

Influence of medium pressure UV lamp in hot tub water treatment on disinfection by-products concentration

Agnieszka Włodyka-Bergier*, Tomasz Bergier

Department of Environmental Management and Protection, Faculty of Mining Surveying and Environmental Engineering, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland, Tel. +48 12 617 47 57; Fax: +48 12 617 50 76; emails: wlodyka@agh.edu.pl (A. Włodyka-Bergier), tbergier@agh.edu.pl (T. Bergier)

Received 17 October 2019; Accepted 30 March 2020

ABSTRACT

The article presents the results of the research on the influence of medium pressure UV lamp on the concentration of disinfection by-products (DBPs) in hot tub water. The lamp was installed in the water treatment system of the hot tub, located in the AGH swimming pool. The studies were conducted for 2 weeks. In the first week the lamp was switched off and water was treated by coagulation and pressure filtration on anthracite-sand filters after that disinfected with sodium hypochlorite. In the second week, treated water was additionally radiated by a medium pressure UV lamp, in an average dose of 205 mJ/cm². The water samples were taken every day from Monday to Friday. In these samples the concentration of the following parameters was measured: inorganics chloramines and halogenated organic DBPs [trihalomethanes (THM), haloacetic acids (HAA), and chloral hydrate (CH)]. The research results showed that the application of medium pressure UV lamp efficiently decreases the concentration of chloramines, however, in regards to organic DBPs it may cause a significant increase in the concentration of CH. The concentration of THM and HAA increased statistically insignificantly.

Keywords: Disinfection by-products; Swimming pool water; UV radiation

1. Introduction

Swimming water is treated in a closed cycle, in which usually organic matter is removed with rapid filtration on one- or multilayer pressure filters (after dosing coagulants) and then water is chlorinated. However such a system is sometimes incapable to guarantee the proper quality of water. For this reason, the low or medium pressure UV lamps are more and more often employed in swimming water treatment, prior chemical disinfection. The main reason for applying these lamps is to support the disinfection process [1–4] and to decrease the concentration of combined chlorine in swimming pool water [5–8]. Both low and medium pressure UV lamps can decrease the concentration of combined

chlorine by 50%–70% [8–10]. Generally inorganic chloramines (mono-, di- and trichloramine) may be degraded by UV radiation, however, the rate of this process depends on the UV wavelength. Afifi and Blatchley III [11] reported that the application of medium pressure UV lamp (dose 60 mJ/cm²) in swimming water treatment technology caused a decrease in the concentration of mono- and dichloramine about 1.5 times. In the case of a low-pressure lamp, these authors also observed the decrease in the concentration of these substances, but significantly lower. The concentration of trichloramine in the experiments by these authors was lower while a medium-pressure lamp was applied in comparison to low pressure one, however higher than in water only chlorinated. The research by Soltermann et al.

* Corresponding author.

[10] on model solutions showed that the rate of photodegradation of chloramine is higher with a higher number of N–Cl bonds, while irradiated with medium pressure UV lamp. In a case of the low-pressure UV lamp, the rates of removal of the mono- and dichloramine were similarly high. Inorganic chloramines are the primary by-product of pool water disinfection and can negatively affect the health of swimming pool users. In the case of mono- and dichloramine, such negative effects were not observed, but they can be precursors of nitrosamine, which is very harmful to health [12]. Trichloramine is more volatile than other inorganic chloramines and is easily transferred to pool air, thus inhalation is the dominant way of exposure to this compound [12–14]. Trichloramine is characterized by an irritating, strong odor and even brief exposure causes coughing or irritation of the skin, eyes, or respiratory tract, probably also asthma. This compound may also cause changes in biomarkers in the lungs, however, available toxicological data on trichloramine are limited [12,13,15]. Chloramines as inorganic compounds are difficult to remove in conventional pool water treatment processes, thus the use of UV lamps to reduce their concentration in pool water is so crucial.

In real facilities, water cycles in closed loops, thus water after irradiation is chlorinated, and water after chlorination is radiated. The constant process of by-products formation occurs, as well as their photodegradation. UV irradiation of chlorinated water causes the occurrence of an advanced oxidation process, which may influence the quantity and quality of organic matter, as well as inorganic substances [2,16]. Due to the reports by Soltermann et al. [10] the secondary processes, which are probably connected with the formation of hydroxyl radicals, play a crucial role in the degradation of trichloramine. The combination of UV and chlorine, as an advanced oxidation process, differently influences on organic matter in water than UV irradiation applied alone.

Water disinfection with UV, followed by chlorination, may cause also important changes in the concentration of halogenated organic water disinfection products [17,18]. UV radiation may also change a structure of natural organic matter, causing the increase in the concentration of molecules with low molecular weight, biodegradability, and a ratio of the hydrophilic fraction to hydrophobic one. The molecules of organic matter with high molecular weight, after UV irradiation of water, become more aliphatic, more carboxylic and carbonyl groups are generated. In water radiated with UV several compounds were identified, such as low-molecule carboxylic acids, acetic acids, keto acids, and aldehydes [4,17,19]. UV causes preferential degradation of organic matter in water and an increase of concentration chromophore compounds of low molecular weight [19]. Free radicals, formed as a result of advanced oxidation processes, react very rapidly with several chemical compounds, especially with aromatic ones [20], for this reason the concentration of aromatic compounds decreases in these processes, and some part of organic matter can be mineralized [21,22].

