



Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: A lab-scale study[☆]



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ABSTRACT

UV dechloramination has become a very popular process for reducing the concentration of chloramines in public swimming pool water. As the effects of this process on the formation of disinfection by-products (DBPs) remain a controversial issue, a bench-scale study has been undertaken to examine the impact of UV dechloramination on the formation of various DBPs. Four pool water samples were exposed to UV radiation at 254 nm in the presence of free chlorine ($[\text{Cl}_2]_0 = 3 \text{ mg L}^{-1}$) and then chlorinated in the dark for 24 h ($[\text{Cl}_2]_0 = 3 \text{ mg L}^{-1}$). High UV doses (up to 47 kJ m^{-2}) were used to simulate cumulative UV doses received by real pool waters. The data showed that UV irradiation led to a 90% photodecay of free chlorine for UV doses ranging from 13 to 20 kJ m^{-2} , to the formation of chlorate ion (0.05–0.11 mol of chlorate/mole of free chlorine decomposed) and to a significant increase in the chlorine demand of pool water during the post-chlorination step. UV exposure followed by post-chlorination did not significantly affect the formation of haloacetic acids, led to a small increase in the concentrations of adsorbable organic halogen (AOX) and of chloral hydrate and markedly increased the formation of trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane), dichloroacetonitrile, 1,1,1-trichloropropanone and chloropicrin.

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1. Introduction

Chlorine gas and sodium or calcium hypochlorite are the most common chemicals used for the disinfection of swimming pool water. According to the French regulations, the concentration of hypochlorous acid (HOCl) in water and the pH must be kept between 0.4 and $1.4 \text{ mg Cl}_2 \text{ L}^{-1}$ and 6.9 and 7.7, respectively [1]. Besides its disinfecting properties, chlorine reacts with contaminants introduced in water by the bathers to produce numerous undesirable disinfection by-products (DBPs), such as inorganic chloramines and organohalogenated by-products [2–8].

Abbreviations: AOX, adsorbable organic halogen; BCAA, bromochloroacetic acid; BCAN, bromochloroacetonitrile; BDCM, bromodichloromethane; CDBM, chlorodibromomethane; CH, chloral hydrate; DBAN, dibromoacetonitrile; DBCAA, dibromochloroacetic acid; DBPs, disinfection by-products; DCAA, dichloroacetic acid; DCAN, dichloroacetonitrile; DCP, 1,1-dichloropropanone; HAAs, haloacetic acids; HANs, haloacetonitriles; MCAA, monochloroacetic acid; TBM, bromoform (tribromomethane); TCAA, trichloroacetic acid; TCAN, trichloroacetonitrile; TCM, chloroform (trichloromethane); TCNM, chloropicrin (trichloronitromethane); TCP, 1,1,1-trichloropropanone; TOC, total organic carbon; THMs, trihalomethanes; TTHMs, total trihalomethanes.

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Among the inorganic chloramines, it is well-known that trichloramine (NCl_3) is very volatile and is a powerful irritant for eye and for the upper respiratory tract [9]. Exposure to trichloramine and to other volatile DBPs in swimming pool water can damage the lung epithelium of swimmers and may be involved in the asthma rise in children and lifeguards [10–12]. The concentration of trichloramine in the atmosphere of indoor swimming pool is not regulated. However, the French Institute of Occupational Health and Safety (INRS) has recommended a comfort limit value of $0.5 \text{ mg NCl}_3 \text{ m}^{-3}$ [9]. The concentration of combined chlorine in water must not exceed $0.6 \text{ mg Cl}_2 \text{ L}^{-1}$ in French public pools [1]. In order to meet this regulation, more than 500 French public pools have been equipped with a UV reactor during the last decade. Several UV systems equipped with Low Pressure (noted as LPUV) or with Medium Pressure (MPUV) lamps have been approved by the French Ministry of Health for dechloramination purposes [13]. In the pool water treatment chain, the UV reactor is inserted between the sand filter and the on-line injection point of the disinfectant. UV systems are usually operated at UV doses of 600 J m^{-2} . In current applications, UV dechloramination is an efficient process for decreasing the concentration of combined chlorine because pool water is continuously recirculated through the UV reactor [13]. For a turnover period of pool water of about 1.5 h, the cumulative dose of UV received by water is approximately equal to 10 kJ m^{-2} daily and therefore, the UV treatment will theoretically remove 90% of trichloramine after

