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Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool

Delphine Cassan [a,*], Béatrice Mercier [a], Françoise Castex [b], André Rambaud [c]

[a] UPRES 2991, Efficience et Déficience Motrices, Faculté des Sciences du Sport, Université Montpellier 1, 34090 Montpellier, France

[b] CNRS UMR 5160, Faculté de Pharmacie, B.P. 14491, Université Montpellier 1, 34093 Montpellier Cedex 5, France

[c] CNRS UMR 5569, Hydrosciences, Faculté de Pharmacie, B.P. 14491, Université Montpellier 1, 34093 Montpellier Cedex 5, France

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Abstract

The aim of our study was to determine the impact of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool. An indoor swimming pool was equipped with two medium-pressure UV lamps. We collected eight samples of water daily over a four-weeks period and measured total and free chlorine, pH, water temperature, bacteriological parameters, total organic carbon and trihalomethanes. During the first week, which served as control, medium-pressure UV lamps were turned off. During the next three weeks, medium-pressure UV lamps were kept on 24 h per day. The third week, we reduced the level of the injected chlorine into water, and the last week we also reduced the water renewal volume by 27%. Our results showed that bacteriological parameters remained within allowable french limits. When medium-pressure UV lamps were kept on, total, free and active chlorine levels were significantly increased ($P < 0.001$), whereas combined chlorine level were significantly decreased ($P < 0.001$ and $P < 0.05$, respectively). The levels of chloroform and bromodichloromethane were significantly increased when medium-pressure UV lamps were kept on ($P < 0.001$), whereas chlorodibromomethane and bromoform levels significantly decreased ($P < 0.05$ and $P < 0.001$, respectively). The additional formation of chloroform and bromodichloromethane may be explained by the increase in active chlorine and by radicalizing mechanisms initiated by UV radiation.

Keywords: Ultraviolet lamps; Chlorination; Chloramines; Trihalomethanes

1. Introduction

Swimming pool water needs to be disinfected in order to minimize the risk of microbiological pollution, to avoid outbreaks of waterborne diseases and to protect swimmers from infection. Traditionally, chlorine is used to disinfect swimming pools. This disinfectant must be present continually and in sufficient concentrations in

* Corresponding author. Tel.: +33 467 415 728; fax: +33 467 415 708.
E-mail address: delphine.cassan@univ-montp1.fr (D. Cassan).

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Nomenclature

$CHBr_2Cl$	chlorodibromomethane
$CHBr_3$	bromoform
$CHBrCl_2$	bromodichloromethane
$CHCl_3$	chloroform
DBPs	disinfection by-products
DPD	*N*,*N*-diethylparaphenylenediamine
THMs	trihalomethanes
TOC	total organic carbon
TTHM	total trihalomethanes

order to protect against survival of newly introduced pathogens.

Swimmers and all bathers release, into water, organic compounds, microorganisms and nitrogenous substances such as urea, creatinine coming from urine, perspiration, hair, mucus, saliva or skin particles, viruses, bacteria, cosmetics. Upon into water these substances produce, in reaction with chlorine, various compounds called disinfection by-products (DBPs) (Beech et al., 1980) like combined chlorine named chloramines and trihalomethanes (THMs).

Among chloramines, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3) are routinely measured in swimming pool water. Indeed combined chlorine maximal value allowable in chlorinated pool is 0.6 mg l^{-1} (JORF, 1981). Moreover chloramines are susceptible to induce respiratory, ocular and skin irritations in lifeguards and swimmers (Hery et al., 1995; Massin et al., 1998). The THMs such as chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) are rarely measured and no guideline specifies the total THMs concentrations allowed in swimming pool water. The relative concentration of different THMs depends on the disinfectant type. Chloroform is the major product when hypochlorous acid (HOCl) is used (Judd and Jeffrey, 1995). According to the literature, chloroform concentration in swimming pools ranges from 14 to 198 μg l^{-1}; the other THMs are present in lower values (Lahl et al., 1981; Aggazzotti et al., 1990, 1993; Cammann and Hubner, 1995).

