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Effects of UV-based treatment on volatile disinfection byproducts in a chlorinated, indoor swimming pool

Mehrnaz Zare Afifi [a], Ernest R. Blatchley III [a, b, *]

[a] *Lyles School of Civil Engineering, Purdue University, West Lafayette, IN 47907, USA*
[b] *Division of Environmental & Ecological Engineering, Purdue University, West Lafayette, IN 47907, USA*

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ABSTRACT

Ultraviolet (UV) irradiation and chlorination are commonly used together in treatment of swimming pool water because they function as complementary disinfectants and because UV-based processes have been shown to promote photodecay of chloramines. However, UV-based treatment also has the potential to promote formation of some disinfection byproducts (DBPs). As a result, the overall effects of UV irradiation with chlorination on swimming pool chemistry remain unclear. To address this issue, a three-year study was conducted in a chlorinated, indoor swimming pool under three different operating conditions: conventional chlorination (1st year) which served as a control, chlorination augmented by MP UV irradiation (2nd year), and chlorination augmented by LP UV irradiation (3rd year). Water samples were collected from the pool for measurement of pH, temperature, total alkalinity, free and combined chlorine, eleven volatile DBPs, and urea concentration. After installation of MP UV, the concentrations of most volatile DBPs decreased; similar effects were observed after inclusion of LP UV. Collectively, these results imply an overall improvement in water quality as a result of the inclusion of the both UV systems. In general, MP UV was more efficient than LP UV for reducing the concentrations of most of the volatile DBPs measured in this pool. However, a need exists to standardize the application of UV systems in recreational water settings.

1. Introduction

Disinfection is necessary in swimming pools to minimize the risk of exposure to microbial pathogens. Traditionally, chlorine has been the preferred disinfectant in swimming pools; however, important drawbacks of swimming pool chlorination have been identified, including limited efficacy against some microbial pathogens, particularly C. *parvum* (Craik et al., 2001; Hijnen et al., 2006), and the formation of potentially harmful disinfection by-products (DBPs), including: trihalomethanes (THMs), chloramines (NH_2Cl, $NHCl_2$, NCl_3, and CH_3NCl_2), haloacetonitriles (HANs), and cyanogen halides, mostly via reactions between free chlorine and natural organic matter that swimmers introduce to the pool (*e.g.* sweat, urine, hair, skin particles, mucus, saliva and cosmetics) (Beech et al., 1980; Kim et al., 2002; Li and Blatchley, 2007; Kristensen et al., 2009; Weaver et al., 2009; LaKind et al., 2010).

In recent years, combined UV/chlorine treatment has been applied with increasing frequency to swimming pool water because the radiation from both common UV source types (low pressure [LP] and medium pressure [MP] Hg lamps) is known to be effective for inactivation of *C. parvum* (Craik et al., 2001; Hijnen et al., 2006). UV irradiation at germicidally-active wavelengths has also been shown to cause photodecay of chloramines; however, UV irradiation promotes the formation of dichloroacetonitrile ($CNCHCl_2$) and cyanogen chloride (CNCl), and also promotes free chlorine consumption (Cassan et al., 2006; Li and Blatchley, 2009; De Laat et al., 2010; Weng et al., 2012, 2013; Weng and Blatchley, 2013).

UV irradiation can alter organic matter in water by reducing molecular size, total organic carbon (TOC) content, and color (Corin et al., 1996). UV irradiation also has the potential to alter the concentrations of many DBPs in water (Weng and Blatchley, 2013; Weng et al., 2013), but reports to date of the effects of UV systems on water chemistry in chlorinated pool facilities have been largely anecdotal. In addition, there are uncertainties about the UV source type (*i.e.*, LP or MP Hg lamps) to use as a secondary

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* Corresponding author. Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN 47907, USA.
E-mail address: blatch@purdue.edu (E.R. Blatchley).

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disinfectant in swimming pool facilities.

Sharpless and Linden (2001) demonstrated that NO_3^- will photodecay when exposed to UV radiation at wavelengths of less than 240 nm to form NO_2^-. In the presence of free chlorine in solution, NO_2^- will be rapidly oxidized back to NO_3^- (Diyamandoglu et al., 1990; Margerum et al., 1994), thereby promoting free chlorine consumption. Therefore, NO_3^- represents a homogeneous photocatalyst for degradation of free chlorine when subjected to radiation with $\lambda < 240$ nm.

Liviac et al. (2010) and Plewa et al. (2012) illustrated that UV-based treatment may be beneficial for reduction of genotoxicity and cytotoxicity in chlorinated swimming pool water or drinking water treatment systems. No UV dose-dependent information was related to these toxicity responses, but MP-based systems yielded lower cytotoxicity than LP-based systems.

Liu et al. (2006) demonstrated that the formation of THMs, HAAs, and CNCl are promoted as a result of secondary UV exposure in chlorinated water. Cassan et al. (2006) reported an increase of $CHCl_3$ and $CHCl_2Br$ formation as a result of MP UV irradiation, while Beyer et al. (2004) reported a decrease in THM concentrations in a similar study. However, Weng et al. (2012) reported that $CHCl_3$ concentration was essentially unchanged as result of UV irradiation. Kristensen et al. (2009) presented results from a long term study for comparison of pool water treatment with and without UV irradiation; no effect on THM concentration in swimming pool water was observed to result from inclusion of UV treatment.

Shah and Mitch (2012) demonstrated that the formation of halonitromethanes was promoted with MP UV and pre/post chlorination. Regulated THMs and HAAs were not affected by UV pretreatment at disinfection doses (40–186 mJ/cm^2). However, in other studies that involved higher doses (*e.g.* 1000 mJ/cm^2), THM formation increased by as much as 30–40% (Reckhow et al., 2010; Lyon et al., 2012; Linden et al., 2012).

UV irradiation is effective for photodegradation of *N*-nitrosamines, including *N*-Nitrosodimethylamine (NDMA) (Stefan and Bolton, 2002). However, Soltermann et al. (2013) demonstrated that UV irradiation of pool water can promote NDMA formation because of the presence of chloramines and alkylamines. Therefore, despite the photolability of *N*-nitrosamines, UV treatment of waters containing precursors for *N*-nitrosamine formation can result in a net *N*-nitrosamine production.

The combined application of chlorination and UV irradiation also provides opportunities for formation of reactive intermediates, including $HO^\bullet$ (Nowell and Hoigné, 1992; Feng et al., 2007). However, the formation of $HO^\bullet$ from free chlorine photolysis is a relatively inefficient process, largely because of the low absorptivity of free chlorine species. At a dose of 60 mJ/cm^2, which is typical of UV systems used in swimming pools, HOCl concentration will be reduced less than 2% (Feng et al., 2007). Therefore, $HO^\bullet$ production from HOCl photolysis is likely to be an inefficient process with UV systems in pools.

In general, volatile DBPs will behave as intermediates in pools when UV/chlorine treatment is applied. The formation of some volatile DBPs (*e.g.*, inorganic chloramines, CH_3NCl_2, CNCl, and $CNCHCl_2$) involves reaction pathways that are opened by UV irradiation, when followed by chlorination. However, for each of these compounds, at least one mechanism of loss from solution is known to exist, including hydrolysis or oxidation (sometimes promoted by free chlorine), photolysis, and liquid → gas transfer. Therefore, it is expected that the concentrations of these compounds may increase immediately after inclusion of UV-based treatment and/or the introduction of DBP precursors, followed by a period in which the concentrations of these compounds decrease. However, the timescales for formation and decay of these compounds are known to vary widely. For some volatile DBPs, such as chloroform, photolysis is expected to be less important than volatilization (Hansen et al., 2013).

This research involved a three-year study to characterize water quality in a chlorinated, indoor pool facility under three operating conditions: conventional operation, based on chlorination, as a control condition (1st year), conventional chlorination augmented with MP UV irradiation for (2nd year), and conventional chlorination augmented with LP UV irradiation (3rd year). The time frame for each operating condition was selected to allow examination of seasonal changes (*i.e.*, heating, ventilation, and air conditioning [HVAC] system operation), diurnal changes, building operations, and different patterns of pool use (*i.e.*, bather load).

