

IMPACT OF CHLORINE AND MONOCHLORAMINE ON ULTRAVIOLET LIGHT DISINFECTION

Banu Örmeci

Department of Civil and Environmental Engineering
Duke University, Durham, NC

Gina A. Ishida

Department of Environmental Science and Engineering
University of North Carolina, Chapel Hill, NC

Karl G. Linden

Department of Civil and Environmental Engineering
Duke University, Durham, NC

ABSTRACT

Chlorination of water during treatment upstream of the disinfection process may possibly influence the effectiveness of ultraviolet (UV) inactivation in three ways: (1) chlorine and monochloramine may absorb UV light and interfere with the delivery of UV light to the targeted microorganisms, (2) oxidation of organic matter by chlorine may alter the UV absorbance, and (3) UV irradiation may photo-dechlorinate the active chlorine species. In this study, degradation rate of free chlorine and monochloramine under monochromatic and polychromatic UV light was determined in raw, treated, and deionized water samples. UV absorbance spectra of chlorine and monochloramine were also measured in raw, treated, and deionized water samples. The impact of chlorine-based UV absorbance on delivery of UV for disinfection was investigated. The results of this study indicate that chlorine is degraded during UV disinfection at typical UV doses although the extent of degradation is dependent upon the type of chlorine species, the water quality, and the type of UV irradiation (mono- or poly-chromatic). The transmission of UV irradiation in a 1 cm pathlength is slightly effected by the presence of chlorine and monochloramine, decreasing the available UV energy by up to 2.25 %. However, the addition of chlorine can serve to decrease the UV absorbance under certain water quality matrices.

Introduction

Prechlorination is an important tool for maintaining the water quality and efficiency of a treatment plant. Although the primary use of chlorine is for disinfection, chlorine can also be used to control the taste and odor, remove color and turbidity, and aid coagulation and filtration in a treatment plant. Depending on the purpose of prechlorination, chlorine may be added at various points during the treatment process such as before coagulation, sedimentation, or filtration. Prechlorination doses required to maintain a substantial (1 mg/L) free residual chlorine in water is closely related to water quality and increases when organic and inorganic matter concentration is high in water. Prechlorination doses of 16 mg/L have been reported in the literature (White, 1999).

Prechlorination of water during the treatment process may possibly influence the effectiveness of ultraviolet (UV) disinfection. Chlorine and monochloramine present in the prechlorinated water may absorb the UV light and interfere with the delivery of UV radiation to the targeted microorganisms. 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. Other interactions that involve chlorine and UV disinfection processes include the impact of chlorination on the presence of organic matter in the water (thus UV absorbance) and the impact of UV at practical disinfection doses on dechlorination. Therefore, it is important to understand how chlorine and monochloramine behave under UV irradiation. The objectives of this research are to determine 1) how the presence of chlorine and monochloramine affects the efficiency of UV disinfection, 2) the kinetics of chlorine and monochloramine decay under monochromatic and polychromatic UV light, and, 3) the effect of water quality on the interaction of UV absorbance and chlorine and monochloramine decay.

Background

Chlorine reacts with organic and inorganic matter in water by oxidation and substitution reactions. One of the most important reactions for chlorine is the formation of chloramines in the presence of ammonia. This reaction converts chlorine to mono-, di-, and trichloramines depending on the pH, temperature, contact time, and initial ratio of chlorine to ammonia in water. Monochloramine is known to be a weaker and slower disinfectant compared to free chlorine, but its use in disinfection is preferred when chlorine residuals are difficult to control. Monochloramine is more effective against biofilms (LeChevallier et al., 1988), stays in the water distribution system longer, and is cheaper compared to free chlorine. Both free chlorine and monochloramine form organic monochloramines in the presence of organic nitrogen (e.g., amino acids and proteins). The reaction of free chlorine with organic nitrogen is instant, whereas monochloramine takes several minutes (White, 1999). Presence of natural organic matter in water accelerates the decay of monochloramine via oxidation and reduction reactions (Vikesland et al., 1998).

Photochemical reactions also play an important role in the decay of chlorine compounds. During the photolysis of HOCl and OCl⁻, various primary reactive intermediates are formed which are rapidly converted into secondary photooxidants such as OH and Cl radicals (Buxton and Subhani, 1982; Molina et al., 1980). In the presence of organic material, two chain reactions have been proposed in which organic solutes and HOCl may act as chain promoters and OH and Cl radicals as chain carriers (Oliver and Carey, 1977; Nowell and Hoigne, 1992a). Formation of these radicals increases the degradation rate of organic compounds. Nowell and Hoigne (1992b) have reported that organic probe molecules resistant to photolysis decayed when they were exposed to UV or sunlight in the presence of chlorine.

Materials and Methods

Three different water samples were used in this study: 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 beginning of the

treatment plant prior to any treatment. Treated water was collected from the top of the settling tank after the coagulation-flocculation process and before the sand filtration. In the treatment plant, chlorine was injected into the pipes during the transfer of water from the settling tanks to the sand filters, therefore settled water, having no chlorine, was chosen over chlorinated filtered water to be used in this research. The third water sample was deionized water (Hydro, Research Triangle Park, NC). Unlike treated water and raw water, deionized water did not contain any organic and inorganic matter and served as a control in the experiments.