In order to produce better quality water with a lower level of harmful chemicals, ultraviolet (UV) light treatment has been investigated. Traditionally, UV radiation is used to inactivate microorganisms by absorption. The germicidal wavelength is 253.7 nm (Morgan, 1989). Two types of lamps are used to disinfect swimming pool water: low-and medium-pressure UV lamps. The low-pressure lamps emit a maximum energy output at a wavelength of 254 nm and the medium-pressure lamps emit energy at wavelengths from 200 to 600 nm. To study the effects of UV radiation on DBPs, we have chosen the medium-pressure lamps because of their large spectral range.

The aim of the present study was to determine the effects of medium-pressure UV lamps radiation on the water quality in a chlorinated indoor swimming pool and to determine whether the level of the combined chlorine, injected chlorine and water renewal volume could be reduced. We investigated the effects of these lamps on physicochemical, chemical and bacteriological parameters.

2. Materials and methods

2.1. The swimming pool

This study was carried out in an indoor public swimming pool in Montpellier, France. The swimming pool installation is presented in Fig. 1. The pool (25×15 m) was approximately 1050 m^3 in volume. The circulation of water was about 360 m^3 h^{-1} and the water turnover time was about 3 h. Sodium hypochlorite was used as disinfectant without stabilizing agent. The pH correction was made by hydrochloric acid adjunction. The hydrochloric acid and sodium hypochlorite dosing pumps were automatically controlled by respectively a chlorine meter and a pH meter. The pH demand was determined at 7.5 and the chlorine demand via hypochlorite at 1.9 mg l^{-1}. The filtration system was composed of two sand filters with anthracite. The circulating drawing water was from both the base and the wall outlets of the pool. The mean of the water renewal was 54 m^3 per day. The pool water came from the public network. There were neither air flow nor dehumidifier. Academics students, high school pupils and swimmers from swimming clubs frequented the pool.

2.2. Medium-pressure UV lamps

Two medium-pressure UV lamps (UV MP 240, BIO-UV SA, Lunel, France) were installed on the water circuit, after the sand filters and before the dosing pumps of sodium hypochlorite and hydrochloric acid (Fig. 1). The pool was equipped with two lamps of 4 kW, giving a total nominal input of 8 kW. The UV output watts, at the germicidal wavelength of 254 nm, was 1.2 kW (15% of the initial input watts), with an average amount of UV-C of 145 mJ cm^2 and the transmittance of the water of the pool was 98% out of 10 mm.

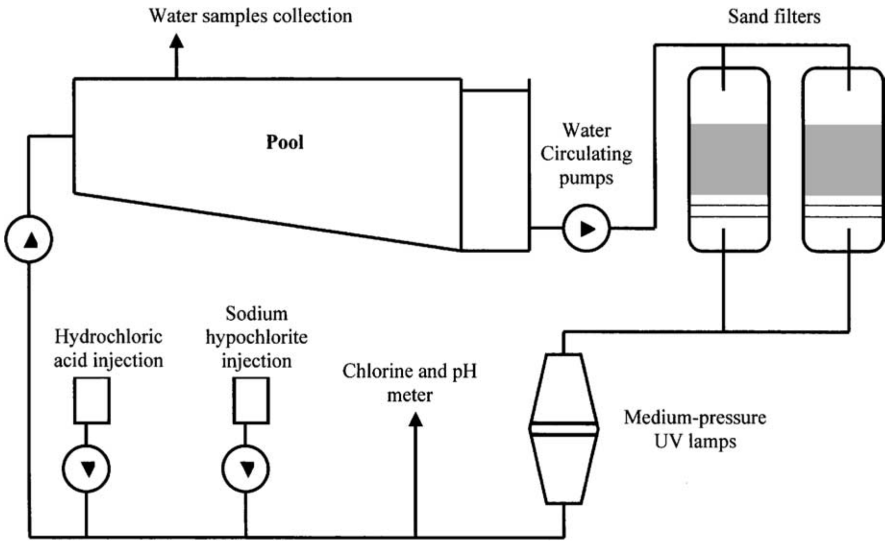

Fig. 1. Swimming pool installation.

