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Disinfection by-product formation of UV treated swimming pool water

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Abstract

Water samples from 3 indoor swimming pool facilities were tested to evaluate UV-induced effects on swimming pool water chemistry. Concentration change of several DBPs was investigated in experiments including medium pressure UV treatment with and without chlorine and post-UV chlorination. Post-UV chlorine consumption increased, dose-dependently, with UV treatment dose. A clear absence of trihalomethane formation by UV and UV with chlorine was observed. The post-UV chlorination clearly induced formation of DBPs; however, for the total trihalomethanes (TTHM), the inductions were not more than what could be replicated by performing the DBP formation assay with higher chlorine concentrations to simulate extended chlorination. Post-UV chlorination of water from a swimming pool that continuously uses UV treatment to control combined chlorine could not induce secondary formation of DBPs. The trihalomethane induction might result from a kinetic increase in formation by UV. However, this does not imply that higher trihalomethane concentrations would occur in pools that apply continuous UV treatment. The bromine fraction of the halogens in the formed trihalomethanes increased with UV dose, which indicates that UV breaks bromine atoms from larger molecules participating in trihalomethane production during the post-UV chlorination. No significant effect on DBP formation was observed by the photo-inducible radical forming molecules NO_3^- and H_2O_2 , which may either occur occasionally in high concentrations in pool water or be added in a DBP reducing treatment process, respectively.

Keywords

DBP formation assay; medium pressure UV lamp; Post-UV chlorination; trihalomethane

INTRODUCTION

Chlorine is extensively used due to its efficiency to deactivate viruses and bacteria. However, chlorine reacts with organic matter, enhancing DBP formation, which is suspected to be genotoxic. To reduce combined chlorine concentration in the pools, medium pressure (MP) ultraviolet (UV) lamps are used but these may produce chloroform. So far, there are several studies with contradictory results regarding the effects of UV in DBP formation (Beyer et al., 2004; Cassan et al., 2011, 2006; Kristensen et al., 2009; Cimetiere and De Laat, 2014).

It is believed that radicals reacting with organic matter dissolved in pool water resulted in activated compounds, which produced significantly more chloroform (THM) when subsequently chlorinated. In chlorinated water, direct photolysis of hypochlorous acid (HOCl) can produce hydroxyl and chlorine radicals (Nowell and Hoigne, 1992; Watts and Linden, 2007) which are used as an

Advanced oxidation process (AOP) to remove contaminants (Sichel et al., 2011). Hydrogen peroxide is also used for chloroform prevention in combination with UV (Appel, 2013). Since nitrate already exists in natural water, and after being exposed to UV light, creates hydroxyl radicals, so it is also used as an AOP (Lyon et al., 2012).

In the present study, the effect of chlorine, nitrate, and hydrogen peroxide as radical initiators was investigated via addition prior to UV irradiation. The concentration change of 4 well known volatile DBPs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) was investigated in authentic swimming pool water with a medium pressure UV-lamp. The DBP and more specific total trihalomethane (TTHM) level measured after UV and post-UV chlorination was compared with a sample without UV exposure. Water from a third swimming pool using continuous UV treatment was exposed to UV in the laboratory to investigate whether further UV could induce DBP formation.

METHODS

Reagents

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

Water characterization

Colorimetric reactions were used to quantify chlorine, hydrogen peroxide, nitrate, and nitrite. For characterization of the pool water, a cell test kit (LCK 310, Hach Lange, Germany) was used to measure free and total chlorine.

During experiments the residual chlorine was determined using 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid-diammonium salt (ABTS), as described by Pinkernell et al. (2000).

Hydrogen peroxide was determined using potassium TiO-oxalate (Antoniou and Andersen, 2014), while test kits (NO₃⁻ 09713 and NO₂⁻ 114776, Merck, Germany) were used to determine nitrate and nitrite.

