

Practical Paper

UV disinfection of chlorinated water: impact on chlorine concentration and UV dose delivery

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ABSTRACT

Prechlorination of water upstream of an ultraviolet (UV) disinfection process may possibly influence the effectiveness of UV inactivation through the absorbance of UV radiation. Alternatively, UV may act to destroy chlorine, reducing the residual in water. Monochromatic UV light was more effective in degrading monochloramine whereas polychromatic UV light was more effective in degrading free chlorine. The extent of degradation varied with the type of chlorine species, water quality and type of UV irradiation (mono- or polychromatic). However, decay of chlorine and monochloramine at typical UV disinfection doses ($< 100 \text{ MJ/cm}^2$) was negligible. The transmission of UV irradiation was affected slightly by the presence of chlorine and monochloramine, and these effects on inactivation of MS2 coliphage were modeled for LP – and MP-UV reactors. The presence of 1 mg/L free chlorine or monochloramine decreased the inactivation of MS2 coliphage by less than 0.1 log for a LP-UV reactor. For the MP-UV reactor, MS2 inactivation decreased by between 0.1 and 0.3 log.

Key words | chlorine, monochloramine, photolysis, ultraviolet irradiation, water treatment

INTRODUCTION

Prechlorination is an important tool for maintaining the water quality and efficiency of a treatment plant. Although the primary use of chlorine in a treatment plant is for disinfection, chlorine can also be used to control the taste and odor, remove color, aid in coagulation and filtration and minimize biological growth in a filter. Depending on the purpose of prechlorination, chlorine may be added at various points in the treatment process such as before coagulation, sedimentation or filtration. The prechlorination dose required to maintain a free residual concentration of chlorine in water is closely related to water quality, and is typically around 1 mg/L. However, it may increase up to 12 mg/L when the organic matter and inorganic species concentration is high in water (White 1999).

Prechlorination during the water treatment process may possibly influence the effectiveness of downstream ultraviolet (UV) disinfection. Recently, due to increasingly stringent regulations in the United States over chlorinated

disinfection byproducts and the chlorine resistant pathogen *Cryptosporidium parvum*, interest in the application of ultraviolet (UV) light for disinfection has accelerated. Chlorine and monochloramine present due to the practice of prechlorination may absorb UV light, interfering with the delivery of UV radiation to the targeted microorganisms. Alternatively, UV irradiation may decay chlorine residual via photolysis, leading to undesirable dechlorination. In addition, photooxidants formed during the photolysis of chlorine and monochloramine may further react with organic matter present in water and change the properties of UV-absorbing constituents. Therefore, it is important to better understand the fate and effect of chlorine and monochloramine under the application of UV irradiation for disinfection. The objectives of this study were to determine: 1) how the presence of chlorine and monochloramine affects the transmission of UV radiation and subsequent inactivation and 2) the extent of chlorine and

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monochloramine decay under monochromatic and polychromatic UV light for three waters that represent different water qualities. Chlorine and monochloramine chemistry in the presence of organic and inorganic matter and ultraviolet light is very complex. This study was not geared toward detailing the photodecomposition kinetics and rate constants of chlorine and monochloramine decay in natural waters. Rather, the goal of this study was to investigate how the presence of residual free chlorine and monochloramine in treated water entering a UV reactor system may affect the practice of applying UV irradiation to water.

BACKGROUND

Chlorine and monochloramine present in water may be involved in a variety of chemical reactions such as with ammonia, inorganic ions and natural organic matter. Photochemical reactions also play an important role in the decay of chlorine and monochloramine compounds in water. UV irradiation facilitates the destruction of bonds between Cl–Cl or NH₂–Cl molecules by forcing one of the paired electrons into an antibonding orbital. The resulting unstable molecules are easily reduced to Cl[–] ion hydrates. Organic and inorganic species in natural water can have a substantial influence on the photolysis of chlorine in the presence of UV light (Nowell & Hoigne 1992a, b). Chain reactions that occur in the presence of organic matter and chlorine increase the photodecay rate for both chlorine (Oliver & Carey 1977) and other organic constituents in water (Nowell & Hoigne 1992b).

There is growing interest in using UV light for the disinfection of drinking water because UV does not produce any known harmful disinfection byproducts and is effective at low doses against some target pathogenic microorganisms such as *Cryptosporidium parvum* and *Giardia lamblia*. The recent draft of the EPA UV Disinfection Guidance Manual (USEPA 2003) suggests that typical UV doses employed for water disinfection will be in the range of 15–130 mJ/cm², but in rare cases doses up to 300 mJ/cm² may be required for the inactivation of viruses. Of the pathogens of interest in drinking water, viruses are most resistant to UV disinfection followed by bacteria and protozoa. Certain water quality parameters have an

important effect on the performance of UV disinfection systems, and variations in water quality, such as the presence of particles, water treatment chemicals and algae, will affect the dose delivery to the pathogens.