2.3. Protocol

During the first week (W1), which served as control, the medium-pressure UV lamps were turned off and the injected chlorine into water determined at 1.9 mg l^{-1}. Beginning with the second week (W2) the medium-pressure UV lamps were kept on 24 h d^{-1} until the end of the study. The third week (W3), the injected chlorine into water was reduced to 1.4 mg l^{-1} by lowering the instruction of the chlorine meter. The fourth week (W4), the volume of water renewal was reduced to 27%. The pH was maintained at 7.5 over the 4-week period.

Each day and for the 4-week period, eight samples of water were collected at 2-h intervals. These samples were withdrawen directly in the pool, at 30 cm below the water surface, always at the same place, where the flow of water was the lowest, at the opposite of the water repression. The number of people using the swimming pool and the water renewal volume were noted.

2.4. Analysis

Differents parameters were measured by standard methods:

(1) *Physicochemical parameters:* the DPD (*N*,*N*-diethylparaphenylenediamine) method was used to determine total and free chlorine. The red color's intensity was analysed by photometry with operating wavelength at 520 nm (Palintest® Pooltest 25 Photometer). The activator solution provided is used to determine total chlorine (USEPA, 1983). Total chlorine is the sum of free and combined chlorine. Active chlorine was calculated in accordance with free chlorine, pH and water temperature. The pH was measured using phenol red indicator test; the yellow-to-red color's intensity was analysed by photometry (Palintest® Pooltest 25 Photometer). The chlorides was measured by chloridol indicator test, the clear-to-milky color's intensity was analysed by photometry (Palintest® Pooltest 25 Photometer). To avoid interassay variability, two different water samples, for each parameter, were assayed and the mean values were taken as the representative values.

(2) *Chemical parameters:* total organic carbon (TOC) was measured by a TOC meter (Tekmar–Dorhman Phoenix 8000 TOC Analyser) (NF EN 1484). The uncertainty of measurement was 9% with the amount of 2 mg C l^{-1} and 6% with 5 mg C l^{-1}. The THMs (chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$) and bromoform ($CHBr_3$)) analysis were carried out by gas chromatography according to the NF EN ISO 10301-3:1997 (AFNOR, 2001).

(3) *Bacteriological parameters:* revivable aerobic bacteria were measured by counting the colony grown at 37 °C in a nutrient agar culture medium (NF EN ISO 6222). A membrane-filtration method allowed the detection and enumeration of total coliforms (NF EN ISO 9308-1:2000), thermotolerants coliforms (NF T 90-414) and pathogenic staphylococci (NF T 90-421(A)) (AFNOR, 2001).

2.5. Statistical analysis

Data are presented as mean ± SD. Statistical evaluation of the raw data was performed using one-way

ANOVA followed by Scheffe's post-hoc test. After obtaining a statistically significant F test from the ANOVA, the Scheffe's test was used to determine the significant differences between group means in an analysis of variance setting. The P-value represents the probability of error that is involved in accepting our observed result as valid, that is, as "representative" of the population. The P-value of .05 was considered as a significance level of acceptation.

3. Results

The frequentation and the water temperature were not significantly different over the four-weeks period and the bacteriological quality of water was maintain within allowable French limits (JORF, 1981). Physicochemical, chemical and bacteriological parameters values over the four-weeks period are shown in Table 1.

3.1. The first week

The values are regarded as control. Free and combined chlorine values ranged from 1.26 to 2.2 mg l^{-1} and from 0.1 to 0.94 mg l^{-1}, respectively. Active chlorine values ranged from 0.74 to 1.58 mg l^{-1} while pH values ranged from 7.1 to 7.5. Chlorides values ranged from 145 to 310 mg l^{-1} Cl, while TOC values ranged from 1.6 to 2.1 mg l^{-1} C. Total THMs (TTHMs) values ranged from 28.3 to 43.7 μg l^{-1}, $CHCl_3$ ranged from 19.9 to 35.1 μg l^{-1}, $CHBrCl_2$ from 4.4 to 5.8 μg l^{-1}, $CHBr_2Cl$ from 2 to 3.5 μg l^{-1} and $CHBr_3$ ranged from 0.8 to 2.2 μg l^{-1}.