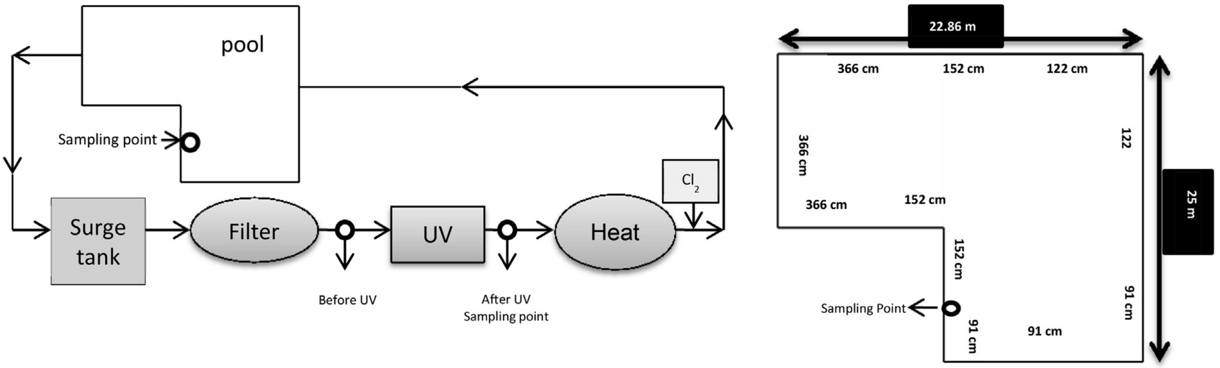
This study was designed to address two basic questions. First, should UV irradiation be included as part of swimming pool water treatment? And second, assuming that the answer to these questions is at least sometimes yes, which of the common sources of UV radiation (LP or MP Hg lamps) should be used?

2. Methods and materials

2.1. Facility description

Water chemistry was monitored at the indoor swimming pool facility five days per week during the academic year (nominally August–June) and once per week during summer (the pool was not open for use in the summer) under each of the operating conditions described above. In the 2nd and 3rd years of this experiment, UV reactors (MP and LP, respectively) were installed at the indoor pool as a secondary disinfection process. These reactors were provided by Engineered Treatment Systems, LLC (Beaver Dam, WI). The reactors were selected by the manufacturer for this application in a manner that is consistent with commercial swimming pool applications. The MP UV reactor was model ECF220-8V (EST Technology) that housed two MP lamps. The LP UV reactor was model SAG720A120 (*Chlorking* Sentry UV) that housed six LP UV lamps. Both UV reactors were operated under conditions that yielded a nominal UV dose of 60 mJ/cm^2 (253.7 nm equivalent), as defined by the internal, proprietary operating algorithms of the manufacturers. The UV reactors were installed in the recirculation system of the pool facility to treat the entire recirculated flow, immediately downstream of the two sand filters and before calcium hypochlorite dosing pump (Fig. 1a). LP lamps emit radiation predominately at a characteristic wavelength of 254 nm, while MP lamps emit photons in a wide range (*i.e.* 200–400 nm), which includes lower wavelengths ($\lambda < 240$ nm) where absorption by NO_3^- can be strong (Linden et al., 2012) and where chloramine photolysis has been shown to be more efficient (Li and Blatchley, 2009); therefore, N-DBP behavior may be more dynamic when MP UV is used with chlorine than when chlorination is used alone or with LP UV.

As indicated in Fig. 1b, this facility houses an L-shaped pool that contains 770 m^3 of water. One leg of the “L” is a six-lane, 22.86 m (25-yard) pool, while the other leg of the “L” is a six-lane, 25 m pool. The air space of this facility has a volume of approximately 3200 m^3, and the HVAC system at the facility is operated at roughly nine air changes per hour. All of the air brought into this facility by the HVAC system was from the outside (*i.e.*, no air recirculation). The mean hydraulic detention time for water in the pool was approximately 5 h. Free chlorine was applied to the pool in the form of $Ca(OCl)_2$ from an erosion feeder. Free chlorine feed rate was controlled by the signal from an ORP controller, which was set at a value of 814 mV. Tap water was added to the pool as needed to maintain water level. The pool has not undergone total water replacement (*i.e.*, emptying followed by re-fill) in several years; this operational approach is common among pools in the United States.



(a) (b)

Fig. 1. (a) Schematic of pool facility and UV/chlorine systems used to treat water. (b) Plan view of indoor swimming pool facility. The open circles indicate locations of water sample collection.

2.2. Sample collection and analysis

Water samples were collected in 25 mL Nalgene polyethylene bottles with polypropylene screw caps. Samples were collected from approximately 30 cm below the pool water surface without head-space. Samples were always collected at a fixed location to avoid complicating issues associated with spatial variability. One important consideration relates to the locations of chlorine control hardware and the sample collection point. As in most pools, chlorine control in this pool is accomplished by instrumentation that is included in the recirculation system. On the other hand, the samples were collected from 30 cm below the surface at a fixed location in the pool. This is relevant because pools are not well-mixed systems; in fact, they are strongly stratified. Consequently, measurements of controlled parameters, such as free chlorine or pH, in the pool are commonly quite different from those collected at the point of control. Following installation of the UV systems, water samples were also collected from taps located immediately before and after the UV reactor (Fig. 1a). Water samples were transported to the Environmental Engineering Laboratories at Purdue University and then subjected to a battery of analytical procedures (Table 1). Supporting material section SI.1 includes additional information regarding the analytical methods that were applied for this study.

The project was conducted in a manner that did not interfere with use of the pool. As such, the project did not involve control of several parameters that are likely to influence water quality, including: operation and maintenance of the pool, operation of the HVAC system, and use of the pool by swimmers. During the period of this study, the pool was used for swimming lessons and physical education classes by high school and middle school students as well as competitive swimmers on high school and club teams. Section SI.2 illustrates the nominal bather loading of the pool during the research period. The pool was closed during summers.

3. Results and discussion

Summaries of measurements of fundamental water quality parameters (pH, temperature, and, total alkalinity) are included in sections SI.3, SI.4, and SI.5, respectively. These parameters will influence the dynamic behavior of residual chlorine and DBPs in pools. For example, Hansen et al. (2012) and Singer (1999) showed that by reducing pH, THM formation was reduced while formation of HAN and NCl_3 were promoted. Lian et al. (2014) demonstrated that formation of CNCl and NCl_3 from chlorination of uric acid is favored at pH = 6.0 as compared to higher pH values. Blatchley and Cheng (2010) demonstrated that low pH conditions favor NCl_3 formation from chlorination of urea. Of particular interest was a slow but steady increase of pH from roughly 7–8 when the pool experienced consistently heavy use, then during summer pH steadily decreased when the pool was closed. This increase of pH will reduce the effectiveness of free chorine as an oxidant and disinfectant, but increase the rate of hydrolysis/oxidation of some nitrile compounds (*e.g.*, CNCl and DCAN). The shift of free chlorine speciation that would accompany this pH change will also influence the rates of DBP formation.