one day of treatment (Table S1 in the Supplementary material). It must also be emphasized that UV dechloramination of swimming pool water will also decompose free chlorine because hypochlorous acid and hypochlorite ion absorb UV light [14]. In pure water, the photodecomposition rate of free chlorine at 254 nm is slower than the rates of photolysis of mono- and dichloramine and is significantly faster in the presence of organic solutes [14]. The mechanisms of photodecomposition of chloramines and free chlorine are quite complex and are not well elucidated. Recent works showed that inorganic chloramines are decomposed by UV light into inorganic radicals and nitrite ions as intermediates and into ammonium, nitrite, nitrate and nitrous oxide as stable end-products [15–17]. Free chlorine photolysis leads to the formation of hydroxyl radicals and chlorine atoms as transient species which can further react with free chlorine to produce chloride ions and other oxychlorine species [15,18–20].

Most of the reactions initiated by UV photolysis of chloramines and free chlorine are currently unknown but these reactions may affect the production of DBPs. To our knowledge, only four full-scale studies on the effects of UV dechloramination on the concentrations of DBPs in swimming pool have been published. The data obtained by Gérardin et al. [21] with reactors equipped with LPUV and MPUV lamps and by Cassan et al. [22] with a reactor equipped with MPUV lamps showed that UV dechloramination may increase the concentrations of trihalomethanes (THMs) in water by up to 250%. On the other hand, no significant effect of UV irradiation on THM concentrations was observed by [23] (LPUV and MPUV lamps) and by Vrillet [24] (LPUV lamps). It is difficult to explain the discrepancy between the conclusions of these studies because many factors can affect the production of THMs such as the pool attendance, hydraulic residence time, UV dose, UV wavelength, free chlorine concentration and loss of volatile DBPs by stripping.

In order to better understand the effects of UV dechloramination on the formation of DBPs, laboratory experiments have been carried out in the present study under fully controlled conditions. Four pool water samples were exposed to UV light in a photoreactor equipped with a LPUV lamp in the presence of free chlorine ($[\text{Free chlorine}]_0 = 3 \text{ mg L}^{-1}$) and at UV doses up to 47 kJ m^{-2} which correspond to typical cumulative UV doses received by real swimming pool waters for residence times ranging from 5 to 10 days. After exposure to UV light, pool water samples were post-chlorinated ($[\text{Free chlorine}]_0 = 3 \text{ mg L}^{-1}$). The effects of UV doses on the chlorine demands and on the formation of DBPs during the post-chlorination treatment have been investigated.

2. Materials and methods

2.1. Preparation of solutions

All solutions were prepared from reagent-grade chemicals and purified water delivered by a Millipore system (Milli-RX75/Synergy 1985). The stock solution of sodium hypochlorite ($\approx 3 \text{ g Cl}_2 \text{ L}^{-1}$) was prepared in purified water by dilution of a commercial solution of sodium hypochlorite (13% Acros Organics) and addition of hydrochloric acid to adjust the pH to about 8.5–9.0 and then stored in the dark at 4 °C. Free chlorine concentration in the stock solution was determined just before use by iodometric titration.

Dilute solutions of free chlorine ($3 \text{ mg Cl}_2 \text{ L}^{-1}$) were prepared in phosphate buffered water ($[\text{TOC}] \leq 0.1 \text{ mg C L}^{-1}$, $\text{pH} = 7.4$) and in tap water of the city of Poitiers ($[\text{TOC}] = 0.4 \text{ mg C L}^{-1}$, $\text{pH} = 7.4$) in order to compare the photodecomposition rates of free chlorine in various types of water.