A Shimadzu ASI-V UVC/Persulphate analyzer was utilized for the quantification of the remaining in the samples.

Pool water

Pool water was collected from public swimming pools (two main practice basins and a hot water therapy basin (Denmark)). The two practice basins are typical public pools, temperature 26 °C, sand filter with flocculation, a side stream activated carbon filter and a hydraulic retention time (HRT) of 4 h. The hot water therapy basin has a much higher bather load and a faster development of combined chlorine, due to the higher temperature (34 °C); hence, it is operated with medium pressure UV lamps in a side stream of about 20% of the circulation, in order to effectively control the combined chlorine concentration. The pool has sand filters and the HRT is just 0.5 h.

Filling water for the swimming pools came from the public distribution network, which is based on non-chlorinated ground water. Water samples were collected during regular operating hours and were analyzed immediately after their collection, upon which the pool water quality (pH, NO₃⁻, free and combined chlorine) were determined.

DBPs Analysis

The analyses were performed by Purge&Trap GC-MS as previously published by Hansen et al. (2012a).

UV treatment

UV treatment was performed in a quasi-collimated beam apparatus with a doped medium pressure lamp ($P = 700 \text{ W}$, ScanResearch, Denmark) with enhanced output in the lower range (200-240 nm), compared to standard mercury medium pressure lamp, as it is described by Hansen et al. (2013b).

DBP formation with chlorine

After UV exposure, chlorine was added to the samples (post-UV chlorination) based on the chlorine consumption, in order to achieve a chlorine residual after 24 h of either 1-3 mg/L (typical chlorine levels) or 31-33 mg/L (high chlorine levels). The chlorine consumption was determined in pre-experiments and concentrations were measured by ABTS. The pH was adjusted to 7.1 and the samples were stored at $25 \text{ }^\circ\text{C}$. After 24 h, the residual chlorine was determined and the samples were analyzed the same day for DBPs.

Experiment

This study was carried out as laboratory batch experiments to ensure controlled experimental conditions. In general, a sample of pool water was spiked with a radical initiator (Cl_2 , NO_3^- or H_2O_2) and then UV irradiated. The irradiation time varied corresponding to $\frac{1}{2}$ - 2 days dose of UV in the real treatment situation. After exposure, the sample was either analyzed for DBPs or chlorine was added (post-UV chlorination), and allowed to react for 24 h before DBP analysis.

The water was analyzed for DBPs before UV exposure in order to establish initial values, after UV exposure, and after post-UV chlorination to investigate whether DBPs are formed during UV irradiation or after reaction with chlorine.

Three samples were not exposed to UV light (Dark) by covering the sample with a piece of cardboard, but otherwise treated the same way. One sample was a control for the handling of samples during UV exposure and was not post-UV chlorinated, but directly analyzed for DBPs. The two other samples were post-UV chlorinated and were controls for the formation potential of the pool water without UV exposure.

Since chlorine concentration varied in the collected pool water, chlorine was added so 3 mg/L was present before UV exposure. Some experiments were conducted without chlorine to investigate the effect of high and typical chlorine concentrations.

To examine the effect of nitrate, some samples were spiked with 11.1 mg/L NO_3^- -N (50 mg/L NO_3^-) prior to UV exposure. When hydrogen peroxide was added until the concentration was 1.0 mg/L after reaction with the chlorine residual from the pool. The radiation time varied. The prolonged exposure time was necessary to achieve 80% removal of H_2O_2 through photolysis, as it is applied by the company Pool Water Treatment (Rotterdam, Netherlands) for pool treatment (Appel, 2013).

Water from the hot water therapy basin was only used in selected experiments to examine the possibility to induce formation of DBPs in pool water already treated with UV light.