The experiments on the influence of UV radiation on the concentration of disinfection by-products (DBPs) in swimming water, conducted on the real facilities, are presented in only a few publications. Cassan et al. [9] in the research realized in the indoor swimming pool, in two-week series, found out that a medium pressure UV lamp applied in a

combination with chlorination caused the increase in the concentration of trichloromethane (TCM) and bromodichloromethane (BDCM), and the decrease of dibromochloromethane (DBCM) and tribromomethane (TBM). Kristensen et al. [8] in the research with low and medium pressure UV lamps did not observe an influence of UV on the concentration of trihalomethanes (THM). While Beyer et al. [23] in the research with a medium pressure UV lamp, observed the increase of the concentration of the sum of THM from 32–44 µg/L to 21 µg/L, after four-week treatment with UV technology. Afifi and Blatchley III [11] were conducting a three-year research project, in which during the first year water was only chlorinated, in the second one – additionally irradiated with a low-pressure UV lamp, and in the third one the chlorination was combined with low-pressure UV lamp. Their results showed that medium pressure UV lamp causes the decrease of concentration of several chlorination by-products in comparison with low-pressure UV lamp and chlorination alone. Exposure to even trace amounts of toxic micro-contaminants in pool water can affect the health of users. Kramer et al. [24] conducted the studies on concentrated pool water samples, using the UMU test on bacteria *Salmonella typhimurium*, and they received particularly high cytotoxic and genotoxic results for haloacetonitriles (HAN) and chloropicrin. Among the analyzed DBPs from the group of THM and haloacetic acids (HAA), genotoxic effects were observed for brominated THM, dibromo-, bromochloro- and dichloroacetic. In the case of chloral hydrate (CH), genotoxic and cytotoxic effects were observed only at very high concentrations, not occurred in real pool water (185 mg/L). In other studies Hansen et al. [14] conducted on a model pool water solution, genotoxicity, and cytotoxicity studies on Chinese hamster ovary cells showed that the most toxic effects were observed for HAN, lower for HAA, whereas for THM this kind of effect was not noticed. The addition of bromide ions caused a drastic increase in the cytotoxicity of the tested samples. Similar trends have been observed for genotoxicity.

There are no reports or articles regarding the application of medium pressure UV lamps in the water treatment technology of hot tub, which is a relatively difficult facility (high chlorine concentration, high temperature). For this reason, our goal in this article is to study the influence of medium pressure UV lamp on the quality of water in the hot tub, functioning in the AGH swimming pool. The analyzed dose of UV radiation was relatively high – it was approximately 205 mJ/cm². The experiments were conducted in two one-week series – in the first week the lamp was switched off, in the second one – switched on. The following parameters were analyzed in water: organic DBPs from the group of THM, HAA, and CH, as well as inorganic chloramines (mono-, di- and trichloramine). The utilitarian goal of this research is to evaluate if it is rational to use medium pressure UV lamps to treat water in the hot tub.

2. Materials and methods

The research was conducted on the real facility – the hot tub with hydromassage, installed on the AGH swimming pool facility, which is a complex of indoor swimming pools (Krakow, Poland). The basic technical parameters of the studied tub are given in Table 1.

Table 1
The technical parameters of study object – hot tub

| Parameter | Value |
|-----------------------------------|--|
| Dimensions | 3.82 m × 2.5 m; depth 0.9 m |
| Water cycle flow rate | 46 m ³ /h |
| Active volume of expansion tank | 10 m ³ |
| Coagulant dose ^a | 0.5–1.0 ml/m ³ |
| Filtration | multilayer pressure filter |
| Number of filters | 1 (dimension 1.4 m) |
| Filtration rate | 30 m/h |
| Water temperature | 32°C |
| UV lamp | Medium pressure UV lamp by BestUV |
| UV dose | 205 mJ/cm ² (201–209 mJ/cm ²) |
| Free chlorine concentration, mg/L | 0.7–1.0 |

^apolyaluminum chloride, the concentration of Al³⁺ 1.2%

To test the influence of the medium-pressure UV lamp on the quality of pool water, a two-week experience was carried out. In the first week, after water was replaced in the tub and in its technological system, the series of samples were taken while the UV lamp was switched off. Thus water was treated in a classic system, included coagulation with polyaluminium chloride, filtration on a multilayer rapid filter, disinfection with sodium hypochlorite. In the second week, water was replaced again. The UV lamp was switched on, and it was installed after rapid filtration and prior chemical disinfection. The AL1.1500 lamp by BestUV was used. It is a flow medium pressure lamp with one 1,500 W filament. The dose of UV radiation was controlled by the lamp power and water flow rate. The UV dose during the experiments was measured using the UV lamp built-in sensor and displayed on the control panel. A relatively high UV radiation dose (205 mJ/cm²) was used. The decision to conduct the experiments in one-week series was caused by the fact that water in the hot tub is exchanged at least once a week.