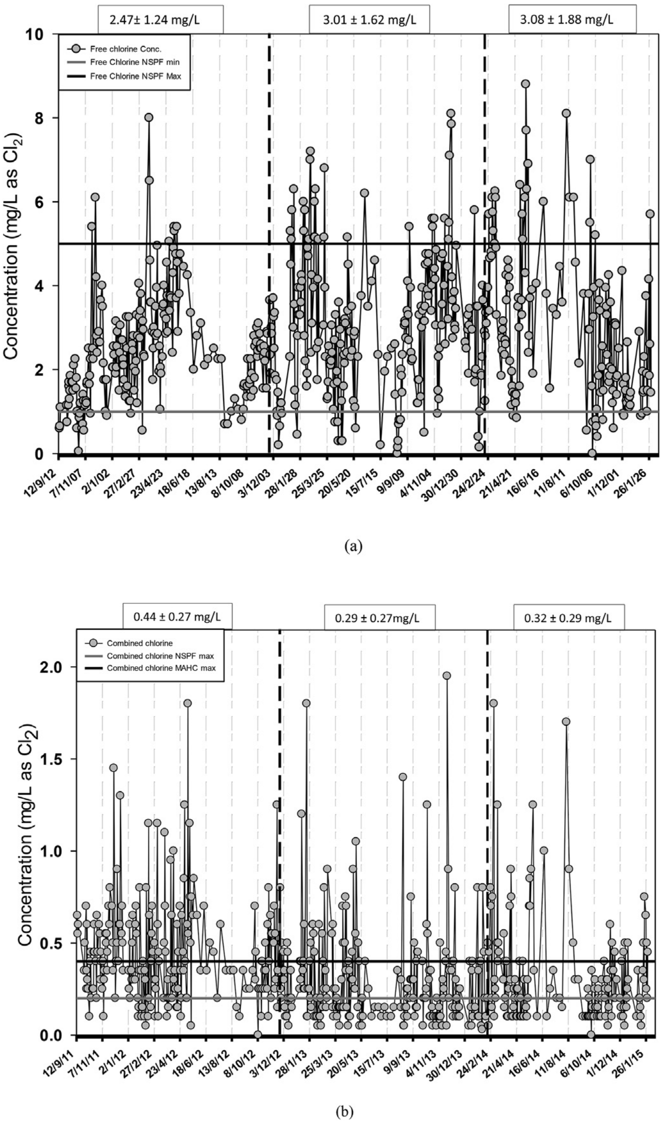
One of the motivations for inclusion of UV systems in pools is to reduce the concentrations of inorganic and organic chloramines. Germicidal UV radiation has been shown to cause photodecay of these compounds (Li and Blatchley, 2009; De Laat et al., 2010; Weng et al., 2012). However, UV irradiation has also been demonstrated to open reaction pathways that may lead to re-formation of chloramines following post-UV chlorination (Weng et al., 2013). To examine this issue, measurements and calculations of chloramine concentration changes across the LP UV system were compared. The calculations were based on the behavior of pure photolytic reactions in dilute solutions. For these conditions, the concentration of a photochemically-active compound following exposure to LP UV radiation can be calculated. Measured and calculated

Table 1
Analytical methods used for characterization of chemistry in swimming pool water samples.

Methods	Target analytes	References
Membrane Introduction Mass Spectrometry (MIMS)	Volatile DBPs including: NH_2Cl, $NHCl_2$, NCl_3, $CHCl_3$, $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$, CNCl, CNBr, $CNCHCl_2$, and CH_3NCl_2	(Weaver et al., 2009); (Shang and Blatchley, 1999); (Li and Blatchley, 2007)
Colorimetric DPD/KI with portable photometer	Free and combined chlorine	APHA-AWWA-WEF, 1995
Antipyrine digestion/colorimetric method	Urea	Prescott and Jones, 1969
Portable pH meter	pH and temperature	
Alkaphot (Palintest) tablets with portable photometer	Total alkalinity	

changes in chloramine concentration are summarized in section SI.6. For a single pass through the UV reactor, calculated and measured changes in chloramine concentration were subtle. More generally, measured changes in DBP concentrations across the UV reactor system (*i.e.*, single pass) were small (data not shown). Therefore, substantial changes in DBP concentrations associated with inclusion of UV systems in pools are attributable to the effects of multiple passes through the UV system, along with the effects of continuous exposure to +1-valent chlorine.

Time-course summaries of liquid-phase concentration measurements are presented in Figs. 2–10. These figures should be interpreted as follows: the dashed grey vertical lines indicate every 8th Monday during the sampling period. As appropriate, solid horizontal lines represent concentration limits or guidelines for each compound. The dotted horizontal lines indicate detection limits for volatile DBPs by MIMS. The dashed vertical lines indicate the dates when MP UV and LP UV was installed at the pool. Also included in these figures are calculated values of the mean ± standard deviation (described hereafter as “observed concentrations”) of measured concentrations for each compound over each time period of the study. Graphical summaries of the distributions of measurements for each of the three project periods are presented in the form of box-and-whisker diagrams for each compound in section SI.7. Comparisons between the three different water treatment operation conditions were performed by the student's t-test. A two-tailed p-value of <0.05 was considered statistically significant.



(a)

(b)

Fig. 2. Time-course measurements of (a) free and (b) combined chlorine concentration as measured by the DPD/KI spectrophotometric method.

3.1. Free and combined chlorine

The National Swimming Pool Foundation (NSPF) has established a guideline range for free chlorine concentration in pools of 1–5 mg/L (all residual chlorine concentrations reported as Cl_2), with an ideal range of 2–4 mg/L (NSPF, 2010). As shown in Fig. 2a, during year 1 the free chlorine concentration exceeded the NSPF guideline upper limit eight times and fell below the recommended minimum value 15 times. The observed free chlorine concentration was 2.47 ± 1.24 mg/L in the control period. For the period of inclusion of MP UV at the pool, free chlorine exceeded the NSPF maximum limit 30 times and fell below the minimum value 22 times, with observed concentration of 3.01 ± 1.62 mg/L. For the period of inclusion of LP UV at the pool, free chlorine exceeded the NSPF upper limit 23 times and fell below the lower limit 14 times, with observed concentration of 3.08 ± 1.88 mg/L. These free chlorine excursions had direct and immediate effects on the concentrations of several volatile DBPs in year 1; however, the excursions that were observed after inclusion of MP UV resulted in no or smaller increases in the concentrations of most DBPs that were measured in this study compared to first and third year.

The generally more erratic behavior of free chlorine following inclusion of UV reactors was apparently related to the ORP controller and also the difficulties that pool operators experienced in controlling free chlorine after the UV reactors were installed. In part, the variability in free chlorine concentration was probably attributable to the increased rate of free chlorine consumption that results from inclusion of UV, as described by Weng et al. (2012) and Cimetiere and De Laat (2014). The increase in free chlorine consumption with inclusion of UV is largely attributable to opening of new or faster reactions for chlorine to participate in than in the absence of UV (Weng et al., 2012). To a lesser degree, direct photolysis of free chlorine, which leads to the formation of OH• and Cl• radicals, may also have contributed (Feng et al., 2007; Watts and Linden, 2007). These radicals tend to react unselectively with natural organic matter (NOM) to promote formation of some DBPs (Metz et al., 2011). Cimetiere and De Laat (2014) observed that UV-based water treatment of chlorinated swimming pool promotes formation of by-products that are more reactive with chlorine than their respective parent compounds. Linden et al. (2012) reported that free chlorine consumption will not be significantly changed at typical disinfection UV doses (<186 mJ/cm^2) in once-through systems. At higher UV doses (186–1000 mJ/cm^2) or in recirculating systems, chlorine demand will increase; however, this behavior is likely to be site-specific. Watts and Linden (2007) illustrated that the chlorine demand for MP UV systems was higher than for LP UV systems, primarily because of differences in free chlorine photolysis rates between these UV system types. As described previously, UV systems that emit radiation with $\lambda < 240$ nm (*e.g.*, MP UV) will also experience photocatalytic decomposition of free chlorine because of the presence of NO_3^-. It is relevant to note that NO_3^- concentrations in pools can be quite high, with reported values as high as 129 mg/L (Li et al., 2016) (note: nitrate concentrations were not measured in this study).