Data treatment

The data treatment was conducted using MS Excel and Prism Graph Pad. The results of the different treatments were compared with an one-way ANOVA with Tukey's Multiple Comparison Test with 95% confidence level. For all the different treatments there were triplicates (or five replicates for $\text{UV}_{1d}/\text{Cl}_2, \text{Cl}_2$ and $\text{Dark}/\text{Cl}_2, \text{Cl}_2$). The treatments were grouped according to significant difference ($P < 0.05$). All treatments with insignificant difference were given the same letter. The error bars in the figures indicate the standard deviation among the replicates.

RESULTS AND DISCUSSION

Water samples from 3 indoor swimming pool facilities were tested to evaluate UV-induced effects on swimming pool water chemistry. The 4 investigated DBPs were detected in the collected pool water, indicating that UV is not responsible for the creation of the entire amount of these by-products. The experiments were conducted as batch experiments and thus the DBP formation may be different in a long-scale experiment where the water is treated continually with UV light.

Chemical characterization of pool water

For the 3 indoor pool water used for the experiments, the initial pH ranged from 7.10 to 7.24. The TOC, free chlorine, and combined chlorine concentrations were measured and ranged from 1.58 to 2.14 mg/L, 0.44 to 1.37 mg/L, and 0.17 to 0.36 mg/L, respectively. Regarding the nitrate analysis, untreated water sample was analyzed and exhibited initial concentrations ranging from 2.2 to 6.1 mg/L NO_3^- -N. Having determined the initial nitrate concentration, some water samples were spiked with nitrate stock solution in order to have nitrate concentrations in the beginning of the experiment equal to 11.1 mg/L NO_3^- -N. After UV exposure, nitrate spiked samples were analyzed for nitrite. The nitrite concentration was 0.20 and 0.45 mg/L-N.

Chlorine consumption

The chlorine consumption varied greatly among the treatments, the lowest chlorine consumption is observed in solely chlorinated samples (Dark/ Cl_2 , Cl_2 : Figure 1). Chlorine consumption tends to increase with increasing chlorine concentration (Dark/ Cl_2 , Cl_2 vs. Dark,High Cl_2). The highest chlorine consumption is observed in post-UV chlorinated samples and it appears to be proportional to the prolonged exposure time (UV $_{1/2d}$ / Cl_2 , Cl_2 vs. UV $_{1d}$ / Cl_2 , Cl_2 vs. UV $_{2d}$ / Cl_2 , Cl_2 vs. UV $_{3.4d}$, Cl_2).

According to Weng et al. (2012), the concentration of nitrite in irradiated water samples is increasing after the depletion of chlorine, due to nitrate photolysis. Nitrite formation might increase chlorine consumption since nitrite is oxidized by chlorine to form nitrate (Diyamandoglu et al., 1990). However, no change could be detected in the chlorine consumption in the experiments with added nitrate (UV $_{1d}$ / Cl_2 , Cl_2 vs UV $_{1d}$ / Cl_2 / NO_3^- , Cl_2).

In the experiment with addition of hydrogen peroxide as radical initiator, the chlorine consumption was similar to the samples with prolonged UV exposure (UV $_{3.4d}$ / H_2O_2 , Cl_2 vs UV $_{3.4d}$, Cl_2).