The water samples were taken from Monday to Friday, in both research week. Every day, 2 samples were taken to run double measurements of each analyzed parameter. In those samples, besides basic water quality parameters (nitrogen compounds, indicators of quantity and quality of organic matter), the following parameters were determined: free and combined chlorine, selected organic chloramines, halogenated organic DBPs (THM, TCM, BDCM, DBCM, TBM, CH, HAA, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA)). The water samples were also tested microbiologically; the total number of microorganisms was determined at 22°C (psychrophiles) and 36°C (mesophiles); R2A culture medium was used. Incubation time was 7 and 5 d, respectively for 22°C and 36°C. Prior to analysis the temperature of tested samples was adjusted to 25°C.

Halogenated organic by-products were analyzed with Trace Ultra DSQII GC-MS by Thermo Scientific (USA). The helium was used as a carrier gas. Separation of the compounds was done on a RxiTM-5ms capillary column by Restek (USA) (film thickness 0.5 µm, column length 30 m, column diameter 0.25 mm). THM and CH were extracted with methyl tert-butyl ether (MTBE) by liquid–liquid

method with the addition of sodium sulfate. HAA from the water was extracted with acid–liquid extraction with MTBE, then their acid esterification was conducted, using a solution of sulfuric acid in methanol (10%) at 50°C for 1 h. For THM and CH analysis on gas chromatography–mass spectrometry the chromatography column was heated up from 35°C (9.5 min) to 200°C (0 min) with a temperature rate of 40°C/min. For HAA analysis the chromatography column was heated up from 40°C (0 min) to 100°C (5 min) with a temperature rate of 40°C/min, and afterward to 200°C (0 min) with a rate of 8°C/min. The detection limit for all these compounds was 0.05 µg/L.

The concentration of free and combined chlorine was determined with a colorimetric method with N,N-diethyl-p-phenylenediamine (DPD). The concentration of mono-, di- and trichloramine was measured accordingly to the DPD/KI method [25]. Chlorine and chloramine concentrations were measured with Aurius 2021 UV-VIS spectrophotometer by Cecil Instruments (UK). The detection limit of this method was 0.03 mg/L. Dissolved organic carbon (DOC) was determined by the oxidation of organic matter in the liquid phase. The detection limit of this method was 0.3 mg/L. Specific ultraviolet absorbance (SUVA) was determined as the ratio of absorbance at 254 nm (measured with Aurius 2021 UV-VIS) and DOC. The concentration of total nitrogen (TN), ammonium nitrogen (N-NH₄), nitrite nitrogen (N-NO₂), and nitrate–nitrogen (N-NO₃) was determined photometrically with Nanocolor tests and Nanocolor UV-Vis spectrophotometer by Macherey-Nagel (Germany). Detection limits for nitrogen compounds were TN – 0.1 mg/L; N-NH₄ – 0.01 mg/L; N-NO₂ – 0.002 mg/L; N-NO₃ – 0.02 mg/L. The concentration of organic nitrogen was calculated as the difference between total and inorganic nitrogen. Conductivity and pH were determined with electrometric methods.

We studied if the medium pressure UV lamp, employed in the pool water treatment system, caused the changes in concentration of each analyzed DBPs on a statistically significant level ($p < 0.05$). The statistical analyses were performed with R Studio (Ver. 1.0.143). Shapiro–Wilk normality test and homogeneity of variance (Levene-type test by lawstat package) were done prior to the main

statistical analysis. In the cases of normal and homogeneous variance – analysis of variance with the post-hoc Tukey's HSD test was used. In all other cases, the Dunn test (from dunn.test package) was used.

3. Results and discussion

3.1. Basic and microbiological parameters

Table 2 presents the basic and microbiological parameters of swimming pool water taken from the studied hot tub, in options with the medium pressure UV lamp switched off and on.

Comparing the parameters of tub water quality in these two variants, the importance of the organic matter nitrification should be noticed. The concentration of organic nitrogen in the first experimental week was 0.55 mg/L, while in the second one – 0.84 mg/L. The concentration of organic carbon was similar in the first and second weeks (3.20 and 3.10 mg/L respectively). However, the SUVA parameter was lower in the Cl₂/UV variant, indicating a reduction of high molecular weight compounds and aromatic ones by UV radiation. The average concentration of combined chlorine was 0.43 mg/L in the first week (UV lamp off) and 0.22 mg/L in the second one (UV on). Polish Legal Regulations [26] regarding chlorine concentration (max. 0.3 mg/L) were met only when the UV lamp was used. UV radiation causes the formation of an advanced oxidation process (Cl₂/UV) hence the increase in nitrate–nitrogen concentration when the lamp was switched on. In only chlorinated water the nitrate–nitrogen concentration was 2.90 mg/L, but in water additionally radiated with UV lamp it was 3.48 mg/L; which corresponds to nitrate concentration of 10.77 and 12.92 mg/L, respectively. In Polish legislation [26], the difference between water concentrations in the basin and filling water cannot exceed 20 mg/L, thus the use of UV lamps did not raise nitrates to such a level that water quality standards were exceeded.