The concentration of combined chlorine was statistically significantly lower after inclusion of MP UV (0.29 ± 0.27 mg/L) (p-value: 7.1×10^{-8}) and LP UV (0.32 ± 0.29 mg/L) (p-value:

3.1×10^{-5}) than in the control year (0.44 ± 0.27 mg/L). Despite the fact that combined chlorine concentration was slightly lower after inclusion of MP UV than LP UV (year 2 and 3 comparison), the difference was statistically insignificant (p-value: 0.56). Kristensen et al. (2009) reported that both MP UV and LP UV systems were effective for control of combined chlorine; however, LP UV was less effective than MP UV. NSPF (2010) has established an upper limit guideline of 0.2 mg/L (as Cl_2) for combined chlorine concentration, as measured using DPD/KI. More recently, a guideline value of less than 0.4 mg/L (as Cl_2) for combined chlorine has been established under the Model Aquatic Health Code (2014) (Fig. 2b). The concentration of combined chlorine fell below the NSPF recommended maximum value (0.2 mg/L) 22 times (10%) and fell below the MAHC guideline value (0.4 mg/L) 97 times (47%) during the control year, while combined chlorine concentration fell below NSPF maximum guideline 90 times (39%) and fell below MAHC guideline 164 times (72%) after inclusion of MP UV. After inclusion of LP UV, the combined chlorine concentration fell below the NSPF maximum guideline 55 times (36%) and fell below the MAHC guideline 111 times (73%). This behavior is consistent with the photodecay of inorganic and organic chloramines that has been reported for UV-based treatment (Li and Blatchley, 2009; Weng et al., 2012; Kristensen et al., 2009; Cassan et al., 2006).

Along with the continuous photodecay of combined chlorine by UV treatment, formation (or reformation) of combined chlorine may also be observed when precursors are being introduced to the pool (*i.e.*, when swimmers are in the pool) (Kristensen et al., 2009; Weng et al., 2013), which suggests that the (re)formation of combined chlorine may be faster than photodecay by UV treatment during periods of heavy pool usage. In this study, the average concentration of combined chlorine after inclusion of UV treatment was less than in the control year.

3.2. Trihalomethanes (THMs)

The formation of THMs without using UV treatment has been associated with several factors including: the type of disinfectant (Judd and Jeffrey, 1995), pH (Singer, 1999), temperature (Chu and Nieuwenhuijsen, 2002), free chlorine concentration (Montiel, 1980; Judd and Jeffrey, 1995; Kim et al., 2002), precursor type and concentration (Larson and Rockwell, 1979), TOC concentration (Chu and Nieuwenhuijsen, 2002), bather loading and their activities (Chu and Nieuwenhuijsen, 2002), the presence of carbon tetrachloride (CCl_4) in the chlorine supply (Montiel, 1980), and the presence of other constituents, such as copper (Blatchley et al., 2003), bromide, and ammoniacal nitrogen (Doré, 1989). As described previously, the literature includes conflicting information regarding the effects of UV on THMs.

Kristensen et al. (2009) reported a general trend of increasing maximum daily total trihalomethane (TTHM) concentration with increasing bather loading; however, the correlation between these parameters was poor. This weak correlation may be influenced by formation of TTHM by different pathways, as well as the other factors that affect THM formation (see list above). For example, TTHM formation due to direct reactions of free chlorine with bather's skin particles has been reported to be fast (Erdinger et al., 2005). On the other hand, TTHM formation from organic macromolecules that are released from bather's skin tend to be slow (Glauner et al., 2004).

THMs measured in this study included chloroform, dibromochloromethane, dichlorobromomethane, and bromoform. However, the concentrations of dichlorobromomethane and dibromochloromethane in the target pool were consistently low or below the detection limit in all samples, so measured values of the concentration of these compounds are not included herein.

Chloroform was the dominant THM by mass. Fig. 3 illustrates time-course chloroform concentration measured by MIMS in this study. The chloroform concentration exceeded the Danish and German standards for the maximum concentration in swimming pools in almost all samples. As described earlier, THM formation can be promoted at alkaline pH conditions (Singer, 1999; Hansen et al., 2012). Interestingly, despite the fact that higher pH and free chlorine excursions occurred more often after inclusion of UV reactors (year 2 and 3) than in the control year, the concentration of chloroform tended to be lower and less variable in the second and third year than in the control year. The observed chloroform concentration in the control year was 74.51 (±36.88) μg/L, whereas after inclusion of MP UV and LP UV these values decreased to 60.22 (±24.04 μg/L) and 52.19 (±24.53 μg/L), respectively (p-values: 4.21×10^{-6} for MP UV and 4.46×10^{-11} for LP UV compared to control year). Liu et al. (2006) observed the concentration of chloroform to be generally higher under MP UV water treatment than LP UV water treatment, which is consistent with this study (p-value: 2.40×10^{-3}). This observation can be explained by the polychromatic emission pattern of MP UV lamps which includes UVA (315–400 nm) and UVB (280–315 nm) radiation. It has been reported that UVA and UVB irradiation can generate lower molecular weight organic acids from cleavage of large natural organic matter molecules (Dahlén et al., 1996). In this study, LP UV irradiation was more effective than MP UV for decreasing chloroform concentration.

Cassan et al. (2006) observed promotion of chloroform formation after inclusion of MP UV and suggested that the additional formation of chloroform could be explained by reactions with Cl• radicals produced through the photolysis of free chlorine. However, other studies have indicated that OH• radical is the predominant photo-oxidant from free chlorine photolysis, while the accumulation of Cl• radicals is negligible in the presence of organic compounds acting as radical scavengers (Nowell and Hoigné, 1992; Feng et al., 2007; Watts and Linden, 2007). Zheng et al. (1999), and Nowell and Hoigné (1992) reported reductions of TTHM concentration by using UV irradiation in pre-chlorinated drinking water due to both lower free chlorine concentration to react with organics and degradation of organics from the OH• radicals. Spiliotopoulou et al. (2015) reported no effect of UV irradiation on chloroform concentration in water samples with and without free chlorine present. In addition, in a long-term study of a public pool by applying both UV treatment and without UV treatment, Kristensen et al. (2009) showed no effect of UV on THM

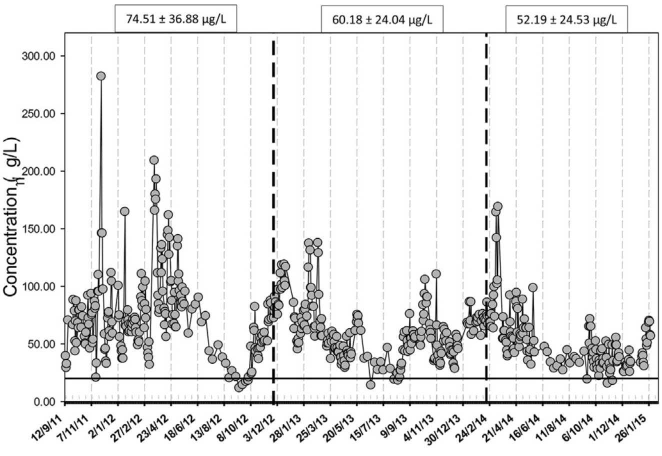


Fig. 3. Time-course measurements of chloroform ($CHCl_3$) concentration. The solid horizontal line indicates the Danish and German standards of 20 μg/L.

concentrations in a pool that was treated by several types of UV reactors. Beyer et al. (2004) reported a decrease in THM concentrations in a similar study.

Among the four THMs, brominated THMs are more effective at absorbing UV radiation between 200 and 300 nm than $CHCl_3$ (Nicole et al., 1991; De Laat et al., 1991) (see section SI.8). As shown in Figure SI.8, as bromination increases, molar absorptivity increases as well. The effect of this behavior is that brominated THMs are more susceptible to UV photodegradation than $CHCl_3$ (Chen et al., 2010; Lekkas and Nikolaou, 2004; De Laat et al., 1991).

The bromoform concentration decreased by applying MP UV from 1.26 (±2.99 μg/L) in the control year to 0.45 (±0.55 μg/L) after inclusion of MP UV at the swimming pool. Bromoform concentration increased after the LP UV reactor was installed at the pool to 1.45 (±1.64 μg/L); the differences between these values and those of the control year were statistically insignificant (p-value: 0.44) (see Fig. 4).