MATERIALS AND METHODS

Three water samples were used in this study to evaluate chlorine–UV interactions over a range of water qualities: raw water, treated water and deionized water. Raw water and treated water were taken from the Williams Water Treatment Plant, Durham, NC. The raw water was collected from the reservoir of the treatment plant prior to any treatment. Treated water was collected from the effluent of the sedimentation basin following coagulation and flocculation processes, but before filtration, to avoid the addition of chlorine during the filtration step. Pre-filtered water is not normally used for UV disinfection, but given the goal of this study, it was deemed acceptable as a source of “treated water”. Treated and raw water samples were transferred to the laboratory within 15 minutes and stored in the dark at 4°C throughout the room-temperature experiments. The third water sample was deionized water (Hydro Services and Supplies, Research Triangle Park, NC). Unlike treated water and raw water, deionized water did not contain significant organic and inorganic matter and thus served as a control in the experiments.

Water samples having an initial free chlorine and monochloramine concentration of 4–5 mg/L were prepared using fresh household bleach (1.5 mg/mL stock solution prepared from 5.25% sodium hypochlorite, Clorox[®]) and 100 mg/L monochloramine stock solution. The chlorine and monochloramine concentrations used were higher than those typically used for drinking water practices, but were chosen to allow measurement of the chlorine decay over a broad range of UV doses. A working stock of 100 mg/L monochloramine, on a weight-to-weight ratio, was prepared by mixing 4 mg of ammonia to 1 mg of chlorine, which in moles gives nearly a 10:1 ratio of NH₃ to Cl[–]. Monochloramine stock solution was prepared by adding 0.37 mL Clorox[®] to 100 mL 0.01 M pH 9.5 K₂HPO₄ buffer and 0.081 g NH₄Cl to 100 mL of the same buffer, and combining these two mixtures slowly. Free chlorine and combined chlorine

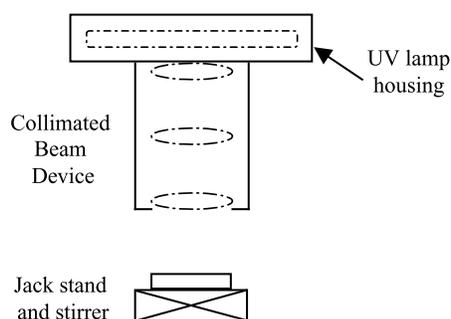


Figure 1 | Picture of a typical benchscale UV exposure collimated beam instrument.

concentrations were determined using a combination of DPD ferrous titrimetric and DPD colorimetric methods (*Standard Methods* 1998).

Samples that contained chlorine or monochloramine were exposed to monochromatic (253.7 nm) and polychromatic (200–400 nm) UV irradiation in bench scale “collimated beam” type instruments and the decrease in the chlorine and monochloramine concentrations were measured over the duration of the experiments. **Figure 1** illustrates a typical collimated beam instrument where a spatially homogenous beam of UV radiation is produced to irradiate the sample. The monochromatic UV unit contained four 15 W low-pressure (LP) lamps (Sankyo Denki G15T8, Japan) housed in a shuttered box. The polychromatic UV unit, manufactured by Calgon Carbon Corp. (Pittsburgh, PA), contained a single 1 kW medium-pressure (MP) lamp (Hanovia Ltd., #6806A441, NJ). All irradiation experiments were conducted in the dark and samples were not exposed to daylight. A spectrometer (S2000, Ocean Optics, Inc., Dunedin, FL) calibrated using a NIST (National Institute of Standards and Technology) traceable

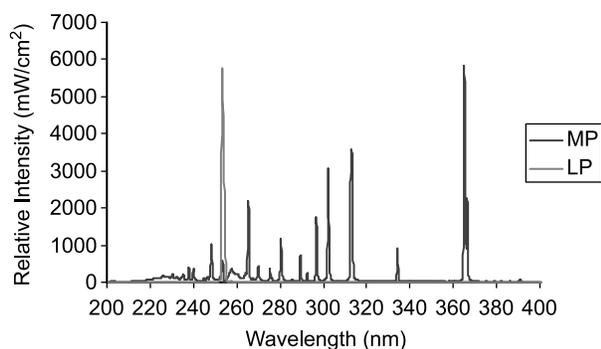


Figure 2 | The emission spectrum of the LP and MP lamps used in the experiments.

D₂ lamp (Oriel, Inc., Stratford, CT) was used to determine the MP lamp spectrum. The emission spectra of the LP and MP lamps are illustrated in **Figure 2**. The irradiation incident to the water sample was measured using a radiometer with a UV detector (Model No. IL 1700 SED 240, International Light, Newbury Port, MA) calibrated at 254 nm to standards traceable to the NIST. The UV dose calculations for the LP and MP lamps were performed according to the methods provided on the website of the [International Ultraviolet Association \(http://www.iuva.org\)](http://www.iuva.org). The average irradiance in the solution irradiated with the LP lamp was calculated by incorporating the incident irradiance, petri factor (ratio of the average surface irradiance to the center irradiance), the sample UV 254 absorbance and sample depth of the water, using an integration of the Beer–Lambert law (*Morowitz 1950; Bolton & Linden 2003*). The germicidal irradiance for the MP lamp was calculated in a fashion similar to the LP lamp but also included the variation in radiometer sensor responsivity over the UV wavelengths, the lamp output between wavelengths 200 and 300 nm and a germicidal weighting (*Linden & Darby 1997*).