The average number of mesophilic bacteria was 41 cfu/mL in the variant with the medium-pressure UV lamp switched off and 6 cfu/mL with it switched on. While the average number of psychrophilic bacteria was respectively 127 cfu/mL and only 10 cfu/mL. Although UV light can degrade organic matter to smaller particles and increase the content of biodegradable organic carbon [4,17,19], UV radiation improves the microbial stability of water. The increased content of bacteria in the case of chlorination alone indicates that even in swimming pools equipped with water-air aerosol devices (including a hydromassage bath), elevated the concentration of free chlorine (0.7–1.0 mg/L) may be insufficient. Although the R2A medium was used for microbiological analysis, which results in significantly higher results of the number of microorganisms compared to a standard medium, it can be observed that after using the UV lamp the number of psychrophiles dropped to below the limit (100 cfu/mL) [26]. This shows that the use of a UV lamp can support the disinfectant effect of chlorine.

3.2. Chloramines

Fig. 1a presents how the concentration of combined chlorine changed along with the time of the experiment (a number of days since water exchange), while Fig. 1b is the share of individual inorganic chloramines in the analyzed variants of the technological system.

In a variant with the UV lamp switched off, the concentration of combined chlorine was increasing along with time – from 0.25 mg/L on the first day of the experiment to 0.54 mg/L on the last one. When the UV lamp was switched on, the concentration of combined chlorine was in a range between 0.19 and 0.25 mg/L, and its accumulation in time was not observed. Except for the first day, the statistically significant differences between the variants with the UV lamp on and off were observed for the concentration

Table 2
Quality of swimming pool with medium pressure UV lamp switched off (Cl₂) and on (UV/Cl₂)

| Water quality parameter | Unit | Cl ₂ | | | UV/Cl ₂ | | |
|-------------------------|----------------------|-----------------|---------|---------|--------------------|---------|---------|
| | | Mean | Minimum | Maximum | Mean | Minimum | Maximum |
| N-NH ₄ | mg/L | 0.03 | <0.02 | 0.03 | <0.02 | <0.02 | <0.02 |
| N-NO ₂ | mg/L | <0.002 | <0.002 | <0.002 | 0.004 | <0.002 | 0.01 |
| N-NO ₃ | mg/L | 2.90 | 2.50 | 3.90 | 3.48 | 2.40 | 4.20 |
| TN | mg/L | 3.48 | 3.20 | 4.10 | 4.34 | 3.10 | 4.80 |
| Organic N | mg/L | 0.55 | 0.17 | 0.97 | 0.84 | 0.48 | 1.08 |
| DOC | mg/L | 3.20 | 1.40 | 5.51 | 3.10 | 2.74 | 3.53 |
| SUVA | m ⁻¹ L/mg | 1.27 | 0.72 | 2.25 | 0.77 | 0.33 | 1.46 |
| pH | – | 7.19 | 7.14 | 7.23 | 7.22 | 7.18 | 7.30 |
| Free chlorine | mg/L | 1.28 | 0.78 | 2.01 | 1.32 | 0.58 | 1.84 |
| Combined chlorine | mg/L | 0.43 | 0.25 | 0.54 | 0.22 | 0.19 | 0.25 |
| THM | µg/L | 20.34 | 6.09 | 33.09 | 23.06 | 8.05 | 36.42 |
| CH | µg/L | 26.91 | 7.25 | 44.15 | 112.85 | 92.88 | 140.17 |
| HAA | µg/L | 49.37 | 38.71 | 59.73 | 60.73 | 40.01 | 78.49 |
| Mesophiles | cfu/mL | 41 | 15 | 94 | 6 | 2 | 16 |
| Psychrophiles | cfu/mL | 127 | 36 | 248 | 10 | 5 | 20 |

of combined chlorine. The difference in the concentration of combined chlorine between the results obtained in the first week of the experiment and the second one in which the lamp was switched on was statistically significant ($p = 0.0001$). The medium pressure lamp, installed in the hot tub water treatment system, proved to effectively remove all inorganic chloramines, but only in a case of mono- and dichloramine, these effects were statistically significant. The concentration of NHCl_2 decreased by 55% – from 0.29 mg/L in the first week to 0.13 mg/L in the second week, when the lamp was switched on. The average concentration of NH_2Cl in the variant with the UV lamp switched on was 0.06 mg/L and was 34% lower than one obtained for the first week (0.09 mg/L). These effects were statistically significant ($p = 0.0094$ and 0.0001 for mono- and dichloramine respectively). The studies have also shown the effective removal of trichloramine – up to 44% of NCl_3 was removed; from the concentration of 0.06 mg/L in the variant with UV lamp switched off to 0.03 mg/L with it switched on, however, this effect was not statistically significant ($p = 0.0888$). As far as UV trichloramine removal is concerned, the results of other authors are inconclusive. Soltermann et al. [10] showed that water, which was treated with a medium pressure UV lamp, before it flows to a swimming pool, has a significantly lower concentration of trichloramine than without a lamp. However in swimming pool water, such differences were

not observed. It may indicate that UV radiation effectively photodecays trichloramine, on the other hand it increases the reactivity of organic matter, through its degradation, which causes more intensive the trichloramine formation in chlorinated water. In the research by Afifi and Blatchley III [11] water, irradiated with a medium pressure UV lamp, contained more trichloramine than chlorinated water, but less than water irradiated with low-pressure UV lamp. In our study, presented in this article, lower concentrations of trichloramine in water treated with medium pressure UV lamp were compared to untreated water, but UV dose (205 mJ/cm^2) was almost 3.5 times higher than one used by Afifi and Blatchley III [11] (60 mJ/cm^2) in the research mentioned above. Thus an application of UV in large doses can effectively reduce trichloramine, even in such a difficult object as a hot tub with hydromassage.