Since brominated compounds tend to be more photosensitive than their chlorinated analogs, the increase in $CHBr_3$ (in 3rd year) concentration after inclusion of UV reactors suggests that by applying the combination of UV/chlorine water treatment, the reformation rate of $CHBr_3$ was faster than its photodecay in the LP UV reactor (Cimetiere and De Laat, 2014).

Hansen et al. (2013) studied the photodegradation of THMs by MP UV lamp output in a lab-scale study; they observed that bromoform degraded faster than the other chloro, bromo THMs and the degradation rate decreased with substitution of chlorine (bromoform > dibromochloromethane > bromodichloromethane > chloroform). It is known that the C—Br bond (280 kJ/mol typ., corresponding to photon energy at $\lambda = 428$ nm) is weaker than the C—Cl bond (397 kJ/mol typ., corresponding to photon energy at $\lambda = 301$ nm) (White, 1992).

Spiliotopoulou et al. (2015) reported that by increasing UV exposure time, the concentration of chloroform decreased while the formation of brominated THMs increased; this behavior may be attributed to the cleavage of the bonds between organic compounds and bromine as a result of UV irradiation, thereby providing a mechanism for bromide formation. Subsequent addition of chlorine would result in oxidation of Br^- to +1-valent bromine, thereby leading to HOBr production (White, 1992). The HOBr produced by this process would then be available to participate in reactions that lead to formation of brominated DBPs, including THMs. According to Heeb et al. (2014), the rate constants for hypobromous acid reactions with organic molecules are up to three orders of magnitude higher than for HOCl. Hence, bromine can be transferred from the larger brominated molecules to smaller volatile DBPs such as dibromochloromethane and bromoform (Spiliotopoulou et al., 2015).

3.3. Halonitriles

Halonitriles that were measured in this study included dichloroacetonitrile [DCAN], cyanogen chloride [CNCl] and cyanogen bromide [CNBr]. Weng et al. (2012) demonstrated that UV_{254} irradiation enhanced formation of DCAN and CNCl as long as free chlorine was present in solution. The rate-limiting step in the formation of chlorinated nitriles involves cleavage of N—Cl bonds (Reckhow et al., 2001; Na and Olson, 2006; Li and Blatchley, 2007; Weng et al., 2012). UV irradiation has been demonstrated to be effective for cleavage of N—Cl bonds (Li and Blatchley, 2009; Weng et al., 2012, 2013; Weng and Blatchley, 2013).

The rates of DCAN formation and decay tend to be slow in swimming pools and this behavior appears to depend largely on pool usage (Zare Afifi and Blatchley, 2015). L-histidine and L-arginine have both been demonstrated to be effective precursors for formation of DCAN (Weng et al., 2012; Li and Blatchley, 2007). Moreover, UV irradiation has been demonstrated to promote formation of DCAN from these amino acids in chlorinated water samples. However, previous research has also indicated that DCAN will undergo hydrolysis in aqueous solution (Reckhow et al., 2001). No measurements of DCAN precursors were included in this study.

As illustrated in Figs. 2 and 5, the free chlorine excursions during year 1 led to rapid increases in the concentration of DCAN, but no or smaller increases were observed during free chlorine excursions after inclusion of UV reactors. One possible explanation is that long-term use of UV exposure leads to decrease in the concentrations of organic precursors that are responsible for DCAN formation.

By comparing the DCAN concentration for the chlorination only water treatment (year 1) and after inclusion of MP UV as a secondary disinfectant in this pool (year 2), it appears that DCAN formation was promoted after MP UV was installed, which is consistent with the observations of Spiliotopoulou et al. (2015); the observed concentration of DCAN under the chlorination condition was 7.96 (±4.83) μg/L, whereas after inclusion of MP UV, these values were increased to 10.1 (±3.28) μg/L (p-value: 3.36×10^{-7}). However, by comparing the observed DCAN concentration between year 1 (7.96 (±4.83) μg/L) and year 3 (after inclusion of LP UV) (7.67 (±4.32) μg/L), DCAN concentration in these two years was statistically indistinguishable (p-value: 0.55). Results here are in contrast

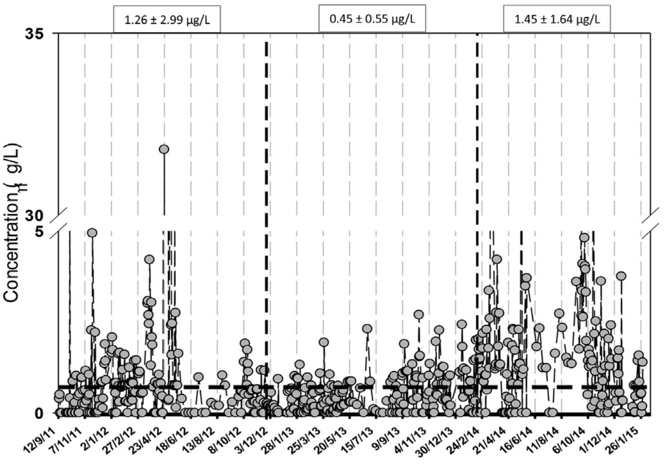


Fig. 4. Time-course measurements of bromoform ($CHBr_3$) concentration as a function of sampling date. Note vertical-axis break from 5 to 30 μg/L.

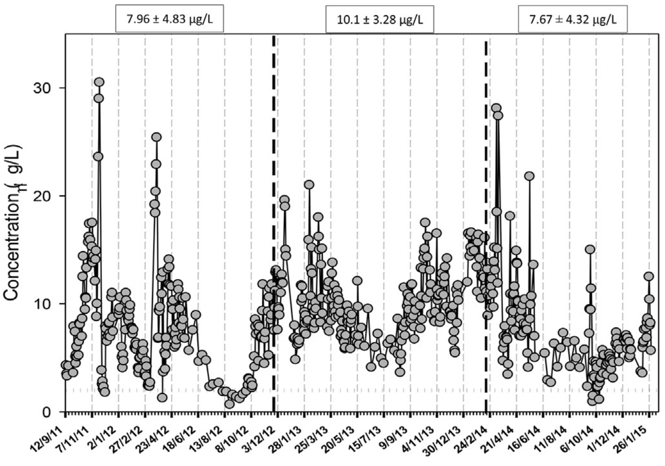


Fig. 5. Time-course measurements of dichloroacetonitrile ($CNCHCl_2$) concentration.

with Cimetiere and De Laat (2014) and Weng et al. (2012) for LP UV based on lab-scale studies, wherein DCAN concentration increased after water samples were exposed to LP UV irradiation, followed by post-chlorination.

According to Weng et al. (2012), as long as free chlorine is present in the solution, DCAN formation will be promoted by UV_{254} irradiation. On the other hand, DCAN is unstable in the presence of free chlorine and the decomposition rate of DCAN is accelerated by increasing both pH and residual free chlorine dose in solution (Hansen et al., 2013; Reckhow et al., 2001). As observed from SI.3 and Fig. 1, both pH and free chlorine concentration tended to be higher in year 3 than in year 1 or 2, and these characteristics may have contributed to the decrease of DCAN concentration after inclusion of LP UV in this pool.

Cyanogen chloride is known to behave as an intermediate in chlorinated swimming pools because it can be produced and oxidized rapidly (Zare Afifi and Blatchley, 2015) and it is volatile (Weng et al., 2011). Thus, CNCl concentration in pool water can be expected to change rapidly. CNCl is produced from reactions between free chlorine and a number of precursors in pools, including amino acids and uric acid (Lee et al., 2006; Na and Olson, 2006; Lian et al., 2014). OCl^- has been demonstrated to catalyze the oxidation of CNCl (Na and Olson, 2004). The combined application of UV_{254} irradiation and chlorination has been demonstrated to promote CNCl formation from L-histidine, L-arginine, and glycine up to the point of free chlorine depletion (Weng et al., 2012; Weng and Blatchley, 2013). More generally, it has been demonstrated that UV_{254} exposure of chlorinated imidazole and guanidine compounds can contribute to CNCl formation (Weng and Blatchley, 2013). In addition, it has been observed that CNCl formation can be promoted from UV irradiation of chlorinated creatinine samples and photolysis of dichloromethylamine (Weng et al., 2013).