The UV doses used in these experiments ranged between 0–1500 mJ/cm² in increments of 100 mJ/cm². It is important to point out that the typical UV dose used for disinfection is usually between 15–130 mJ/cm² for potable waters, but higher UV doses were needed in this study to be able to show chlorine and monochloramine decay and determine the decay rates. Thus, the UV dose range used in this study includes both those used for disinfection (<100 mJ/cm²) and those that may be used for contaminant photolysis and advanced oxidation (>500 mJ/cm²). The irradiance of the MP lamp was greater than that for the LP lamp. However, the intensity of the incident irradiation was altered by adjusting the distance between the sample and the UV lamps such that the exposure time was the same for a particular UV dose with either lamp type. Each dose step of 100 mJ/cm² corresponded to an exposure time of approximately 4 minutes for all water samples. Consequently, an experimental run took approximately 1 hour to complete. For the samples that were kept in the dark, the concentrations of chlorine and monochloramine were also measured at 4 minute intervals. UV dose (mJ/cm²) was calculated as the product of the average germicidal

UV irradiance (mW/cm^2) multiplied by the exposure time (s).

Samples of 300 mL were placed in a crystallization dish and stirred at the same rate with a magnetic stirrer during the irradiation period to achieve a well-mixed sample. The control samples that were not irradiated were also mixed at the same rate. Therefore, any chlorine loss through volatilization was controlled for all samples. A sample volume of 5 mL was withdrawn from the exposure dish after each dose of $100 \text{ mJ}/\text{cm}^2$ to measure the residual chlorine or monochloramine concentration in the sample. The large size dish with a wide mouth ($125 \times 65 \text{ mm}^2$) was chosen to minimize the change in water depth during the exposure experiments. The depth of the 300 mL water sample was reduced from 2.6 cm to 2.1 cm after 15 withdrawals of 5 mL samples. The change in the sample depth was accounted for in the determination of UV dose at each time point. Absorbance spectra scans (200–400 nm) of samples containing 1, 3 and 5 mg/L chlorine or monochloramine were measured in a 1 cm quartz cell using a Varian Cary 100 Bio UV-visible spectrophotometer (Varian Analytical Instruments, Walnut Creek, CA) right after the addition of chlorine and monochloramine. Turbidity (Hach Company, Hach 2100N Turbidimeter, Loveland, CO), pH (Cole Parmer Instrument Company, pH 100 series, Vernon Hills, IL) and total organic carbon (Apollo 9000, Tekmar-Dohrmann, Cincinnati, OH) present in each of the waters tested were determined prior to each experiment.

REACTOR MODELING METHODS

Figure 3 displays the reactors that were used to numerically model the effect of chlorine residual absorbance on UV disinfection. In Figure 3(a), a single low-pressure (LP) pilot-scale UV reactor, where the lamp is oriented parallel to the inlet flow direction, was used to simulate the effects of residual chlorine species under monochromatic conditions. The LP-UV reactor was operated at a flow rate of 7.6 gpm with the water absorbance conditions at 254 nm discussed in a later section. Figure 3(b) displays a two-lamp medium pressure (MP) full-scale reactor where the lamps are oriented perpendicular to the inlet flow direction. The MP-UV reactor was operated at a flow rate of 3.0 MGD with the water spectral absorbance conditions discussed in the following section.

In this study, a finite-volume-based commercial CFD code PHOENICS (CHAM, England) was used. The transport of the microorganisms through the UV reactors was simulated using an Eulerian approach, which characterizes the organisms as a continuous reacting scalar (Ducoste *et al.* 2005). The simulation of a reacting scalar requires the solution of the mass, momentum, turbulence and convective–reaction transport equations. The renormalized group (RNG) two-equation $k-\epsilon$ model was used to characterize the turbulence in the UV reactor (Wilcox 1998).

The local fluence rates in the UV reactor were computed using the RAD-LSI model (Liu *et al.* 2004).

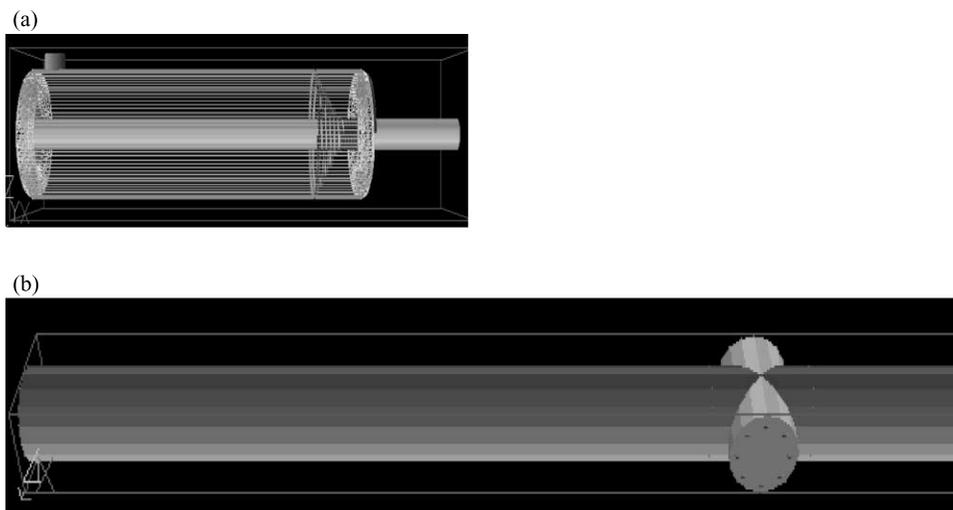


Figure 3 | Test UV reactors: (a) single LP-UV reactor, (b) dual lamp MP reactor.