3.3. Halogenated organic DBPs

Fig. 2a presents the total concentration of by-products in the subsequent days of observation in both water treatment options, while Fig. 2b is the average concentrations of the individual DBPs in the first week of the experiment, in which water was only chlorinated, and in the second one, in which water was irradiated with UV, prior its disinfection with the sodium hypochlorite.

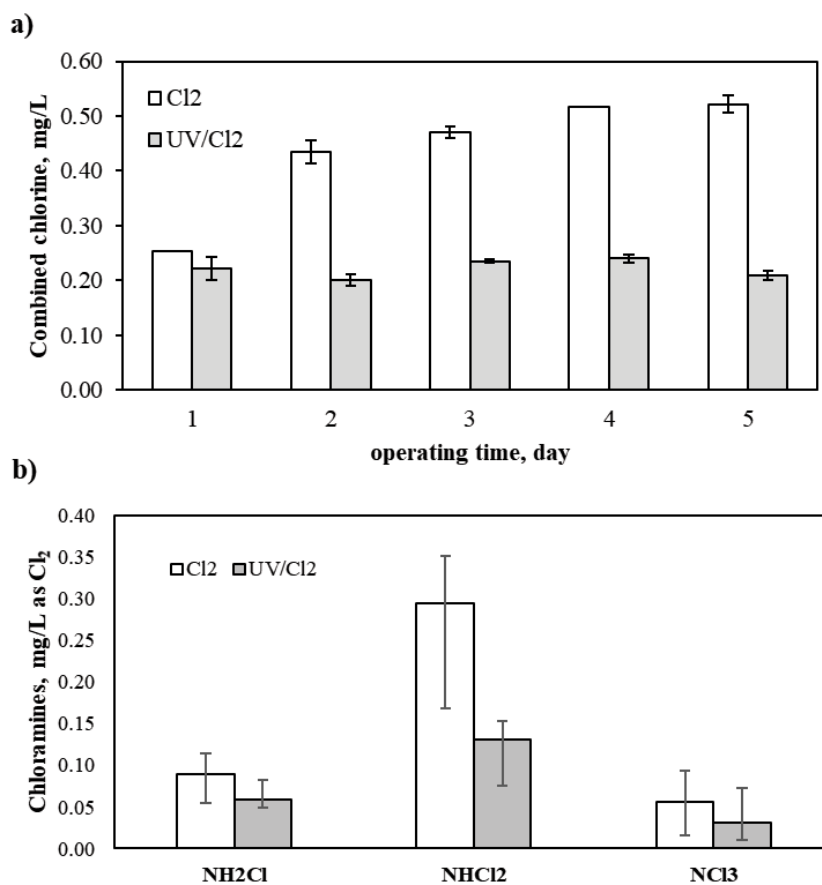


Fig. 1. Concentration of (a) combined chlorine and (b) chloramines in water samples with medium pressure UV lamp switched off (Cl_2) and on (UV/ Cl_2).

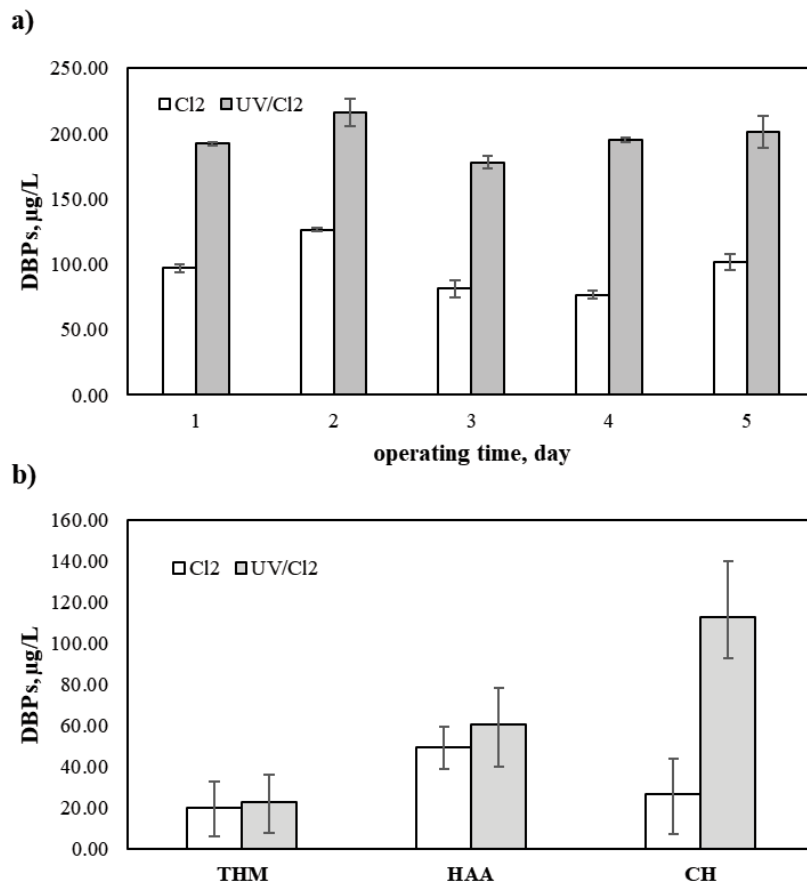


Fig. 2. Halogenated organic by-products in the water samples taken from the hot tub with medium pressure UV lamp switched off (Cl₂) and on (UV/Cl₂), (a) DBPs concentration in a function of time and (b) average concentrations of individual DBPs.