3.2. The second week: Effects of UV radiation only

Total chlorine ($P < 0.01$) and free chlorine ($P < 0.001$) mean values increased significantly. Combined chlorine mean value (range from 0.0 to 0.9 mg l^{-1}) decreased significantly by 31% ($P < 0.05$) while active chlorine mean value (range from 1 to 1.72 mg l^{-1}) increased significantly by 21% ($P < 0.001$). Total THMs values ranged from 85 to 105.9 μg l^{-1}; $CHCl_3$ and $CHBrCl_2$ mean values increased significantly by 185% ($P < 0.001$) and by 210% ($P < 0.001$) respectively, whereas $CHBr_3$ mean value decreased significantly by 48% ($P < 0.001$).

3.3. The third week: Effects of UV radiation and reduction of the injected chlorine into water

Total chlorine mean value decreased significantly vs W2 ($P < 0.001$) whereas free chlorine mean value increased significantly vs W1 ($P < 0.001$). Active chlorine mean value (range from 1.14 to 1.68 mg l^{-1}) increased significantly by 23% vs W1 ($P < 0.001$) and combined chlorine mean value (range from 0 to 0.4 mg l^{-1}) was reduced significantly by 64% vs W2 ($P < 0.001$) and by 75% vs W1 ($P < 0.001$). Data on TTHMs ranged from 68.6 to 115.6 μg l^{-1}; $CHCl_3$ mean value increased significantly by 115% vs W1 ($P < 0.001$) and decreased significantly by 24% vs W2 ($P < 0.001$); $CHBrCl_2$ mean

Table 1
Physicochemical, chemical and bacteriological parameters values (mean ± SD) over the four-weeks period

Parameters	Week 1		Week 2		Week 3		Week 4	
	Mean	±SD	Mean	±SD	Mean	±SD	Mean	±SD
Total chlorine (mg l^{-1})	2.4	0.2	2.6	0.3	2.3	0.1	2.3	0.1
Free chlorine (mg l^{-1})	1.7	0.2	2.1	0.2	2.1	0.2	2.1	0.2
Combined chlorine (mg l^{-1})	0.6	0.2	0.4	0.2	0.2	0.1	0.2	0.1
Active chlorine (mg l^{-1})	1.2	0.2	1.4	0.2	1.4	0.1	1.5	0.1
Chlorides (mg Cl l^{-1})	225.3	39.7	238.9	41.1	231.7	31.1	268.7	53.7
pH	7.2	0.1	7.2	0.1	7.2	0.1	7.0	0.5
Aerobic bacteria/ml	0.2	0.2	0.3	0.5	0.1	0.1	0.1	0.3
Total coliforms/100 ml	0	0	0	0	0	0	0	0
Thermotolerant coliforms/100 ml	0	0	0	0	0	0	0	0
Pathogenic staphylococci/100 ml	0	0	0	0	0	0	0	0
Total organic carbon (mg C l^{-1})	1.8	0.1	1.9	0.1	1.8	0.1	1.7	0.0
Total THMs (μg l^{-1})	35.9	6.1	95.2	6.6	74.7	14.2	75.7	11.6
Chloroform (μg l^{-1})	26.7	4.8	76.1	4.7	57.5	10.9	63.7	9.2
Bromodichloromethane (μg l^{-1})	5.1	0.5	15.9	1.4	14.6	2.9	9.2	2.1
Chlorodibromomethane (μg l^{-1})	3.1	0.4	2.7	0.4	2.2	0.3	2.2	0.3
Bromoform (μg l^{-1})	1.0	0.4	0.5	0.0	0.5	0.0	0.5	0.0
Water renewal volume (m^3)	54.4	11.4	54.6	17.4	72.2	9.9	40.0	24.8
Water temperature (°C)	26.9	0.3	27.4	0.6	27.5	0.5	27.3	0.4
Number of persons using the pool	237	102	269	64	296	88	219	70

Sample size $n = 40$ for physicochemical parameters; $n = 15$ for bacteriological parameters, TOC and chemical parameters.

value increased significantly by 185% vs W1 ($P < 0.001$) whereas $CHBr_2Cl$ decreased significantly by 29% vs W1 ($P < 0.001$) and by 21% vs W2 ($P < 0.05$); $CHBr_3$ mean value remained unchanged vs W2 and significantly decreased by 48% vs W1 ($P < 0.001$).