The RAD-LSI model accounts for the reductions in transmittance due to reflection, refraction (bending effect only) and absorption (both in the fluid and through the quartz sleeve) and UV-C lamp efficiency. For MP lamp modeling, a multi-wavelength approach encompassing 20 wavelengths at 5 nm intervals between 200–300 nm was characterized. For each wavelength band, model inputs included water and quartz sleeve transmission, the fraction of lamp power and germicidal efficiency for the challenge microorganism. In this study, the germicidal efficiency for MS2 shown in the US EPA UVDGM (2003) was used.

RESULTS AND DISCUSSION

Variations in water quality, such as UV absorbers (humic and fulvic acids, aromatic organics, nitrates and sulfites, etc.), the presence of particles and water treatment chemicals, affect the irradiation delivery to the pathogens. These factors may also influence the photoreactions with chlorine and chloramines. In order to have a general idea of the quality of the water samples used, the pH, turbidity and total organic carbon (TOC) content of the three water samples were measured as reported in Table 1.

As expected, deionized water was the cleanest of the three samples, having negligible turbidity and TOC. Treated water had lower turbidity and TOC compared to the raw water. The decay rates of chlorine and monochloramine under monochromatic and polychromatic UV light were evaluated for zero-order and first-order kinetics. Free chlorine exhibited a good fit for zero- and first-order decay in DI, and zero-order decay in treated and raw water samples, whereas monochloramine exhibited a good fit for both zero- and first-order decay in all water samples. The decay rates for chlorine and monochloramine as a function of UV dose are

given in Table 2. These decay rates describe the chlorine and monochloramine decay caused by a combination of physical and chemical processes. They are meant to be comparative in nature and are specific to the water samples and exposure conditions used in this study. In addition, the decay rates are reported as dose-based rates reflecting the average UV dose delivered to the water samples. As reported by Bolton & Stefan (2002), the decay rates, reported in units of time^{-1} in UV studies, have little meaning unless several parameters of the irradiation experiments, such as irradiance, absorbance and path length, are known. Because the irradiance of UV light is dependent upon the distance from the lamp in a bench or field reactor (irradiance decreases with distance from the source), it is impossible to compare rates of reaction between different UV systems using units based on the time of exposure. The symbol R_m is used to indicate the decay rate under monochromatic UV and R_p to indicate the decay rate under polychromatic UV. In addition to decay rates, absorbance spectra of representative concentrations of chlorine and monochloramine applied in a typical prechlorination process were measured (presented below) to evaluate the change in the UV absorbance of the water samples due to chlorine addition.

Decay of chlorine and monochloramine

Figure 4(a) illustrates the decay of free chlorine in the deionized water for exposure to monochromatic and polychromatic UV light. An unexposed but otherwise identically treated control sample (dark) was prepared to determine the chlorine loss in the absence of UV photolysis over time. Each dose step of 100 mJ/cm^2 corresponded to an exposure time of approximately 4 minutes for all water samples. All samples were stirred at the same rate, therefore any loss due to volatilization was similar for all samples. The chlorine concentration of the control sample did not show an appreciable decrease, indicating that chlorine loss due to volatilization or chemical reactions with the water constituents were absent for deionized water, as was expected due to the clean water quality. The samples that were exposed to monochromatic and polychromatic UV light exhibited gradual chlorine decay with increasing UV dose. The free chlorine zero-order decay rate under monochromatic UV was slightly higher than the decay rate under

Table 1 | Water quality characteristics of waters used in this study

Sample	pH	Turbidity (NTU)	TOC (mg/L)
DI *	8.00	0	0.25
Treated water	7.00	2.44	3.33
Raw water	7.13	9.61	5.86

*Water quality of the deionized water was not measured on the day of the experiments.

Table 2 | Decay rates of free chlorine and monochloramine in DI, treated and raw water under (LP-) and (MP-) UV irradiation

Sample	Monochromatic (LP-UV)		Polychromatic (MP-UV)		Dark	
	Free chlorine	Mono-chloramine	Free chlorine	Mono-chloramine	Free chlorine	Mono-chloramine
Zero-order decay coefficients						
DI	$R_m = 0.0012$	$R_m = 0.0018$	$R_p = 0.0009$	$R_p = 0.0012$	$R = 0.00003$	$R = 0.00006$
Treated	$R_m = 0.0038$	$R_m = 0.0018$	$R_p = 0.0056$	$R_p = 0.0012$	$R = 0.0008$	$R = 0.0002$
Raw	$R_m = 0.0068$	$R_m = 0.0017$	$R_p = 0.0084$	$R_p = 0.0011$	$R = 0.0015$	$R = 0.0003$
First-order decay coefficients						
DI	N.A.	$R_m = 0.0008$	N.A.	$R_p = 0.0005$	N.A.	N.A.
Treated	N.A.	$R_m = 0.0006$	N.A.	$R_p = 0.0003$	N.A.	N.A.
Raw	N.A.	$R_m = 0.0005$	N.A.	$R_p = 0.0003$	N.A.	N.A.