The accumulation of combined chlorine along with time can be observed in a variant without a UV lamp. However in a case of organic by-products, it was impossible to observe the clear trends of their accumulation or degradation. The average concentration of DBPs in an option with UV varied from 76.69 µg/L on the fourth day of the experiment to 126.58 µg/L on the second day. When the UV lamp was switched on, the lowest concentration of DBPs was observed on the third day (178.05 µg/L), while the highest on the second one (216.29 µg/L). Statistical analysis showed that the sum of DBPs in the first and second week of the experiment differed significantly ($p = 0.0001$). Fig. 2b shows the average concentration of halogenated by-products (THM, HAA, and CH) from the entire observation period, for both hot tub water treatment options. Medium pressure UV lamp had no significant effect on THM concentration in pool water ($p = 0.3251$). In the first week of observation, THM concentration was 20.34 µg/L, whereas, in the second week, when the medium pressure UV lamp was switched on, it was 13% higher (23.06 µg/L). In the case of HAA compounds, a slight increase in their concentration was observed, while they were UV irradiated. However, similarly, as for THM, this was not a statistically significant difference ($p = 0.2984$). The average concentration of HAA was 49.37 µg/L in an option with the UV lamp switched off and 60.73 µg/L with it switched on (23% increase). Considering

CH in these two treated water variants, the irradiation with UV lamp resulted in a large, statistically significant increase (by 319%) of its concentration ($p = 0.0001$). In the first week of the experiment, with the UV lamp switched off, the average CH concentration was 26.91 µg/L, whereas, in the second week, when the medium pressure UV lamp was switched on, the average concentration was 112.85 µg/L.

It is hypothesized that UV radiation only accelerates the formation of the by-product in pool water and that, at a sufficiently long reaction time, their content will be as much as without UV [27]. On the other hand, during UV irradiation the photodegradation of the formed DBPs (including CH) occurs, decreasing their concentration [7]. The increase of CH concentration, observed in our studies, indicates that the precursors, formed as a result of UV degradation of organic matter into smaller molecules, very actively form CH; processes of its decay played a minor role.

Fig. 3 presents the average concentrations of individual compounds in the THM and HAA groups for both water treatment options. The logarithmic scale was used, because of the large differences in presented concentrations.

Our studies showed an increase of TCM concentration (15%), a decrease of BDCM concentration (7%), and an increase of BDCM concentration (47%), as a result of UV irradiation. However the differences between the concentrations of these compounds in the first and second weeks

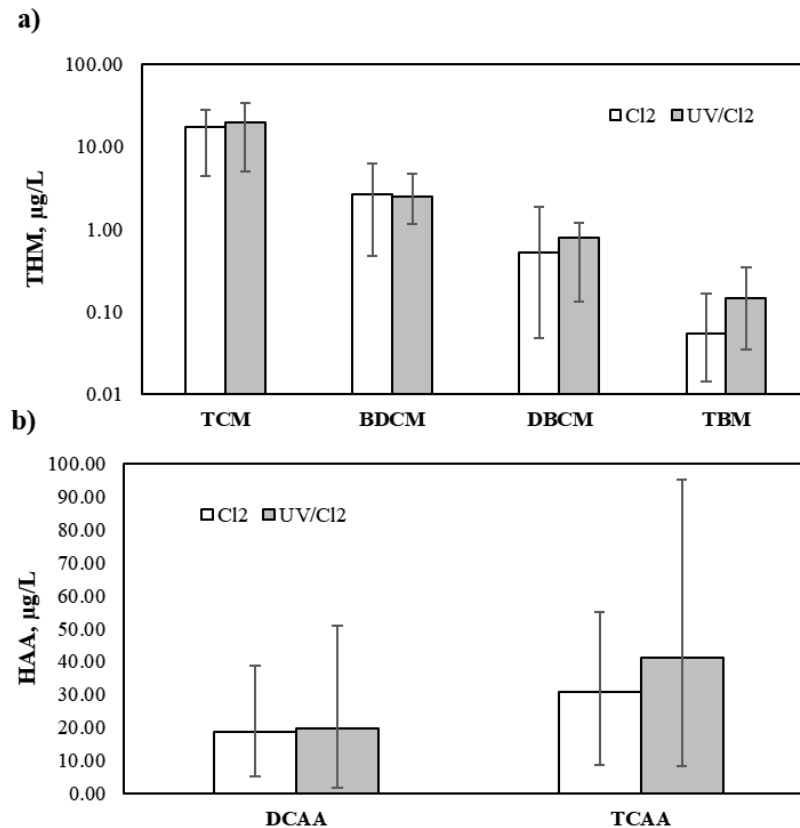


Fig. 3. Distribution of individual compounds in the groups of disinfection by-products (a) trihalomethanes and (b) haloacetic acids.