2.2. Pool water samples

Four water samples were collected from three public indoor swimming pools between 8.00 am and 9.00 am, and used immediately upon arrival at the laboratory (Table 1). All the pools were treated by chlorine gas or sodium hypochlorite and none of them had a UV dechloramination system. Water samples were collected into a 10-L glass bottle. After collection, free and combined chlorine were not quenched by a reducing agent because the time elapsed between sampling and the arrival of the samples at the laboratory did not exceed 30 min. The concentrations of free and total chlorine, total organic carbon (TOC) and nitrate, the pH and the UV absorbance at 254 nm of the four pool water samples have been reported in Table 1.

2.3. UV photoreactor

Photolysis experiments were conducted by using a thermostated cylindrical batch reactor (Fig. S1 in the Supplementary material). All experiments were performed at $25.0 \pm 0.5 \text{ °C}$. The reactor was equipped with a LPUV lamp (Vilber Lourmat, 6 W) emitting at 254 nm. The UV lamp was turned-on during at least 20 min in a separated reactor in order to stabilize light output before introducing the lamp into the photoreactor. The volume of the aqueous solution in the reactor (V) and the angular path length of the reactor (l) were equal to 4.00 L and 6.25 cm,

Table 1

Composition of the four swimming pool water samples and experimental data obtained for the photodecomposition rates of free and combined chlorine and for the molar yields of chlorate in swimming pool waters.

Swimming water sample	Pure water	Tap water Poitiers	0410BLA	0421GAN	0427GAN	0428BEL
Sampling date		April 10, 2010	April 10, 2010	April 21, 2010	April 27, 2010	April 28, 2010
Disinfectant used		Cl ₂ gas	NaOCl	Cl ₂ gas	Cl ₂ gas	NaOCl
UV transmittance at 254 nm (cm ⁻¹)			98.6	98.7	98.8	98.7
Alkalinity (mg CaCO ₃ L ⁻¹)			103	66	67	95
Nitrate (mg L ⁻¹)			46.3	38.0	34.2	39.9
Chlorate (mg L ⁻¹)	0	<0.1	3.96	<0.1	<0.1	3.30
[Free Cl ₂]/[Total Cl ₂] (mg L ⁻¹) ^a	0	<0.05/<0.05	1.08/1.94	2.45/2.8	2.9/3.2	2.2/2.85
pH	7.4	7.2	7.63	7.57	7.57	7.43
TOC (mg C L ⁻¹)	≤0.10	0.35	5.54	2.75	2.82	5.13
[Free Cl ₂] ₀ (mg Cl ₂ L ⁻¹) ^b	3.0	3.0	3.0	3.0	2.9	2.8
[Combined Cl ₂] ₀ (mg Cl ₂ L ⁻¹) ^b	0	0	0.7	0.4	0.3	0.8
Irradiation time for 50% decay of free Cl ₂ (min)	11.75	11.75	6.0	7.5	6.5	4.5
UV dose for 50% decay of free Cl ₂ (kJ m ⁻²)	12.5	12.5	7.0	8.8	7.6	5.3
Irradiation time for a 90% decay of free Cl ₂ (min)	35.5	35.5	17	16	15.5	11
UV dose for a 90% decay of free Cl ₂ (kJ m ⁻²)	41.5	41.5	19.9	18.7	18.1	12.9
Irradiation time for 50% decay of combined Cl ₂ (min)	–	–	11	6.5	11	7
UV dose for a 50% decay of combined Cl ₂ (kJ m ⁻²)	–	–	12.9	7.6	12.9	8.2
Chlorate yield (mol ClO ₃ ⁻ formed/mol Cl ₂ decomposed)	0.09	0.10	nd ^c	0.10	0.05	0.11

^a Values measured immediately after the arrival of the samples in the laboratory.

^b Concentrations determined just before the beginning of the photolysis experiments.

^c The concentration could not be determined accurately in this sample.

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