Weng et al. (2012) and Liu et al. (2006) illustrated that UV exposure increased CNCl formation in chlorinated water samples. However, according to Fig. 6, the difference between CNCl concentrations observed in the first year (observed concentration of 25.2 ± 36.8 μg/L) and after inclusion of UV reactors (observed concentrations of 21.6 ± 32.9 μg/L after inclusion of MP UV and 33.3 ± 43.9 μg/L after inclusion of LP UV) were not statistically significant, with p-values: 0.29 and 0.068 for MP UV and LP UV, respectively. A possible explanation for this behavior might be the higher concentration of free chlorine during year 2 and 3 compared to the control year, which would have increased the rate of oxidation of CNCl, thereby compensating for the effect of UV. However, the difference of CNCl concentration between year 2 and year 3 was statistically significant with p-value: 0.006, which suggested that MP UV was more efficient than LP UV for reducing CNCl concentration in this pool.

The high concentration of CNCl on 5/19/2014 occurred roughly 2–3 h after the walls and floor of the target pool had been scrubbed in response to a spill on the pool deck. It is possible that through this process, some new precursor(s) that contribute to CNCl formation were introduced to the pool and reacted with free chlorine to produce more CNCl.

CNBr concentration decreased by a factor of almost 5.5 after inclusion of MP UV (from 4.05 ± 3.08 μg/L from the first year to 0.73 ± 0.51 μg/L in the second year; p-value: 1.1×10^{-35}), and by a factor of almost 4 after inclusion of LP UV (0.99 ± 1.88 μg/L; p-value: 5.7×10^{-26}) (see Fig. 7), which suggests that UV irradiation reduced the rate of CNBr formation, increased the rate of CNBr decomposition (*e.g.*, by photolysis), or both. As mentioned previously, the reduction of CNBr by UV radiation may be explained by the fact that the presence of bromine in the molecular structure of the compound dramatically increased the removal rate by UV irradiation, since brominated compounds tend to be more photosensitive than their corresponding chlorinated compounds (Chen et al., 2010; Lekkas and Nikolaou, 2004).

The concentration of CNCl in water showed weak, negative correlations to free chlorine concentration under the three operating conditions (SI.9). Although it is clear that free chlorine (specifically OCl^-) will promote oxidation of CNCl, these weak, negative correlations suggest that other factors will also influence the CNCl concentration in pools.

3.4. *Chloramines*

In general, organic (dichloromethylamine) and inorganic (monochloramine, dichloramine, and trichloramine) chloramines can be degraded by UV irradiation. The apparent quantum yields for photodegradation of inorganic chloramines are wavelength dependent; the stable photoproducts of inorganic chloramines include nitrite, nitrate, nitrous oxide, and ammonium (Li and Blatchley, 2009).

Weng et al. (2012) observed that as a result of post-chlorination of UV_{254} irradiated chlorocreatinine, enhancement of formation of organic and inorganic chloramines occurred. Chlorocreatinine is susceptible to UV_{254} irradiation and photodecay of this compound results in formation of a series of intermediates that could

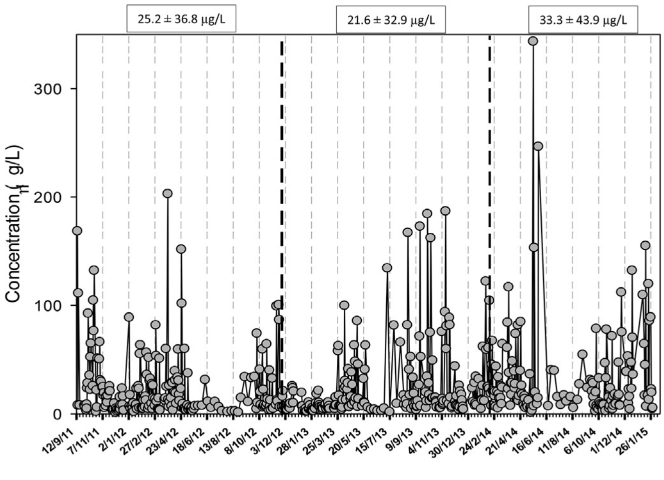


Fig. 6. Time-course measurements of cyanogen chloride (CNCl) concentration.

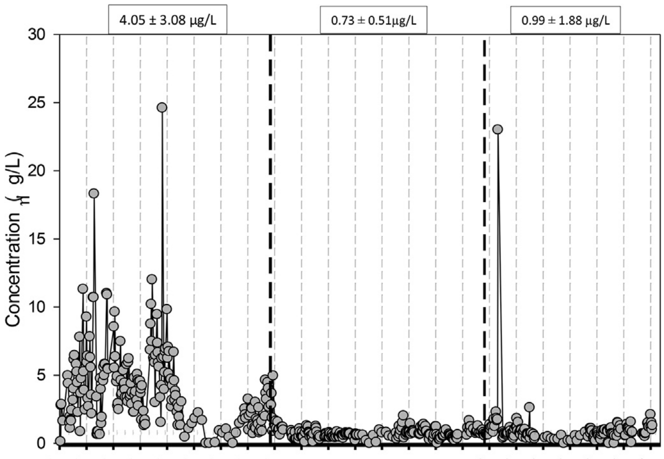


Fig. 7. Time-course measurements of cyanogen bromide (CNBr) concentration.

contribute to formation of organic and inorganic chloramines during post chlorination (Weng et al., 2013). In this same study, dichloromethylamine was formed as an intermediate; its concentration increased when free chlorine was present and decreased after free chlorine was consumed. Experiments involving L-arginine and L-histidine indicated reformation of inorganic chloramines to result from post-UV chlorination (Weng and Blatchley, 2013). According to Weng et al. (2012), after UV_{254} irradiation of chlorinated creatinine, both dichloromethylamine and inorganic chloramines were re-formed, and the resulting concentrations were higher than post chlorination samples without UV exposure. On the other hand, dichloromethylamine and inorganic chloramines, particularly NCl_3, were observed to be susceptible to UV_{254} exposure and they can photodecay by UV exposure (Li and Blatchley, 2009; Weng et al., 2012, 2013).

As shown in Fig. 8a, b, and c, the concentrations of dichloromethylamine, monochloramine, and dichloramine decreased by a factor of roughly 1.5 compared to the first year after inclusion of the MP UV system, with the p-values of 1.55×10^{-16}, 1.6×10^{-6}, and 3.61×10^{-12}, respectively. These results suggest that the rates of photodecay of CH_3NCl_2, NH_2Cl, and $NHCl_2$ with MP UV was higher than the rate of reformation of these compounds by applying UV/chlorine in this pool. After inclusion of the LP UV system, the observed concentrations of CH_3NCl_2, NH_2Cl and $NHCl_2$ decreased slightly compared with the first year, but the differences were statistically insignificant with p-values 0.055, 0.322 and 0.435, respectively. These results are consistent with Li and Blatchley (2007) and Hamel (2007), who illustrated that the photodecay efficiency of chloramines is more efficient by applying MP UV as compared with LP UV at the same dose. Furthermore, the average concentration of free chlorine in the 3rd year was slightly higher than in years 1 and 2, and as discussed previously chloramine concentrations are directly affected by free chlorine concentration.

Weng et al. (2013) conducted experiments involving post-chlorination of UV-irradiated water samples, and they observed that post-chlorination promoted formation of dichloromethylamine and inorganic chloramines, which may have contributed to the higher concentration of chloramines observed in this study after inclusion of LP UV. Also according to Weng et al. (2013), NCl_3 formation was promoted by a factor of 9 by post chlorination.