of the experiment were not statistically significant ($p = 0.534$ for TCM, 0.3812 for BDCM, 0.0562 for DBCM). In the case of TBM, a statistically significant increase in its concentration (169%, $p = 0.0063$) in water irradiated with a medium pressure UV lamp was observed. Despite the observed increase in THM concentration, the water quality standards were not exceeded, which according to Polish law are 100 mg/L for the sum of THM and 30 mg/L for TCM [26]. During the advanced oxidation process (UV/Cl₂) free radicals HO[•] and Cl[•] are formed [2,28]. Cassan et al. [9] consider that the increase of TCM concentration may be caused by the reaction of free chlorine radicals and organic matter, introduced with bathers, by breaking the C–H bond in organic compounds. TCM formation is very fast because the reaction rate of free radicals is very high [20].

Regarding the effect of UV radiation on the formation of brominated derivatives of THM, Spiliotopoulou et al. [27] consider that the UV radiation, emitted by the medium pressure lamp, breaks the bonds between the larger organic compounds and the bromine, thus bromides are released into a solution. It can be explained by the fact that carbon–bromine bond (280 kJ/M) is weaker than carbon–chlorine one (397 kJ/M) [29], so the possibility that UV radiation breaks C–Br bond are greater than for C–Cl one. If chlorine is added after UV irradiation, bromides are oxidized to the hypobromous acid, which is a very strong oxidant. HOBr reacts again with organic matter in water, competing with chlorine, and generate DBPs in a form of bromo- and bromo/chloro-derivatives. The reaction rate of hypobromous acid

with organic compounds is up to three times greater than for chlorine, therefore the bromine is transferred from the larger organic molecules to smaller ones [27,30]. The results of this study confirm this theory and the fact that high doses of UV radiation, emitted by the medium-pressure lamps, can increase the concentration of brominated THM.

The influence of UV radiation on the HAA potential formation was only studied in laboratory tests by Cimetiere and De Laat [6]. These authors irradiated a water sample with the low-pressure lamp and did not observe the unequivocal influence of UV radiation on the dynamics of HAA formation. However they observed the slight increase of ΣHAA , caused by UV radiation. The influence of UV radiation on HAA formation, as in the case of THM, is the result of free radicals' influence on organic matter, especially increasing its potential to form HAA and most likely photodegradation of compounds from this group. Our studies conducted on a hot tub with the medium pressure UV lamp showed an increase in HAA concentration, both for DCAA (5%) and TCAA (34%). However, the results, obtained for the variants with UV lamp switched off and did not differ statistically significantly ($p = 0.5000$ for DCAA was, $p = 0.2984$ for TCAA).

4. Conclusions

The presented studies have shown that the application of medium pressure UV lamps in the hot tub water treatment system can bring many benefits. UV lamp effectively

decreases the concentration of chloramines. Due to the UV disinfecting effect, the microorganisms constantly introduced into the pool water by humans are effectively removed. On the other hand, the constant UV irradiation of chlorinated water, which is the advanced oxidation process, forms the free radicals. They can degrade organic matter to the particles of smaller size, which becomes a precursor of the formation of the by-product, including THM, HAA, and CH. As our studies, carried out on hot tub, have shown the high doses of UV radiation, emitted by the medium pressure lamp (205 mJ/cm²), can significantly increase the concentration of CH (even about 300%).

Acknowledgement

The work was completed under AGH University of Science and Technology statutory research for the Department of Environmental Management and Protection.

