of the concentration of a compound divided with the LC_{50} for that compound. All the LC_{50} was from Chinese hamster ovary cell acute genotoxicity assays and was found in the literature (Plewa et al., 2002, 2008, Muellner et al., 2007). When the pH is changed from 6 to 7 the genotoxic potency is reduced by half (Figure 3 a). However when the pH is increased to 8, the genotoxicity remains almost constant. The presence of bromide in the water increases the genotoxic potency. At pH 7 without bromide the toxicity is $2.4 \cdot 10^{-5}$ but with bromide the toxicity is $6.5 \cdot 10^{-4}$ (Figure 3), which is a factor of 27 in difference. The toxicity of the water was expected to increase, since the toxicity of the bromated containing species is higher than the chlorinated ones. In the experiment without bromide only the HANs contribute to the genotoxicity (Figure 3a), whereas in the experiments with bromide the HAAs add little to the genotoxicity as well (Figure 3b). Kramer et al., (2009) have tested the genotoxicity of water from 11 swimming pools and 48 selected DBPs with a *Salmonella* umu-test. The water was analysed on GC-MS as well. It was found that the genotoxicity of the water samples could be explained exclusively by the HANs.

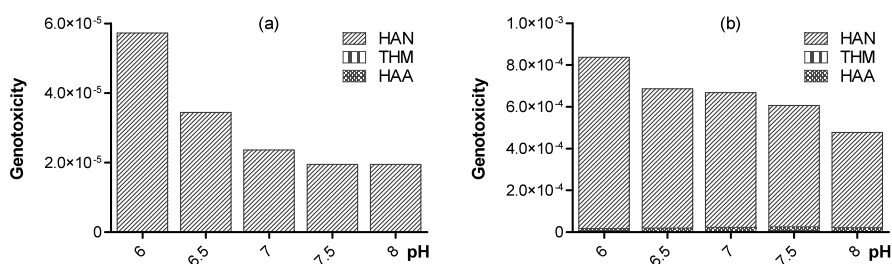


Figure 3 Calculated genotoxicity at different pH values based on measured DBPs in body fluid analogue and chlorine reaction mixtures at constant initial free chlorine (a) and with bromide added (b).

CONCLUSION

It was found that changing the pH affects the formation of DBPs. Even though lowering the pH of the swimming pool might result in a decrease in the concentrations of the legally regulated THM one should be aware of the effect of pH on the other DBPs. These experiments show that the concentration of HANs will increase and HAA formation decrease when changing pH from 7.5 to 6.0. Furthermore it was found that the genotoxic potency of the water increases when lowering the pH. The experiments are laboratory batch experiments and can only indicate what may happen in a swimming pool and further research is necessary.

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