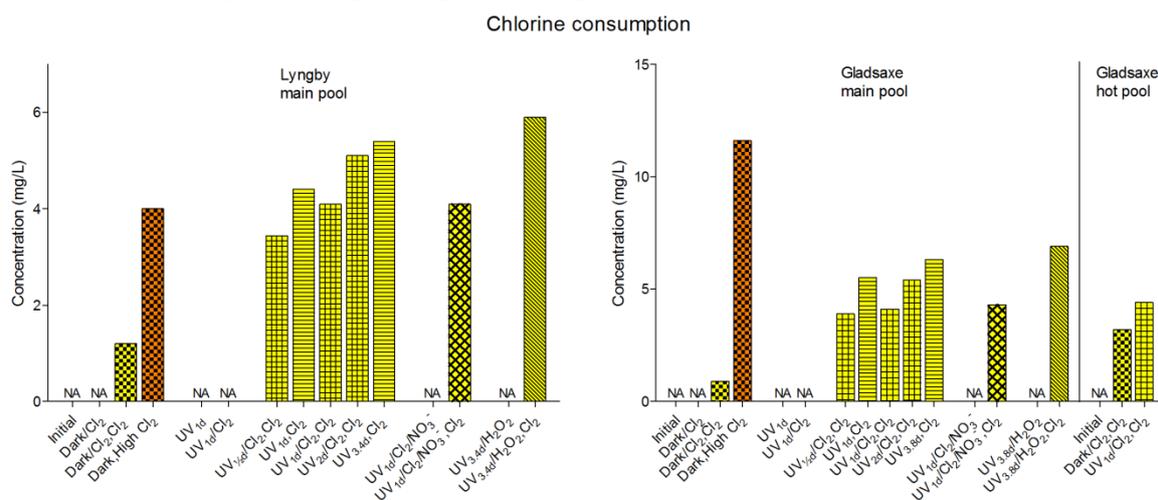


Figure 1. Chlorine consumption in 24h at 25 °C at the different experimental treatments for the three investigated swimming pools. The error bars represent the standard deviation of duplicate analysis.

Formation of volatile by-products

Effect of UV on trihalomethanes

The trihalomethanes only include the chlorinated and brominated trihalomethanes: chloroform, bromodichloromethane, dibromochloromethane and bromoform. We hypothesize that they are formed from the same precursor and the variation among the different species is due to the ratio of bromine to chlorine.

The investigated swimming pools were chlorinated and bromine mainly stems from a low concentration in the source water, thus chloroform was the most pronounced of the THMs (Figure 2). UV treatment of swimming pools has been suspected to create THMs directly in the UV chamber. However, comparing the initial concentrations with the solely UV treated samples, it was seen that the level of the four different THMs was not increase. Thus, the THMs were not formed directly during the UV irradiation. Actually, for the brominated THMs, a reduction was seen for the experimental treatments based exclusively on UV irradiation (UV_{1d}), compared to the initial value (Figures 2). Hansen et al. (2013b) have found that the direct photolysis of THMs increased with increasing amount of bromine incorporated. Therefore, bromoform was the easiest to photolyze, while chloroform was the most difficult (Hansen et al., 2013b). The level of the brominated THMs in the pool water was close to or under the quantification limit. However, the same tendency was found in our results.

Post-UV chlorination of water from a swimming pool that continuously uses UV treatment to control combined chlorine could not induce formation of most DBPs. Both, the matching induction of trihalomethanes from post-UV chlorination and simulated extended chlorination time, and the absence of inducible trihalomethanes in water from a continuously UV treated pool, indicate that literature reports of experimentally induced trihalomethane formation by UV might results from a kinetic increase in formation by UV. However, this does not imply that higher trihalomethane concentrations would occur in pools that apply continuous UV treatment.

The bromine fraction of the halogens in the formed trihalomethanes increased with UV dose, which indicates that UV breaks bromine atoms from larger molecules that participate in trihalomethane production during the post-UV chlorination.