Despite the fact that free chlorine tended to be present at higher concentration after inclusion of UV reactors, the observed concentration of trichloramine in the liquid-phase remained essentially unchanged from year 1 (0.37 ± 0.37 mg/L) to year 2 (0.35 ± 0.25 mg/L) (p-value: 0.45) (Fig. 9). After installation of LP UV, the observed concentration of trichloramine increased to 0.45 ± 0.44 mg/L; however, the difference between these values from year 1–3 was statistically insignificant (p-value: 0.06). Two possible explanations for this behavior could be a fast re-formation of NCl_3 from the reaction of photolysis products of NCl_3 with chlorine, which is consistent with Weng et al. (2013) and Soltermann et al. (2014), and also higher concentration of free chlorine in year 3 than in year 1. On the other hand, by comparing year 2 (MP UV) and year 3 (LP UV) the average NCl_3 concentration was lower after inclusion MP UV than LP UV, which suggests that MP UV is more effective for reduction of NCl_3 concentration than LP UV (p-value: 0.008). This finding is consistent with the findings of Li and Blatchley (2009), who demonstrated that short wavelengths of UVC radiation were more effective for NCl_3 photodecay than long wavelengths.

For the conditions of operation used with this UV system, which were selected to be typical of UV installations in pools, the extent of NCl_3 photodecay appears to have been relatively small for each pass of the water through the system. However, it is important to recognize that UV systems in pools are generally included as part of the recirculating system for pool water. As such, water in a pool will be exposed to UV radiation repeatedly, and the accumulated exposure to UV has the potential to decrease the concentrations of some photolabile compounds, such as NCl_3. In addition, the effect of UV irradiation on NCl_3 concentration in pools depends on the pool size and the recirculation rate; for instance, for pools with a fast turn-over NCl_3 concentration would be expected to be reduced

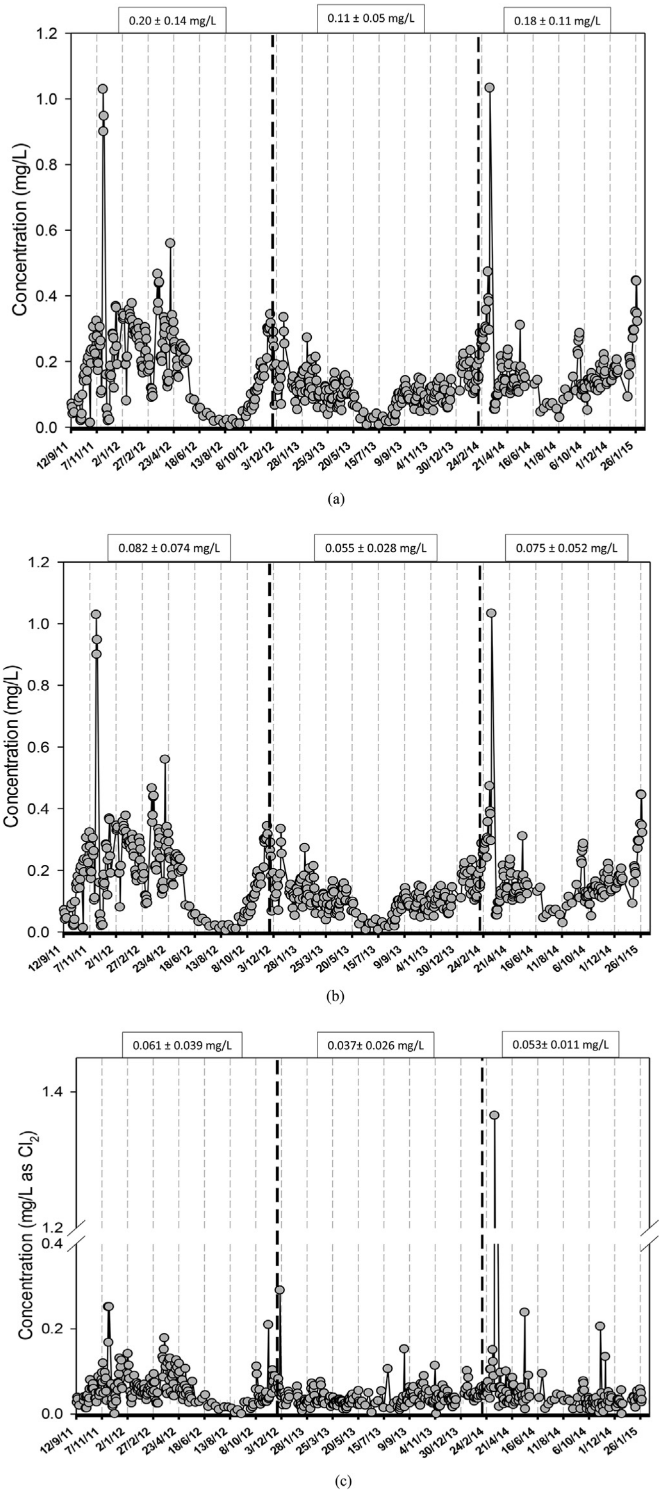


Fig. 8. Time-course measurements of (a) Dichloromethylamine (CH_3NCl_2), (b) Monochloramine (NH_2Cl), and (c) Dichloramine ($NHCl_2$) concentrations.

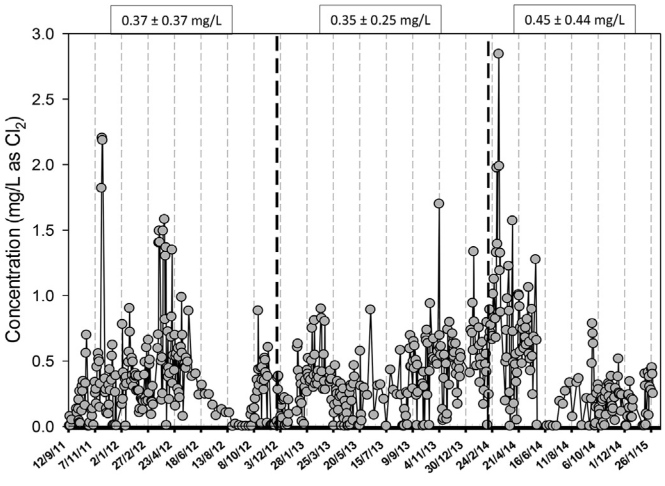


Fig. 9. Time-course measurements of trichloramine (NCl_3) concentration.

more rapidly than in pools with slow turn-over (Soltermann et al., 2014). The effect of UV on NCl_3 concentration in a pool will also be influenced by liquid-phase (non-photochemical) reactions that take place in the pool itself. At present, the balance of the combined effects of photodecomposition and non-photochemical reactions relative to NCl_3 remains incompletely defined. However, according to Soltermann et al. (2014), several factors can influence trichloramine concentration in pools including: free chlorine concentration, recirculation rate, addition of fresh water, bather load, and UV dose. The main factors influencing NCl_3 concentrations in the liquid phase are the free chlorine concentration and UV-based treatment in combination with the recirculation rate through the water treatment system (Soltermann et al., 2014). UV exposure can cleave N—Cl bonds. Also, reducing the free chlorine concentration may represent an important option to decrease NCl_3 concentration. This is because free chlorine can diminish NCl_3 photolysis by reacting with potential UV-induced reaction partners or by quenching OH• radicals (Soltermann et al., 2014). Hence, as long as free chlorine is present in pool water, the reduction of trichloramine is close to the self-decay of NCl_3 in pure water at the same pH. Also, rapid re-formation of NCl_3 in the pool leads to almost the same steady-state trichloramine concentration as without inclusion of UV-based treatment in the pool (Soltermann, 2015).