Units of zero-order decay coefficients are $\text{mg cm}^2/(\text{mJ L})$ and first-order decay coefficients are cm^2/L . The decay coefficients reported here are specific to the water samples and exposure conditions used in this study and are not universal rate constants. The decay of free chlorine in dark is simplified to a zero-order decay in order to be able to compare the decay coefficients for dark, LP-UV and MP-UV.

N.A. stands for not applicable.

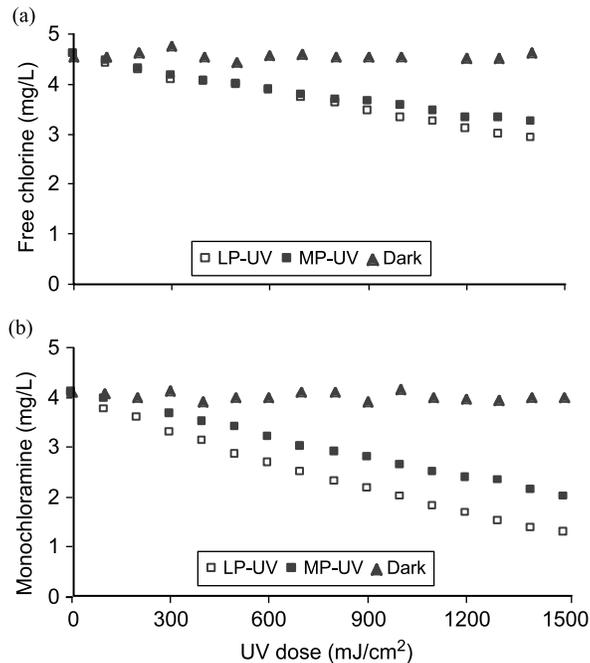


Figure 4 | The decay of (a) free chlorine and (b) monochloramine in deionized (DI) water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light. Note: for “dark” sample, each dose step of $100 \text{ mJ}/\text{cm}^2$ corresponds to an exposure time of approximately 4 minutes.

polychromatic UV light (0.0012 and $0.0009 \text{ mg cm}^2/(\text{mJ L})$, respectively). The decay of monochloramine in deionized water under the same conditions is presented in Figure 4(b). Similar to free chlorine, the monochloramine control sample remained unchanged, indicating that monochloramine loss due to volatilization and chemical reactions was not significant. Monochloramine decayed linearly under monochromatic and polychromatic UV light (0.0018 and $0.0012 \text{ mg cm}^2/(\text{mJ L})$, respectively) but the zero-order decay rates were slightly higher than those of free chlorine. Monochromatic UV was more effective than polychromatic UV light in degrading monochloramine. The decreases in chlorine and monochloramine concentrations in deionized water were attributed to direct UV photolysis.

The decay of free chlorine in the treated water is shown in Figure 5(a). Treated water contained higher levels of organic and inorganic matter compared to the deionized water (Table 1). In the dark control sample, free chlorine exhibited a two-stage decay that was attributed to the chlorine-demanding constituents of the water sample. The initial decay was attributed to the fast chlorine-reacting components, and the secondary decay was attributed to the

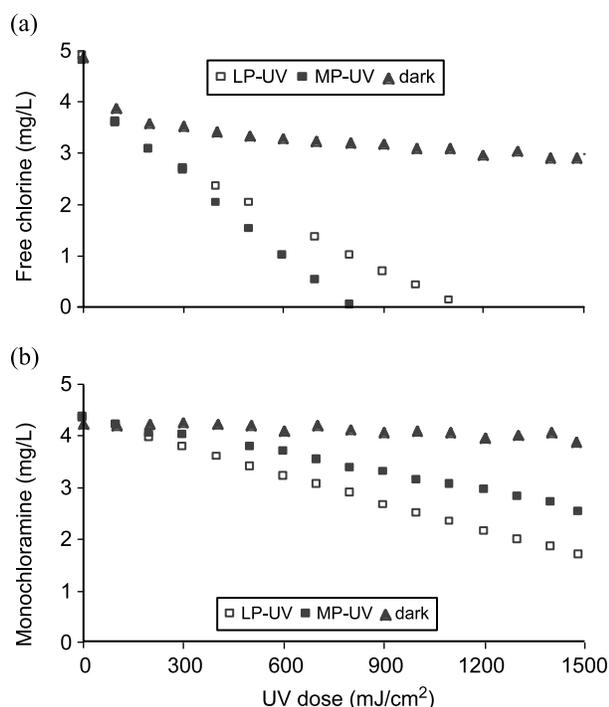


Figure 5 | The decay of (a) free chlorine and (b) monochloramine in treated water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light. Note: for “dark” sample, each dose step of 100 mJ/cm² corresponds to an exposure time of approximately 4 minutes.