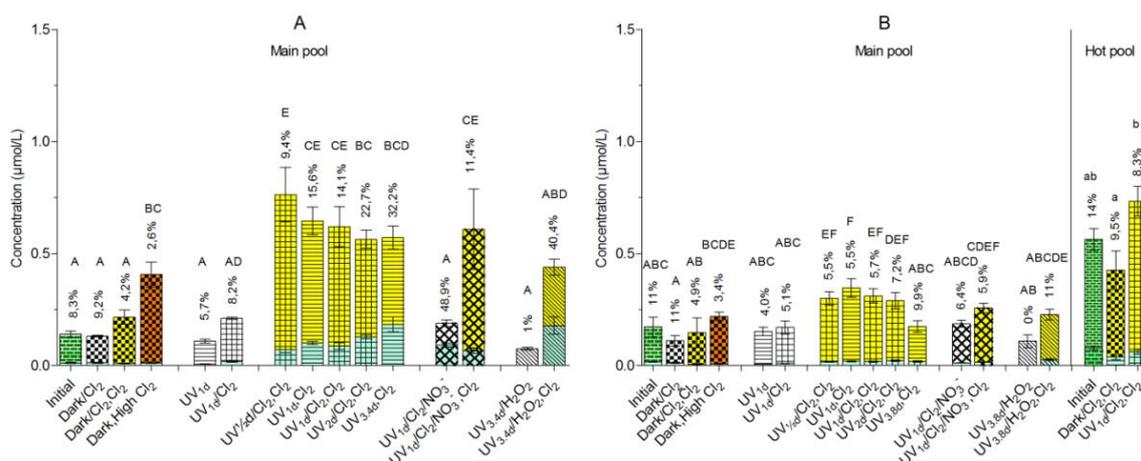


Figure 2. Total trihalomethane formation at different experimental treatments of swimming pool water from A) Lyngby swimming pool and B) Gladsaxe swimming pool. The light green area indicates the amount of bromine incorporated in trihalomethane, which also are given as % bromine per trihalomethane on top of the bar.

The THMs were not formed directly by UV, however, in post-UV chlorinated samples, an increased amount of THM was found. A likely explanation is that UV treatment makes the organic compounds in the pool water more reactive toward chlorine and thereby can act as precursor for

THM formation. So when the activated organic matter meets chlorine again, THMs were formed. Cimetiere and De Laat (2014) found a similar increase in THM formation when chlorinating after UV exposure by low pressure lamp. Increasing the UV exposure time (UV_{1/2d}/Cl₂,Cl₂; UV_{1d}/Cl₂,Cl₂; UV_{2d}/Cl₂,Cl₂; UV_{3.4d},Cl₂) decreased the chloroform formation and increased the formation of the brominated THMs (Figure 2) indicating that the activated organic matter was further photodegradable. The bromodichloromethane was found in higher concentrations than dibromochloromethane and bromoform due to that the available bromine was limited and there had to be more bromine present in order to form dibromochloromethane and bromoform than bromodichloromethane.

It has been hypothesized that UV only accelerates the chloroform formation and that over time the amount of chloroform that is formed in a swimming pool is the same with and without UV (Kaas and Andersen, 2007), since the amount of precursor is limited and the main removal process for pollution is oxidation and mineralization by chlorine (Judd and Bullock, 2003). This was examined by adding a higher chlorine dose in non-irradiated samples (Dark, High Cl₂) to simulate long-term residence time of the water in the basin. In most cases, a significant difference was not found in chloroform levels for post-UV chlorinated samples (UV_{1/2d}/Cl₂,Cl₂; UV_{1d}/Cl₂,Cl₂; UV_{2d}/Cl₂,Cl₂; UV_{3.4d},Cl₂ and UV_{3.8d},Cl₂) and for the samples with simulated longer residence time (Dark,High Cl₂: Figure 2). Thus, the obtained data supported the hypothesis.

Furthermore, examining the THMs as a sum of the four THMs (total trihalomethane; TTHM), it was seen that the post-UV chlorinated sample (UV_{1d}/Cl₂,Cl₂) was not significantly different from the samples with simulated long-term residence time (Dark,High Cl₂: Figure 2).