3.4. The fourth week: Effects of UV radiation, reduction of the injected chlorine into water and water renewal volume

Total chlorine mean value decreased significantly vs W2 ($P < 0.001$) whereas free chlorine mean value increased significantly vs W1 ($P < 0.001$). Active chlorine mean value (range from 1.34 to 1.87 mg l^{-1}) significantly increased by 32% vs W1 ($P < 0.001$) and combined chlorine mean value (range from 0 to 0.4 mg l^{-1}) decreased significantly by 67% vs W1 ($P < 0.001$) and by 52% vs W2 ($P < 0.001$). The chlorides mean value increased significantly by 19% vs W1 ($P < 0.01$) and the pH mean value decreased significantly compared to the first three weeks. The TOC mean value was reduced significantly by 11% vs W2 ($P < 0.01$). Total THMs values ranged from 63.8 to 102.7 μg l^{-1}; $CHCl_3$ mean value increased significantly by 139% vs W1 ($P < 0.001$). On the other hand, $CHBrCl_2$ mean value vs W2 and W3 ($P < 0.001$) and $CHBr_2Cl$ mean value vs W2 ($P < 0.05$) were significantly reduced; $CHBr_3$ mean value remained unchanged vs W2.

4. Discussion

In this study, the microbiological results were found to be in conformity with the quality required by the regulatory agency for public swimming pool in France (JORF, 1981). The number of persons using the swimming pool was not significantly different during the four-weeks period.

Medium-pressure UV lamps radiation in addition to chlorine led to an increase in active chlorine by photolysis of a part of combined chlorine. Consequently, reduction of the water renewal volume and of the injected chlorine into water were possible.

The removal of TOC amount (Week 4 vs Week 2) may be due to a partial mineralization of the dissolved organic material by UV radiation.

During the first week which served as control, we already observed the presence of THMs. According to the literature, the formation of THMs, without UV radiation, depends on several factors: the disinfectant type (Judd and Jeffrey, 1995), the amount of free chlorine (Montiel, 1980; Judd and Jeffrey, 1995; Kim et al., 2002), the amount of DBP precursors such as materials of human origin (Kim et al., 2002) and citric acid contained in urine (Larson and Rockwell, 1979), the amount of TOC (Chu and Nieuwenhuijsen, 2002), the number of bathers and turbulances which they cause (Aggazzotti et al., 1998; Chu and Nieuwenhuijsen, 2002), the increase or reduction of pH (Jiminez et al., 1993; Singer, 1999), the increase of temperature (Chu and Nieuwenhuijsen, 2002), the amount of carbon tetrachloride (CCl_4) present in chlorine (Montiel, 1980) and molecules contained in the public water supply network such as copper (Blatchley et al., 2003), bromides and ammoniacal nitrogen (Doré, 1989).

Our study highlights, for the first time, the additional formation of THMs and particularly of $CHCl_3$ and $CHBrCl_2$ in chlorinated water of an indoor swimming pool using medium-pressure UV lamps. This additional formation is stable over the last three weeks. However $CHBr_3$ and $CHBr_2Cl$ were reduced by the use of UV radiation. Today no European or French guideline specifies the TTHM rates allowed in swimming pool water, only the German Institut for Standardization (1997) suggest a guideline value for the swimming pool water (DIN 19643: THMs < 20 μg l^{-1}). Therefore we choose the World Health Organization (WHO, 1993) TTHM guideline values for drinking water as reference. The drinking water guidelines for the four THMs are 200 μg l^{-1} for chloroform, 60 μg l^{-1} for bromodichloromethane and 100 μg l^{-1} for both chlorodibromomethane and for bromoform. However, the WHO advises that TTHM be taken as a group, which is why national standards are normally set as total THMs. The WHO recommends that the sum of the ratio of the concentration of each trihalomethane to its respective guideline value should not exceed 1. Thus, in this study, TTHM levels were lower than those allowed by the World Health Organization for drinking water and correspond to the literature data (Lahl et al., 1981; Aggazzotti et al., 1990, 1993; Cammann and Hubner, 1995). Five hypothesis may explain the additional formation of THMs:

(1) The homolytic ruptures initiated by UV radiation (Montiel, 1980) on chlorinated water would lead to the formation of free radicals: $HO^\bullet$, $H^\bullet$ and $Cl^\bullet$. Chlorine radical ($Cl^\bullet$) would break the carbon–hydrogen bond (C–H) and would lead to the formation of $CHCl_3$ from human organic matter and active chlorine. This formation is very fast because free radicals life-time is very short. In addition, these reactions formed on the one hand the most stable species (species having the strongest bond energies) and on the other hand the species having the least important steric obstruction. Indeed, to break bromine–carbon bond (Br–C) 297 kJ mol^{-1} is required whereas 356 kJ mol^{-1} is needed to break chlorine–carbon bond (Cl–C). Bromine has more important steric obstruction than chlorine. Lastly, the more chlorine–carbon bond (Cl–C) the more stable the molecule would be. Energy to break bond and steric obstruction

may explain the relative concentration of the following compounds: $CHCl_3 > CHBrCl_2 > CHBr_2Cl > CHBr_3$.

(2) A progressive transformation of $CHBr_3$ into $CHCl_3$ and $CHBrCl_2$ by progressive substitution of bromine atom by chlorine atom may be possible by the following way:

$$CHBr_3 \xrightarrow{h\nu} C^{\bullet}HBr_2 + Br^{\bullet} \xrightarrow{Cl^{\bullet}} CHBr_2Cl$$
$$\xrightarrow{h\nu} C^{\bullet}HBrBr^{\bullet}Cl \xrightarrow{Cl^{\bullet}} CHBrCl_2$$
$$\xrightarrow{h\nu} C^{\bullet}HCl_2 + Br^{\bullet} \xrightarrow{Cl^{\bullet}} CHCl_3$$

However chloroform formation was not exclusively the consequence of the bromoform destruction because the molar assessment of the chloroform level was higher than the bromoform one.

(3) The reduction of $CHBr_3$ by UV radiation may be explain by the fact that $CHBr_3$ has a band absorption included in UV spectral lamp. Moreover to break bromine–carbon bond lowest energy is need than to break the others chlorinated species. It may result in $CHCl_3$ and intermediate brominated compounds ($CHBrCl_2$) accumulation. Indeed medium-pressure UV lamps radiation had removal effect on brominated compounds like bromate (Peldszus et al., 2004).

(4) The increase of active chlorine by photolysis of a part of combined chlorine, may explain this additional formation of chloroform. Indeed, as our results show, when the injected chlorine is reduced (W3), the $CHCl_3$ level significantly decreased.

(5) Lastly, UV radiation may increase the reactivity of organic materials of human origin and lead to this additional formation of THMs. Indeed, Magnuson et al. (2002) underlines the fact that UV radiation, with medium-pressure UV lamps, increases the reactivity of natural organic matter towards chlorination.

Further studies are necessary to check our hypothesis of additional formation of THMs in a chlorinated water with UV radiation.

5. Summary and conclusions

This study investigated the effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool. The following conclusions were drawn: (i) medium-pressure UV lamps radiation led to an increase in active chlorine by photolysis of a part of combined chlorine. Therefore it was possible to reduce the injected chlorine into water and the water renewal volume while maintaining the bacteriological quality of water within allowable limits (ii) medium-pressure UV lamps radiation induced a TOC removal which may result from its partial mineralization, (iii) UV radiation increased the level of total THMs, particularly $CHCl_3$ and $CHBrCl_2$, but removed $CHBr_3$ and $CHBr_2Cl$. However TTHM levels were lower than those allowed by the WHO for drinking water. This additional formation of $CHCl_3$ and $CHBrCl_2$ may be explained by the increase in active chlorine and by radicalizing mechanisms initiated by UV radiation.

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