Science of the Total Environment 443 (2013) 850–856

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Photolytic removal of DBPs by medium pressure UV in swimming pool water

Kamilla M.S. Hansen [a], Raissa Zortea [b], Aurelia Piketty [c], Sergio Rodriguez Vega [d], Henrik Rasmus Andersen [a,*]

[a] Department of Environmental Engineering, Technical University of Denmark, Denmark
[b] Department of Land, Environment and Geotechnology Engineering, Polytechnic University of Turin, Italy
[c] Institute of Chemistry, Industrial and Chemical Engineering and Technology (INP-ENCIACET), National Polytechnic Institute of Toulouse, France
[d] Chemical Engineering, Complutense University of Madrid, Spain

HIGHLIGHTS

- ► UV irradiation is able to degrade all 12 investigated disinfection by-products.
- ► Bromine species are easier to remove than their chlorinated analogues.
- ► UV dose used for combined chlorine was comparable with doses required for DBP removal.
- ► Significant removal of some disinfection by-products in swimming pools is indicated.

ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form 13 November 2012
Accepted 18 November 2012
Available online 14 December 2012

Keywords:
UV treatment
Disinfection by-products (DBP)
Electrical energy per order (EEO)
Swimming pool
Photolysis

ABSTRACT

Medium pressure UV is used for controlling the concentration of combined chlorine (chloramines) in many public swimming pools. Little is known about the fate of other disinfection by-products (DBPs) in UV treatment. Photolysis by medium pressure UV treatment was investigated for 12 DBPs reported to be found in swimming pool water: chloroform, bromodichloromethane, dibromochloromethane, bromoform, dichloroacetonitrile, bromochloroacetonitrile, dibromoacetronitrile, trichloroacetonitrile, trichloronitromethane, dichloropropanone, trichloropropanone, and chloral hydrate. First order photolysis constants ranged 26-fold from 0.020 min^{-1} for chloroform to 0.523 min^{-1} for trichloronitromethane. The rate constants generally increased with bromine substitution.

Using the UV removal of combined chlorine as an actinometer, the rate constants were recalculated to actual treatment doses of UV applied in a swimming pool. In an investigated public pool the UV dose was equivalent to an applied electrical energy of 1.34 kWh $\mathrm{m}^{-3}\,\mathrm{d}^{-1}$ and the UV dose required to removed 90% of trichloronitromethane was 0.4 kWh $\mathrm{m}^{-3}\,\mathrm{d}^{-1}$, while 2.6 kWh $\mathrm{m}^{-3}\,\mathrm{d}^{-1}$ was required for chloral hydrate and the bromine containing haloacetonitriles and trihalomethanes ranged from 0.6 to 3.1 kWh $\mathrm{m}^{-3}\,\mathrm{d}^{-1}$. It was predicted thus that a beneficial side-effect of applying UV for removing combined chlorine from the pool water could be a significant removal of trichloronitromethane, chloral hydrate and the bromine containing haloacetonitriles and trihalomethanes.

1. Introduction

For more than 100 years chlorine has been the preferred disinfectant to ensure the hygienic quality of swimming pool water. Chlorine is the common name for hypochlorous acid (HOCl), which is formed by gaseous chlorine reacting with water. The hypochlorous acid dissociates in water to hypochlorite (OCl^-) ($\mathrm{p}K_a = 7.5$) and the sum of HOCl and OCl^- are known as free chlorine. Hypochlorous acid is significantly more effective than hypochlorite as a bactericide, in preventing cysts and the spreading of spores and inactivating viruses (White, 1992).

It is well documented that chlorine reacts with organic and inorganic matter released from bathers (sweat, saliva, urine, skin residues) to form chlorinated disinfection by-products (DBPs). A recent study identified over 100 DBPs in pool water and reported a higher number of nitrogen-containing DBPs than typically found in chlorinated drinking water with several of the chemicals not identified in drinking water (Richardson et al., 2010). The major concern regarding DBP formation is their effects on human health. Since some DBPs formed in swimming pools are also found in chlorinated drinking water, some studies about genotoxicity, carcinogenicity and health effect risks have been undertaken. However, swimming pool

---

Abbreviations: THM, trihalomethane; HAN, haloacetonitrile; DBP, disinfection by product; EEO, electrical energy per order; EED, electrical energy dose.

* Corresponding author at: DTU Environment, Miljoevej 113, 2800 Lyngby, Denmark. Tel.: +45 4525 1583.

E-mail address: Henrik@ndersen.net (H.R. Andersen).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2012.11.064

waters are significantly more genotoxic than their source tap water (Liviac et al., 2010) which is likely due to the nitrogen-rich precursors released by the bathers. Furthermore, a recent study on bladder cancer found a clear increased risk associated with chlorination by-products in drinking water and indicates that the use of swimming pools further increased the risk (Villanueva et al., 2007).

A common condition affecting swimmers is eye irritation and various compounds such as chlorine, chloramines, haloketones and haloacetic acids have been identified as irritants (Chiswell and Wildsoet, 1989; Erdinger et al., 1998; Zwiener et al., 2007). Erdinger et al. (1998) concluded that the degree of eye irritation resulting from swimming pool waters can only be explained by considering the effects and synergistic action of a number of DBPs in the presence of chlorine. Another effect of DBPs on swimmers is irritation of the respiratory passage and trichloramine has been suggested as the causative compound. Several studies on the association of NCl_3 with respiratory irritation or asthma have been carried out (Bernard et al., 2007; Goodman and Hays, 2008; Hery et al., 1995; Massin et al., 1998; Thickett et al., 2002); however there is still a lack of evidence with which to make a definite conclusion. A recent study performed an in vitro air exposure test using the human alveolar epithelial carcinoma cell line A-549 to conclude that the concentration of NCl_3 alone could not explain the inflammatory effect of air from an indoor swimming pool and that other volatile DBPs must also be contributing to the observed effects (Schmalz et al., 2011).