References

- [1] WHO, Guidelines for Safe Recreational Water Environments, Swimming Pools, Spas and Similar Environments, Vol. 2, World Health Organization, Geneva, 2006.
- [2] M.J. Watts, K.G. Linden, Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water, *Water Res.*, 41 (2007) 2871–2878.
- [3] C. Zwiener, S.D. Richardson, D.M. de Marini, T. Grummt, T. Glauner, F.H. Frimmel, Drowning in disinfection byproducts? Assessing swimming pool water, *Environ. Sci. Technol.*, 41 (2007) 363–372.
- [4] B.A. Lyon, A.D. Dotson, K.G. Linden, H.S. Weinberg, The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment, *Water Res.*, 46 (2012) 4653–4664.
- [5] S.C. Weng, J. Li, K.V. Wood, H.I. Kenttämä, P.E. Williams, L.M. Amundson, E.R. Blatchley III, UV-induced effects on chlorination of creatinine, *Water Res.*, 47 (2013) 4948–4956.
- [6] N. Cimetiere, J. De Laat, Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: a lab-scale study, *Microchem. J.*, 112 (2014) 34–41.
- [7] K.M.S. Hansen, R. Zortea, A. Piketty, S.R. Vega, H.R. Andersen, Photolytic removal of DBPs by medium pressure UV in swimming pool water, *Sci. Total Environ.*, 443 (2013) 850–856.
- [8] G.H. Kristensen, M.M. Klausen, H.R. Andersen, L. Erdinger, F.R. Lauritsen, E. Arvin, H.-J. Albrechtsen, Full Scale Test of UV-Based Water Treatment Technologies at Gladsaxe Sportcentre – With and Without Advanced Oxidation Mechanisms, The Third International Swimming Pool and Spa Conference, London, March 2009.
- [9] D. Cassan, B. Mercier, F. Castex, A. Rambaud, Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool, *Chemosphere*, 62 (2006) 1507–1513.
- [10] F. Soltermann, T. Widler, S. Canonica, U. von Gunten, Photolysis of inorganic chloramines and efficiency of trichloramine abatement by UV treatment of swimming pool water, *Water Res.*, 56 (2014) 280–291.
- [11] M.Z. Afifi, E.R. Blatchley III, Effects of UV-based treatment on volatile disinfection byproducts in a chlorinated, indoor swimming pool, *Water Res.*, 105 (2016) 167–177.
- [12] F. Soltermann, T. Widler, S. Canonica, U. von Gunten, Comparison of a novel extraction-based colorimetric (ABTS) method with membrane introduction mass spectrometry (MIMS): trichloramine dynamics in pool water, *Water Res.*, 58 (2014) 258–268.
- [13] C. Schmalz, F.H. Frimmel, C. Zwiener, Trichloramine in swimming pools – formation and mass transfer, *Water Res.*, 45 (2011) 2681–2690.
- [14] K.M.S. Hansen, S. Willach, M.G. Antoniou, H. Mosbæk, H.-J. Albrechtsen, H.R. Andersen, Effect of pH on the formation of disinfection byproducts in swimming pool water – is less THM better?, *Water Res.*, 46 (2012) 6399–6409.
- [15] N. Bonvalot, P. Glorennec, D. Zmirou, Derivation of a toxicity reference value for nitrogen trichloride as a disinfection by-product, *Regul. Toxicol. Pharm.*, 56 (2010) 357–364.
- [16] J. Jin, M.G. El-Din, J.R. Bolton, Assessment of the UV/chlorine process as an advanced oxidation process, *Water Res.*, 45 (2011) 1890–1896.
- [17] Y.Y. Choi, Y.-J. Choi, The effects of UV disinfection on drinking water quality in distribution systems, *Water Res.*, 44 (2010) 115–122.
- [18] K.G. Linden, A.D. Dotson, H.S. Weinberg, B. Lyon, W.A. Mitch, A. Shah, Impact of UV Location and Sequence on By-Product Formation, Water Research Foundation, Denver, 2012.
- [19] W. Liu, Z.L. Zhang, X. Yang, Y.Y. Xu, Y.M. Liang, Effects of UV irradiation and UV/chlorine co-exposure on natural organic matter in water, *Sci. Total Environ.*, 414 (2012) 576–584.
- [20] R. Schwarzenbach, P. Gschwend, D. Imboden, *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, Hoboken, New Jersey, 2003.
- [21] Q. Han, Y. Wang, H. Yan, B.Y. Gao, D.F. Ma, S.L. Sun, J.Y. Ling, Y.B. Chu, Photocatalysis of THM precursors in reclaimed water: the application of TiO₂ in UV irradiation, *Desal. Water Treat.*, 57 (2016) 9136–9147.
- [22] X.R. Zhang, W.G. Li, E.R. Blatchley III, X.J. Wang, P.F. Ren, UV/chlorine process for ammonia removal and disinfection by-product reduction: comparison with chlorination, *Water Res.*, 68 (2015) 804–811.
- [23] A. Beyer, H. Wörner, R. van Lierop, The Use of UV for Destruction of Combined Chlorine, Fact File of UV in Swimming Pools, USF Wallace & Tiernan, 2004.
- [24] M. Kramer, I. Hübner, O. Rörden, C. Schmidt, Haloacetonitriles – Another Important Group of Disinfection Byproducts in Swimming Pool Water, Swimming Pool and Spa International Conference, London, 2009.
- [25] APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington, 1999.
- [26] Rozporządzenie Ministra Zdrowia z dnia 9 listopada 2015 r. w sprawie wymagań, jakim powinna odpowiadać woda na pływalniach. Dz.U. 2015 poz. 2016 – Regulation of the Minister of Health of 9 November 2015 on the Requirements to be Met by Swimming Pool Water, 2016 (in Polish).
- [27] A. Spiliotopoulou, K.M.S. Hansen, H.R. Andersen, Secondary formation of disinfection by-products by UV treatment of swimming pool water, *Sci. Total Environ.*, 520 (2015) 96–105.
- [28] Q. Zhao, C. Shang, X.R. Zhang, G.Y. Ding, X. Yang, Formation of halogenated organic byproducts during medium-pressure UV and chlorine coexposure of model compounds, NOM and bromide, *Water Res.*, 45 (2011) 6545–6554.
- [29] Y.J. Xiao, R.L. Fan, L.F. Zhang, J.Q. Yue, R.D. Webster, T.-T. Lim, Photodegradation of iodinated trihalomethanes in aqueous solution by UV 254 irradiation, *Water Res.*, 49 (2014) 275–285.
- [30] M.B. Heeb, J. Criquet, S.G. Zimmermann-Steffens, U. von Gunten, Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds – a critical review, *Water Res.*, 48 (2014) 15–42.