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Effect of ozonation of swimming pool water on formation of volatile disinfection by-products – A laboratory study

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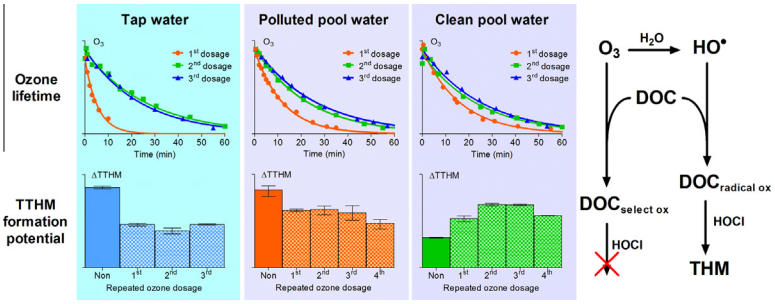
HIGHLIGHTS

- Ozone lifetime in pool water dependent on water quality and previous ozonation.
- Trihalomethane formation decreased after ozonation of polluted pool water.
- Trihalomethane formation increased at low ozone doses in clean pool water.
- High or repeated ozone dosage decreased trihalomethane formation.
- Thus, ozone dosage in swimming pools should be proportional to the water pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozonation experiments were performed using unchlorinated tap water used for filling municipal swimming pools, actual pool water and pool water polluted by addition of fresh tap water and artificial body fluid to evaluate ozone kinetics and water quality effects on formation of volatile disinfection byproducts during subsequent chlorination.

The ozone reaction was observed to behave according to first order kinetics. For tap water half-life was 4 min whilst polluted and unpolluted pool water exhibited half-life of 8 and 11 min, respectively. When ozonation dosage was repeated half-life of ozone was approximated 17–19 min in all samples.

Subsequent chlorination revealed ozone removed reactivity of dissolved organic carbon toward chlorine for tap and polluted pool water, decreasing formation rate of trihalomethanes (TTHM). In pool water higher rates of TTHM formation was observed after the initial ozone dosage, however this decreased with subsequent treatments. For tap and polluted pool water, ozone reacted directly with the pollutants resulting in a short ozone half-life, removing reactivity towards chlorine oxidation and preventing TTHM production. Conversely for pool water samples, due to the long half-life of ozone, the molecule decomposed to hydroxyl radicals. These in turn reacted with aqueous organic matter increasing chlorine reactivity and rates of TTHM formation. Formation of other non-regulated volatile byproducts (e.g. dichloracetonitrile, trichlorpropanone and trichloronitromethane) was observed to increase in pool water with ozone treatment. Thus, ozonation dosage regimes should be designed such that ozone mostly oxidizes fresh pollutants before chlorine is able to react with it.

Abbreviations: AOX, adsorbable organohalogen; DBP, disinfection by-product; DPD, N,N-diethyl-p-phenylenediamine; DIN, Deutsches Institut für Normung; DOC, dissolved organic carbon; HAA, haloacetic acid; HAN, haloacetonitrile; LOQ, limit of quantification; NOM, natural organic matter; THM, trihalomethane; TTHM, total trihalomethane.

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1. Introduction

Chlorine is the most common disinfectant used in public swimming pools. However, chlorine reacts with natural organic matter present in the filling water and pollutants introduced into pool water by bathers forming disinfection by-products (DBPs). The most common DBPs identified in pool water are combined chlorine species (organic and inorganic chloramines), haloacetic acids (HAAs), and trihalomethanes (THMs) [1,2]. The general concern regarding formation of DBPs is their effect on human health since some are genotoxic and thus might be carcinogenic [3]. The main removal mechanisms of the dissolved organic pollutants are oxidation by chlorine and subsequent mineralization.

Ozone is a strong oxidizing agent, with a great variation in reaction times depending on pollutants characteristics. When applied to swimming pool water ozone can oxidize dissolved pollutants (i.e. dissolved organic carbon, DOC; Eq. (1)) which reduces its reactivity with chlorine as both ozone and chlorine are selective oxidants that preferably react with the same parts of organic molecules. As chlorine reactivity of DOC decreases it can be expected that formation of DBPs decreases [4] in pool water following oxidation with ozone:

$$DOC + O_3 \rightarrow DOC_{\text{selectively oxidized}} \quad (1)$$

$$H_2O + O_3 \rightarrow O_2 + 2HO^{\cdot} \quad (HO^{-} \text{ catalyzed, slow at neutral pH}) \quad (2)$$

$$DOC + HO^{\cdot} \rightarrow DOC_{\text{radical oxidized}} \quad (3)$$

If ozone is not consumed quickly by reaction with reducing matter it will decompose to hydroxyl radicals (Eq. (2)) in a competing reaction which rate increases with increasing pH [5,6]. Hydroxyl radicals are non-selective, highly reactive species and thus can oxidize a range of dissolved pollutants (Eq. (3)). Thus, the lifetime of ozone in water depends on pH, DOC concentration, and the quality and functional groups of the DOC. Reaction of organic matter with hydroxyl radicals appears to increase the reactivity towards chlorine and formation of DBPs during chlorination [4,7] properly through introduction of more oxygen containing functional groups and breaking of carbon chains to leave more end-carbons available for oxidation.