Due to the lack of alternatives, the continued use of chlorine as a disinfectant is the most realistic immediate future scenario for public swimming pools. Therefore there is a need to find alternative methods by which to ensure acceptable water quality in the public swimming pools which could be a combination of removing DBP precursors and DBPs themselves. The load of DBP precursors can be reduced significantly by ensuring effective pre-swim hygiene (showering) (Keuten et al., 2012). When DBP precursors are in the water a potential method improvement suggested in literature is to lower the pH in order to reduce the formation of trihalomethanes (THMs) (Kristensen et al., 2007). However, recent studies reported an increased formation of the more toxic DBP group, haloacetonitriles (HANs), when decreasing the pH (Hansen et al., 2012a, 2012b).

One way to remove combined chlorine including NCl_3 is treatment with medium pressure (MP) UV irradiation. In 1976, the first MP UV system was installed in a swimming pool in Denmark and today there are estimated to be 1000–2000 installations in public swimming pools in Europe (Povl Kaas, personal communication). UV light at 222, 254, 288 nm is able to photo degrade inorganic chloramines and showed little or no pH dependence (Li and Blatchley, 2009). A study using MP UV treatment in full stream found up to 32% reduction of NCl_3 in air (Cassan et al., 2011). While another study with MP UV treatment applied to a side stream of the filter return flow reported a decrease in the water concentration of combined chlorine greater than 50% (Kristensen et al., 2009, 2010). However, studies of UV photo degradation of other DBPs are very limited.

UV treatment in a swimming pool has been reported by Cassan et al. (2006) to increase THM levels in the pool while Beyer et al. (2004) reported a decrease in THM levels in a similar study. In a long term study including matched control periods with and without UV treatment in a public pool, Kristensen et al. (2009) showed no effect on THM levels in a swimming pool treated by several types of UV treatment. A mechanism that explains how THM may increase by UV treatment in some cases is given by Glauner et al. (2005) who describe from a laboratory batch experiment of UV treatment of pool water that an increased THM formation potential was induced by the UV treatment when UV treated samples were chlorinated after UV exposure. In public swimming pools chlorine will always be present and since photolysis of chlorine creates radicals (Jin et al., 2011; Sichel et al., 2011) it is possible that some degradation of DBPs may occur by reactions with radicals produced by photolysis of hypochlorite.

The objective of this research was to investigate the photo degradation of 12 of the most common DBPs besides chloramines by UV irradiation with an MP lamp. The investigated DBPs were chloroform, bromodichloromethane, dibromochloromethane, bromoform, dichloroacetonitrile, bromochloroacetonitrile, dibromoacetronitrile, trichloroacetonitrile, trichloronitromethane, dichloropropanone, trichloropropanone, and chloral hydrate. To investigate the possible effect of radical reactions from photolysis of hypochlor experiments were performed with and without the presence of free chlorine. We avoided the possibility of formation of any of the investigated DBP from organic matrix in swimming pool water by performing the experiment on pure chemicals in solution of purified water and we tested the stoichiometrically possible formation of THM from the HANs and chloral hydrate after UV treatment by performing separate experiments with these DBPs.

From the data obtained the first order kinetic constant and the treatment level required to remove 90% of each of the 12 DBP was determined. Furthermore, photolysis of naturally occurring combined chlorine in a public swimming pool was used as an actinometer to compare the UV doses delivered in a full scale UV installation and the laboratory setup. Thus the significance of the actual typical UV treatment dose applied in a swimming pool could be compared to the dose required for photolysis of each of the 12 DBPs.

2. Material and methods

2.1. Reagents

All chemicals and standard solutions were of analytical grade purchased from Sigma-Aldrich.

2.2. Analysis of trihalomethanes and haloacetonitriles

The analyses were performed as previously published in Hansen et al. (2012a). In brief free chlorine was quenched by adding ammonium chloride solution to the vials before they were filled head-space-free with sample. The samples were analysed the same day by Purge and Trap (purge temperature = 30 °C, Velocity XPT Purge and Trap Sample Concentrator, Teledyne Tekmar, with autosampler: AQUATek 70, Teledyne Tekmar) coupled with a GC–MS (HP 6890 Series GC System, 5973 Mass selective detector, Hewlett Packard). This method was also used for the detection of trichloronitromethane, dichloropropanone, and trichloropropanone.

2.3. Analysis of chloral hydrate and haloacetonitriles

For the analysis of the chloral hydrate and HANs a modified version of the EPA 551.1 method was used. A 40 mL borosilicate glass vial was filled with sample without head-space and the samples were stored until the end of the day where all samples were analysed.

To make space in the vial 7 mL of each sample was removed and methyl-tert-butyl ether, internal standard (bromofluorobenzene) and buffer with quenching agent ($Na_2HPO_4/KH_2PO_4/Na_2SO_3$) were added to the vial. Followed by two drops of a colourant (14.85 g L^{-1} 1,10-phenanthrolie $\cdot$ H_2O and 6.95 g L^{-1} ferrosulphate $\cdot$ $7H_2O$) and Na_2SO_4. The vials were shaken for 30 min before the methyl-tert-butyl ether phase was transferred to a GC vial and analysed on a GC–MS (GC 6890N–MSD 5973N, Agilent Technologies). The samples were analysed on the day of collection or stored in the refrigerator for the following day. Details on the method can be found in the Supplementary material.

2.4. Analysis of chlorine and combined chlorine

The concentration of free and total chlorine was measured with a photometer (DR 2800, Hach Lange) using the colorimetric method