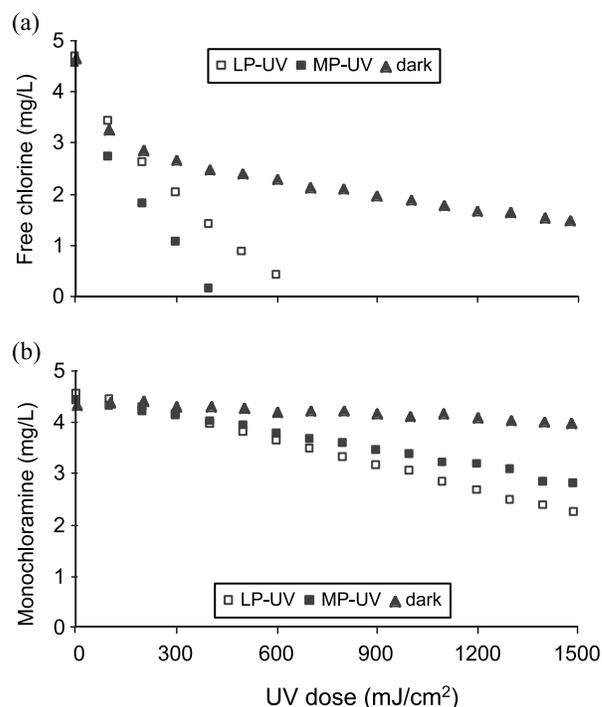


Figure 6 | The decay of (a) free chlorine and (b) monochloramine in raw source water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light. Note: for “dark” sample, each dose step of 100 mJ/cm² corresponds to an exposure time of approximately 4 minutes.

slower reacting components (Vasconcelos *et al.* 1997). In contrast, monochloramine decay was insignificant in the dark (Figure 5(b)). The overall zero-order decay rates of free chlorine under monochromatic ($R_m = 0.0038 \text{ mg cm}^2/(\text{mJ L})$) and polychromatic ($R_p = 0.0056 \text{ mg cm}^2/(\text{mJ L})$) UV irradiation were much higher than the decay rates in deionized water. In fact, all of the free chlorine was consumed after receiving a dose of 800 mJ/cm² with polychromatic UV and 1100 mJ/cm² with monochromatic UV light in the treated water. Monochloramine decayed slower than free chlorine under monochromatic and polychromatic UV light (0.0018 and 0.0012 mg cm²/(mJ L), respectively). Interestingly, in the treated water, monochromatic UV was more effective in decaying monochloramine, whereas polychromatic UV was more effective in decaying free chlorine.

In raw water, which contained the highest organic matter (the poorest water quality) in comparison to the other waters tested, the free chlorine degradation was fastest (Figure 6(a)). Polychromatic UV was again more effective than monochromatic UV light in the degradation

of free chlorine (0.0084 and 0.0068 mg cm²/(mJ L), respectively). The free chlorine concentration in the sample dropped to below the detection limit (10 µg Cl/L as Cl₂) following UV doses of 400 mJ/cm² with polychromatic UV and 700 mJ/cm² with monochromatic UV irradiation. Monochromatic UV light, on the other hand, was more effective in decaying monochloramine (Figure 6(b)). The decay rates of monochloramine in raw water under monochromatic and polychromatic UV light (0.0017 and 0.0011 mg cm²/(mJ L), respectively) were very similar to the decay rates of monochloramine in treated water and did not show a significant change.

The decay rates of chlorine and monochloramine under monochromatic and polychromatic UV light shown in Figures 4–6 and Table 2 include consumption of the chlorine species in the dark in addition to decay from photochemical reactions. The consumption of monochloramine in the dark was minimal in treated and raw water, but the free chlorine consumption in the dark was substantial and its effect on the UV decay rates needed to be accounted for. When the chlorine and monochloramine decay due to the dark

Table 3 | Decay rates of free chlorine and monochloramine in DI, treated and raw water under (LP-) and (MP-) UV irradiation when dark reactions are excluded

Sample	Monochromatic (LP-UV)		Polychromatic (MP-UV)	
	Free chlorine	Monochloramine	Free chlorine	Monochloramine
Zero-order decay coefficients				
DI	$R_m = 0.0011$	$R_m = 0.0018$	$R_p = 0.0009$	$R_p = 0.0013$
Treated	$R_m = 0.0027$	$R_m = 0.0016$	$R_p = 0.004$	$R_p = 0.0010$
Raw	$R_m = 0.0035$	$R_m = 0.0013$	$R_p = 0.0055$	$R_p = 0.0008$
First-order decay coefficients				
DI	$R_m = 0.0003$	$R_m = 0.0007$	$R_p = 0.0002$	$R_p = 0.0004$
Treated	$R_m = 0.0008$	$R_m = 0.0005$	$R_p = 0.0013$	$R_p = 0.0003$
Raw	$R_m = 0.0009$	$R_m = 0.0004$	$R_p = 0.0018$	$R_p = 0.0002$

Units of zero-order decay coefficients are $\text{mg cm}^2/(\text{mJL})$ and first-order decay coefficients are cm^2/mJ .

reactions were excluded from the UV decay rates, the chlorine and monochloramine decay exhibited a good fit to both zero- and first-order kinetics for all water samples, with the decay rates shown in Table 3. The difference between the free chlorine decay rates in the different waters indicates that the decay of chlorine under UV light is not simply the addition of the dark reactions with background water constituents and the light reactions in pure water (i.e. the decay in DI water). Chlorine decay is also affected by UV–water quality and UV–chlorine interactions which may increase the rate of indirect photolysis through the formation of various photooxidants and initiate a series of reactions that eventually consume chlorine and water quality constituents simultaneously. Monochloramine decay did not vary as much as free chlorine, although a slight decrease in monochloramine decay rate was observed in the presence of water constituents. Although a detailed investigation of how water quality may affect the chlorine and monochloramine decay was beyond the scope of this research, results obtained from the treated and raw waters used in this study should hold for most waters.