3.5. *Urea*

By mass, urea is the dominant organic-N compound in human urine and sweat. De Laat et al. (2011) reported urea concentrations ranging from 0.12 mg/L to 3.6 mg/L in swimming pools. Soltermann et al. (2014) illustrated that urea accounted for an average of 66% (ranging from 37 to 85%) of the organic-N compounds in swimming pool samples; therefore, urea represents a major fraction of organic-N compounds in the pool water. Blatchley and Cheng (2010) demonstrated that urea functions as a precursor to NCl_3 production in pools; the rate of NCl_3 formation from chlorination of urea is strongly influenced by pH and Cl:N molar ratio. However, Soltermann et al. (2014) demonstrated that urea is probably not the dominant NCl_3 precursor in pool water. For the conditions that exist in most chlorinated pools, urea reacts with chlorine quite slowly.

In this study the average concentration of urea was, 0.037, 0.032, and 0.036 mg/L under operating conditions of chlorination only, MP UV/chlorine, and LP UV/chlorine, respectively. In general terms, these values suggest that precursor input to the pool was similar during each of the three periods of investigation. Blatchley and Cheng (2010) demonstrated that urea and its chlorinated derivatives are weak absorbers of UV radiation, and are largely unaffected by UV-based processes (Weng et al., 2012).

It is known that the number of swimmers and their activity will affect urea concentration in pools. According to Fig. 10, the urea concentrations during heavy usage were generally higher than during periods of light or no usage of the pool (Zare Afifi and Blatchley, 2015).

4. Conclusions

The following general observations were made based on measures of statistical significance, by examination of data collected in years 2 and 3, and by comparisons of data collected in the various periods of this study:

- Free chlorine excursions had direct and immediate effects on the concentrations of several volatile DBPs; however, the excursions that were observed after inclusion of MP UV resulted in no or smaller increases in the concentrations of most DBPs that were measured in this study compared to the first and third year.
- Despite the fact that free chlorine excursions occurred more often after inclusion of UV reactors (year 2 and 3) than in the control year, the concentration of chloroform tended to be lower and less variable in the second and third year than in the control year. LP UV irradiation was more effective than MP UV for decreasing chloroform concentration.
- Since the brominated compounds are generally more photosensitive than their chlorinated analogs, the increase in $CHBr_3$ after inclusion LP UV suggests that the formation rate of $CHBr_3$ (in 3rd year) was greater than the photodecay rate. MP UV lamps are more efficient than LP UV lamps for the photodegradation of brominated THMs since brominated THMs have a broad absorption band with a maximum near 220 nm.
- DCAN formation was promoted after MP UV was installed, relative to the control year. However, DCAN concentrations in the control year and after inclusion of LP UV were almost identical. Although formation of DCAN can be promoted by UV irradiation, both pH and free chlorine were higher in year 3 than

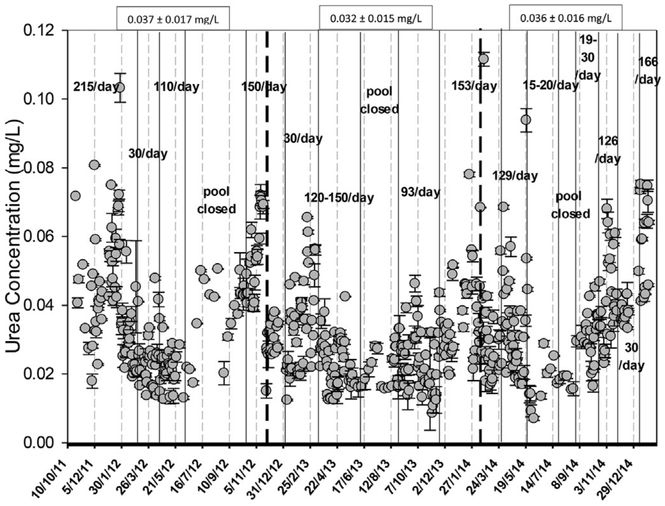


Fig. 10. Urea concentration as a function of time. Data points represent mean of triplicate measurements, while error bars represent the standard deviation. The solid vertical lines indicate periods during which bather load was similar each day; nominal bather load in each period is indicated. Boxes in the graph indicate average ± SD of urea concentration in each operating conditions.

Table 2
Summary of the effects of UV systems on free chlorine consumption and the concentrations of volatile DBPs, combined chlorine, and urea, as measured in a chlorinated indoor swimming pool. All indications are based of tests of statistical significance ($p < 0.05$). For the comparisons indicated on the top row, MP indicates and advantage of inclusion of MP UV; LP indicates and advantage of inclusion of LP UV; Cl_2 indicates an advantage for use of chlorine without UV. Inclusion of both treatments separated by a colon (*e.g.*, MP:LP) indicates no advantage of one treatment vs. the other, based on a test of statistical significance.

Compounds	Cl_2 vs. MP UV	Cl_2 vs. LP UV	MP vs. LP UV	Basis
Free chlorine consumption	Cl_2	Cl_2	MP:LP	Lower rate
Combined chlorine	MP	LP	MP:LP	Lower concentration
$CHCl_3$	MP	LP	LP	Lower concentration
$CHBr_3$	MP	Cl_2:LP	MP	Lower concentration
$CNCHCl_2$	Cl_2	Cl_2:LP	MP	Lower concentration
CNCl	Cl_2:MP	Cl_2:LP	MP	Lower concentration
CNBr	MP	LP	MP	Lower concentration
CH_3NCl_2	MP	Cl_2:LP	MP	Lower concentration
NH_2Cl	MP	Cl_2:LP	MP	Lower concentration
$NHCl_2$	MP	Cl_2:LP	MP	Lower concentration
NCl_3	Cl_2:MP	Cl_2:LP	MP	Lower concentration
Urea	Cl_2:MP	Cl_2:LP	MP:LP	Lower concentration

in year 1 and 2, which may have resulted in decreasing DCAN concentration after inclusion of LP UV in this pool.

- The concentrations of dichloromethylamine, monochloramine, and dichloramine after inclusion of MP UV system in this pool decreased by almost a factor of 1.5 compared to the first year. These results suggest that the rates of photodecay of CH_3NCl_2, NH_2Cl, and $NHCl_2$ with MP UV were higher than the rate of reformation of these compounds by applying UV/chlorine in this pool. After inclusion of LP UV system the average concentrations of CH_3NCl_2, NH_2Cl, and $NHCl_2$ decreased slightly as compared with the first year, but the differences were statistically insignificant, which suggests that the rates of reformation of these compounds were almost the same as rates of photodecay.
- The average concentration of trichloramine remained essentially unchanged from year 1 to year 2. After installation of LP UV, the average concentration of trichloramine increased compared to year 1; however, the differences between these values from year 1 and 3 were statistically insignificant. Two possible explanations for this behavior could be a fast re-formation of NCl_3 from the reaction of photolysis products of NCl_3 with chlorine (NCl_3 re-formation in this pool is higher than photodecay rate of NCl_3 by UV irradiation), and also higher concentration of free chlorine in year 3 (free chlorine promotes NCl_3 formation). On the other hand, by comparing year 2 (MP UV) and year 3 (LP UV) the average NCl_3 concentration was lower after inclusion MP UV than LP UV. This is consistent with previous observations of the photodecay efficiency of chloramines using MP UV as compared with LP UV. Reducing the free chlorine concentration may represent an important option to decrease NCl_3 concentration.
- Urea concentration was essentially unaffected as a result of inclusion of MP or LP UV. Therefore, precursor input to the pool was similar during each of the three periods of investigation.

Table 2 provides a summary of statistically significant differences observed among the effects the three treatments on the ten volatile DBPs and combined chlorine concentration that were measured in this study in the chlorinated, indoor swimming pool. Also included in this tabular summary are comparisons of free chlorine consumption, and urea concentration.

Overall, this study demonstrated that compared to conventional chlorination water treatment in pools, combining UV/chlorine has the potential to reduce the concentration of many volatile DBPs. And between two UV sources, MP UV was generally more effective than LP UV for reducing the concentrations of volatile DBPs in this pool.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.08.064.

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