Generally, most ozonation treatment of swimming pools is undertaken according to the German DIN standard where all or a part of the water is ozonated with a contact time of 3–10 min before destruction of ozone in an activated carbon filter. Destruction of ozone is performed in order to prevent ozone escaping to the air above the swimming pool, however this results in only a small part of the ozone dosage reacting with the treatment targets whilst the main mass of ozone is destroyed [8]. A radically different treatment principle, developed in the USA, is the slip-stream ozonation method which applies a low dose of ozone into a side stream of the filter flow. The low dose of ozone is consumed rapidly by reaction with organic in the main recirculation flow. The ozone dosing is controlled by a redox probe to ensure ozone is not added in excess of the dissolved organic matter present thereby ensuring ozone does not reach the pool. A third treatment principle is the ozone/bromide system where pool water containing bromide is ozonated to oxidize bromide to hypobromous acid, which then acts as a disinfectant [9]. Due to the high concentration of bromide in such systems, ozone is quickly consumed and no bromate is formed [10].

Literature concerning the effects of ozone on DBP formation in swimming pool water is limited. However, general knowledge regarding ozone and reactivity can be found in the literature particularly regarding ozonation of drinking water and wastewater, e.g. von Gunten [11]. For such applications it is seen that the most common DBPs, i.e. THM and HAA, react very slowly with ozone. Furthermore ozone's reaction with nitrogen compounds and chloramine is also relatively slow [8]. However, in a field application of ozone treatment of swimming pool water according to the DIN standard, a 34–48% decrease in chloroform formation potential was achieved depending on ozone contact time [12]. Conversely in a laboratory batch experiment, Glauner et al. [4] obtained only a 12 % reduction of adsorbable organohalogen (AOX) formation potential and 3% reduction in total trihalomethane (TTHM) formation potential after 10 min oxidation by ozone. In a Korean study, ozone/chlorine treated swimming pools had lower levels of DBPs than chlorinated pools [13]. Whilst another study conducted in Canada found no difference on the chloramine level in a pool and spa with chlorine disinfection compared to a pool and a spa with ozone/chlorine treatment [14].

An increased understanding of ozonation in swimming pools (e.g. kinetics of reactions) could help in designing and implementing a more cost effective ozone treatment system and thereby minimize the occurrence of disinfection by-products in swimming pools. Thus, the aim of this current study is to determine the kinetics of ozone consumption with time in pool water and investigate the effect of ozonation on DBP formation. Ozonation experiments were performed to evaluate ozone kinetics and water quality effects on formation of volatile disinfection byproducts during subsequent chlorination. Ozonation was performed on actual pool water collected in a period when bathing attendance was low, in pool water polluted by addition of fresh tap water and artificial body fluids and on unchlorinated tap water used for filling municipal swimming pools. The two pool water illustrate the difference between fresh pollution in the pool and organic matter residuals from long chlorine exposure, while the tap water serves as a general reference to water ozonation.

2. Material and methods

2.1. Reagents

All reagents and chemicals were purchased at Sigma–Aldrich (Denmark) and used as received. The experimental set-up for ozonation was based on a 20 g/h ozone generator from O3-Technology AB (Vellinge, Sweden) which was supplied with dry oxygen gas. Generated ozone was dispersed through a diffuser in a collection bottle containing ultra-pure water, which was immersed in an ice bath so that ozone solubility was maximized. To further increase solubility of ozone, a manometer and valve were placed after the collection bottle and a pressure at 1.4 barG was applied. Based on these experimental conditions, the concentration of ozone achieved in the stock solution was between 80 and 100 mg/L.

2.2. Water samples

2.2.1. Tap water

The tap water stems from the public distribution network, which is comprised of non-chlorinated ground water.

2.2.2. Clean pool water

Pool water was collected from a public swimming pool and used for experiments on the day of collection. The pool for water collection was the main practice basin in Lyngby which is a typical public pool (temperature 27 °C, sand filter with flocculation, and a side stream activated carbon filter) with a hydraulic retention time (HRT) of 4 h. Filling water for the swimming pool is obtained from the public distribution network, which is comprised of non-