UV absorbance of chlorinated waters

The relative impact of addition of 1, 3 and 5 mg/L free chlorine or monochloramine on the UV absorbance spectra of non-chlorinated deionized, treated and raw water

samples is presented in Figures 7 and 8. As illustrated in Figure 7, free chlorine has an absorbance minimum around 254 nm (the LP UV emission) with the absorption maximum of free chlorine below 240 nm and at around 290 nm

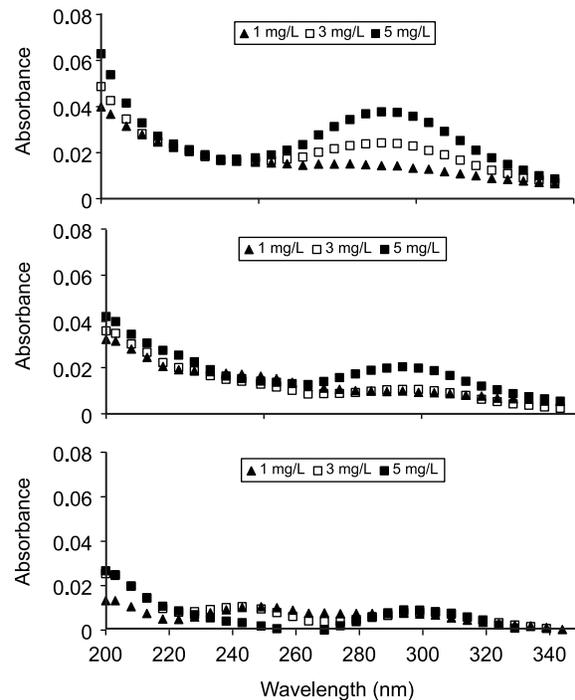


Figure 7 | The absorbance spectra of (a) deionized water (DI), (b) treated water and (c) raw water following a dose of 1, 3 and 5 mg/L free chlorine.

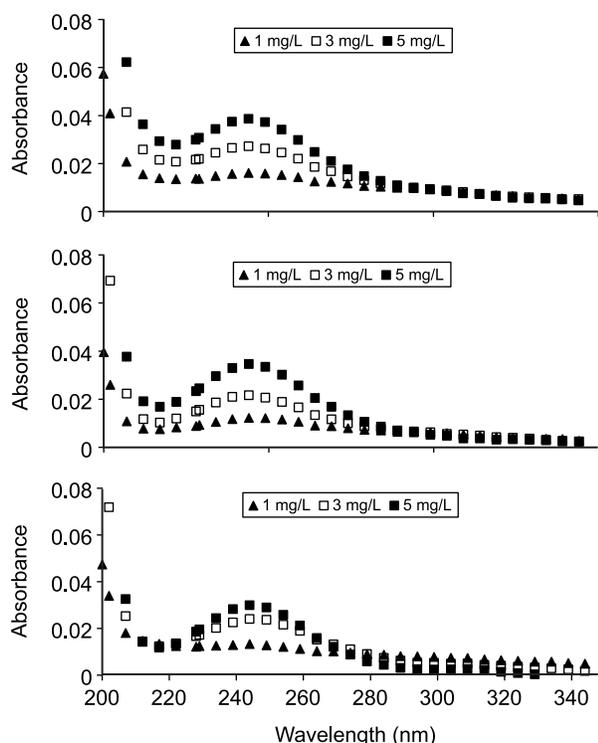


Figure 8 | The absorbance spectra of (a) deionized water (DI), (b) treated water and (c) raw water following a dose of 1, 3 and 5 mg/L monochloramine.

for all water samples, in the wavelength emission range of polychromatic UV light from the medium pressure UV lamp (Figure 2). The absorption maximum of monochloramine, on the other hand, is approximately 240–255 nm, covering the principal low pressure UV lamp output at 254 nm. Above 350 nm, there were no absorbance features of importance for either free chlorine or monochloramine (data not shown). The first law of photochemistry states that only radiation that can be absorbed can produce a photochemical effect. Therefore, when decay rates are based on delivered UV energy, monochromatic UV 254 nm irradiation is more effective than polychromatic UV light in the photochemical degradation of monochloramine (Figure 8). The free chlorine absorbance maximum at approximately 290 nm was most apparent in deionized water, and gradually decreased in the treated and raw water. However, the absorbance spectra peak of monochloramine did not change noticeably between the water samples. The absorbance spectra of free chlorine in deionized, treated and raw water changes as the organic and inorganic matter content of the water sample changes. Monochloramine is

known to be more stable (less reactive) in water as compared to free chlorine. Consequently, a more stable compound would also lead to stability in its absorbance spectra, indicating little change due to reactions with the source water. The minimal decay in the dark (Figures 4–6) provides further evidence of monochloramine stability. The reactivity of free chlorine with the source water, having the effect of decreasing the UV absorbance, implies that prechlorination (causing oxidation) may actually help transmission of UV irradiation. Although this may benefit the application of UV light in water, any addition of chlorine beyond that needed for treatment needs to be balanced with the potential for formation of chlorinated disinfection byproducts.

Impact of chlorine residual on delivery of UV light

In future water treatment practice, the location of a UV treatment process may result in carrying a chlorine residual through a UV reactor. The results showed that the addition of chlorine and monochloramine increases the UV absorbance of the water samples slightly, and therefore decreases the average UV 254 nm irradiance received by the water body. This decrease is small (less than 1% for chlorine and 2.5% for monochloramine, over a 1 cm path length for an addition of 5 mg/L of either species) and is not expected to appreciably change the design dose for a UV disinfection system.