The percentages shown in TTHM (Figures 2) represented the amount of bromine incorporated in the TTHM. The bromine incorporation increases with increasing UV exposure (UV_{1/2d}/Cl₂,Cl₂ vs. UV_{1d},Cl₂; UV_{1d}/Cl₂,Cl₂ vs. UV_{2d}/Cl₂,Cl₂ vs. UV_{3.4d},Cl₂ and UV_{3.8d},Cl₂), especially for the main pool in Lyngby. A likely explanation is that UV broke down the bonds between the organic carbon-based compound and bromine (Figure 3), so that bromide was liberated into the water. The UV treatment also contributed to carbon activation, making it more reactive. When chlorine was added after UV exposure, bromide was oxidized to hypobromous acid (White, 1992), which reacted with the newly formed THM precursors in competition with chlorine, to form Br-Cl-DBPs. Thus, bromine was transferred from the larger brominated molecules to smaller volatile compounds like bromodichloromethane, dibromochloromethane and bromoform.

The experimental treatment of the water from the hot therapy pool in Gladsaxe showed that there

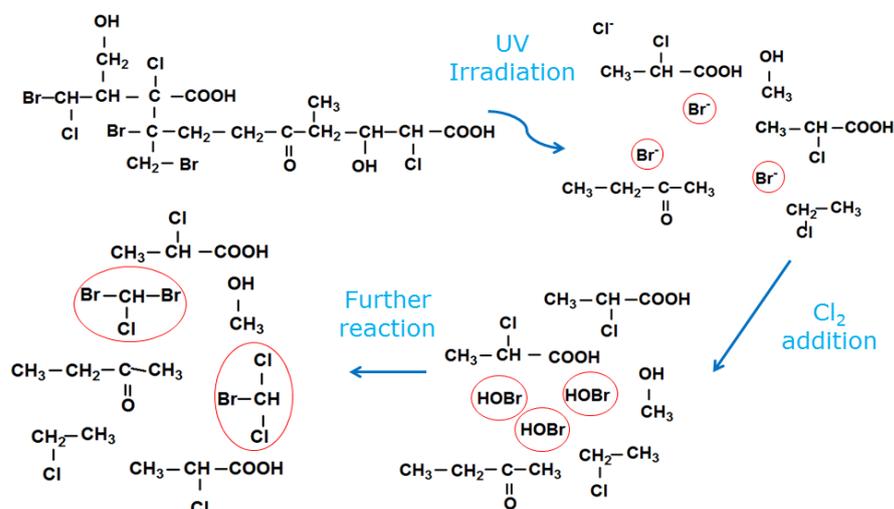


Figure 3. Schematic representation of brominated species formation.

could be slightly more induced TTHM by post-UV chlorination, compared to initial, however this was not significant. The hot water therapy pool had UV as a part of the water treatment to decrease the combined chlorine levels. These results also supported the hypothesis that UV accelerated, but not increased, the THM formation.

Effects of radicals on DBP formation

Hydroxyl radicals from ozone based AOPs have previously been found to activate organic matter in swimming pool water, which formed increased amount of THM when subsequently chlorinated (Glauner et al., 2005). During UV treatment, hydroxyl radicals can be produced by several processes such as photolysis of chlorine, hydrogen peroxide, or nitrate.

To investigate the effect of radicals on the DBP formation, experiments with addition of nitrate, hydrogen peroxide or chlorine were performed. Concerning the effect of either nitrate or hydrogen peroxide on DBP formation, no significant change in the concentrations of TTHM (Figures 2) was observed.

An insignificant change in the concentration of the investigated DBPs was observed for direct photolysis (UV_{1d} vs. UV_{1d}/Cl_2). For the post-UV chlorinated samples, the addition of chlorine before the UV treatment did not significantly affect the formation of the investigated DBPs (UV_{1d}, Cl_2 vs. $UV_{1d}/Cl_2, Cl_2$; Figures 2). Thus, direct formation of DBPs during the UV irradiation by reaction with chlorine radicals appeared unimportant.

CONCLUSION

- UV treatment followed by chlorination amplified THM formation
- Radicals do not significantly affect the THM formation
- THMs are not formed in the UV reactor but in secondary reactions that occur after chlorine addition
- UV treatment amplified the fraction of brominated THM
- UV accelerates THM formation but does not clearly increase the total amount formed

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