Simulations were performed in the LP and MP reactors described earlier to determine the overall impact of chlorine concentration on UV dose delivery. The results are displayed in Table 4 where, for the LP-UV reactor, a 2% and 8% decrease in the log reduction of MS2 was found with deionized water containing 3 mg/L of residual chlorine and monochloramine, respectively. The reduction in the MS2 log inactivation in deionized water was due to the increase in UV absorbance at 254 nm with increasing chlorine species concentration (Figure 7(a)). In the treated water case, the addition of 1 mg/L of residual chlorine showed a 2% drop in MS2 log inactivation and no difference when the chlorine residual was increased to 3 mg/L. When monochloramine was added to the treated water, the results showed no change at 1 mg/L and a 4% drop in log inactivation at 3 mg/L. These results were likely

Table 4 | Impact of residual chlorine and monochloramine on MS2 log inactivation

UV reactor simulations					
Disinfectant	Concentration	Log reduction			
		Monochromatic		Polychromatic	
		Deionized water	Treated water	Deionized water	Treated water
Chlorine	0	1.52	1.53	1.54	1.76
	1	1.50	1.50	1.42	1.51
	3	1.49	1.53	1.32	1.60
Monochloramine	0	1.54	1.53	1.81	1.76
	1	1.50	1.53	1.55	1.80
	3	1.42	1.47	1.25	1.51

due to the interaction between these chlorine species and dissolved constituents found in the treated water body.

Table 4 also displays the MS2 log inactivation in the MP reactor. For simulations conducted with deionized water, the presence of residual chlorine reduced the level of log inactivation by 14% at 3 mg/L while the presence of residual monochloramine reduced the log inactivation by 31% at 3 mg/L. These results were consistent with the change in the absorbance spectra, particularly between 260 and 300 nm for chlorine and between 200 and 270 nm for monochloramine. The larger drop in the log inactivation with the addition of monochloramine was due to the increase in UV absorbance in the wavelengths where a significant amount of UV absorption can occur in the nucleic acids.

When 1 mg/L of residual chlorine was added to treated water, the results showed a 14% reduction in the log inactivation in the MP reactor. However, at 3 mg/L of residual chlorine, only a 9% reduction in log inactivation was predicted. The lower log reduction at 1 mg/L versus 3 mg/L is due to the lower absorbance in the wavelengths between 245–260 nm when the treated water contains 3 mg/L residual chlorine. When the treated water contained 1 mg/L of residual monochloramine, the MP reactor results displayed a 2% increase in MS2 log inactivation. At 3 mg/L

of residual monochloramine, a 14% decrease in the log inactivation was observed. As discussed earlier, the higher sensitivity to monochloramine at higher residual concentrations was due to the change in the water quality absorbance spectra between 230–275 nm, which is the high absorbing region for nucleic acids.

Thus, a chlorine or monochloramine residual that is carried through a treatment plant is unlikely to affect the delivered UV dose for a monochromatic LP-UV reactor. However, the simulated results indicate that a chlorine or monochloramine residual may impact the disinfection performance of a polychromatic UV reactor. The degree to which the chlorine species will impact the MP-UV reactor will depend on the nature of the constituents remaining in the treated water. In some cases, the amount of chlorine residual could enhance the disinfection performance since it is oxidizing compounds that reduce the UV transmissivity. In other cases, the chlorine or monochloramine residual may itself hinder the UV disinfection performance by decreasing the UV transmission. In raw water where the organic matter concentration is high, chlorine addition appears to decrease the absorbance of the water sample, thus improving UV transmission and increasing the average irradiance. Again, this is likely due to chlorine oxidizing the UV absorbing organic matter

present in the raw water sample. The results in this study suggest that site-specific assessment of the water quality (i.e. water absorbance spectral analysis) should be performed in the presence of chlorine or monochloramine residuals to better determine their impact on the UV disinfection performance.

CONCLUSIONS

1. The UV absorbance of free chlorine and monochloramine is relatively small. However, its presence may influence the effectiveness of UV disinfection or the delivery of UV light to the targeted microorganisms, depending upon the water quality and type of UV system.
2. Site-specific assessment of the spectral water absorbance should be performed in the presence of chlorine or monochloramine residuals to determine their impact on the UV disinfection performance.
3. Chlorine and monochloramine in potable water decay steadily when exposed to monochromatic or polychromatic UV light. Total decay of chlorine and monochloramine is very small in the UV dose range that is generally applied for disinfection (15–130 mJ/cm²), and it can be concluded that UV does not have a significant effect on chlorine decay for potable water disinfection.
4. The rate of decay of free chlorine under monochromatic and polychromatic UV light differed among the water qualities tested. Poorer water quality (raw water higher in organic and inorganic constituents versus treated or deionized water) resulted in higher decay rates of chlorine.
5. In contrast to free chlorine, the decay rate of monochloramine under monochromatic and polychromatic UV light was not affected significantly by the water quality ranges tested in this study.
6. Monochromatic UV light was more effective in degrading monochloramine, whereas polychromatic UV light was more effective in degrading free chlorine.

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