Water samples having an initial free chlorine and monochloramine concentration of 4 to 5 mg/L were prepared from fresh household bleach (5.25% sodium hypochlorite, Clorox) and 100 mg/L monochloramine stock solution. Monochloramine stock solution was prepared by adding 0.37 mL Clorox to 100 mL 0.01 M pH 9.5 buffer and 0.081 g NH_4Cl to 100 mL 0.01 M pH 9.5 buffer, and combining these two mixtures slowly. Free chlorine and combined chlorine concentrations were determined using a combination of DPD ferrous titrimetric and DPD colorimetric methods (APHA, 1998).

Samples that contained chlorine or monochloramine were exposed to monochromatic and polychromatic UV irradiation in a collimated beam apparatus and the decrease in the chlorine and monochloramine concentrations were measured over the duration of the experiments. The UV doses used ranged between 0 and 1500 mJ/cm^2 in increments of 100 mJ/cm^2 . 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 under either lamp. Each dose of 100 mJ/cm^2 corresponded to an exposure time of approximately 4 minutes, thus the complete experiment took approximately 1 hour to complete. UV dose (mJ/cm^2) was calculated as the product of the UV irradiance (mW/cm^2) multiplied by the exposure time (s). Samples of 300 mL were placed in a crystallization dish, and stirred continuously with a magnetic stirrer during the irradiation to achieve a well-mixed sample that was homogenous with respect to water constituents and properties. A sample volume of 5 mL was withdrawn from the petri dish after each dose of 100 mJ/cm^2 to determine the residual chlorine or monochloramine concentration in the sample. The large size dish with a wide mouth (125x65 mm) was chosen to minimize the change in the depth of the water 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 at the end of the experiment. The incident irradiation was measured using a radiometer with a germicidal UV detector (IL 1700 SED 240/G/W, International Light, Newbury Port, MA) calibrated over the entire germicidal range to standards traceable to the National Institute of Standards and Technology (NIST). Absorbance spectra scans of samples containing 1, 3 and 5 mg/L chlorine or monochloramine were measured using a Varian Cary 100 Bio UV-visible spectrophotometer (Varian Analytical Instruments, Walnut Creek, CA) from 200 nm to 400 nm.

Turbidity (Hach Company, Hach 2100N, Loveland, CO), pH (Cole Parmer Instrument Company, pH 100 series, Vernon Hills, IL), total carbon, total organic carbon, and

inorganic carbon (Apollo 9000, Tekmar-Pohrmann, Cincinnati, OH) in the treated and raw water were initially determined before starting the experiments.

Results and Discussion

The degradation rates of the chlorine and monochloramine were determined after the UV exposure and compared. In addition, absorbance spectra of representative concentrations of chlorine and monochloramine applied in a typical prechlorination process were determined in raw, treated, and deionized water samples.

Figure 1a illustrates the decay of free chlorine in the deionized water after exposure to monochromatic and polychromatic UV light. An identical sample was kept in the dark over the duration of the experiment. The chlorine concentration of the control sample that was kept in the dark did not show a significant change. Deionized water does not contain any organic or inorganic matter, therefore consumption of chlorine or monochloramine by chemical oxidation and substitution reactions is unlikely to occur. In addition, since the sample was kept in the dark, photolysis cannot take place. The samples that were exposed to monochromatic and polychromatic UV light exhibited a gradual linear decay in chlorine with increasing UV dose. The free chlorine decay rate under monochromatic UV was slightly higher than the decay rate under polychromatic UV light. The decay of monochloramine in deionized water under the same conditions is presented in Figure 1b. The monochloramine concentration was steady in the dark, and under monochromatic and polychromatic UV light, monochloramine exhibited a higher decay rate than free chlorine. Monochloramine also decayed linearly under monochromatic and polychromatic UV light, however monochromatic UV was more effective in degrading monochloramine than the polychromatic UV light. The decreases are attributed to the photochemical reactions induced by UV light.

The decay of free chlorine in the treated water is shown in Figure 2a. The decay rates of chlorine under monochromatic and polychromatic UV irradiation were much higher compared to the decay rates in deionized water. In fact, all of the chlorine was consumed after receiving a dose of 800 mJ/cm^2 with polychromatic UV and 1100 mJ/cm^2 with monochromatic UV light in the treated water. Polychromatic UV was more effective in decaying the chlorine compared to the monochromatic UV light. Free chlorine exhibited an exponential decay in the dark in which chlorine consumption was rapid in the first 10 minutes and then leveled off. In contrast, monochloramine consumption was insignificant in the dark (Figure 2b). Monochloramine decayed slower than free chlorine under monochromatic and polychromatic UV light. In the treated water, monochromatic UV was more effective in decaying monochloramine, and polychromatic UV was more effective in decaying free chlorine.

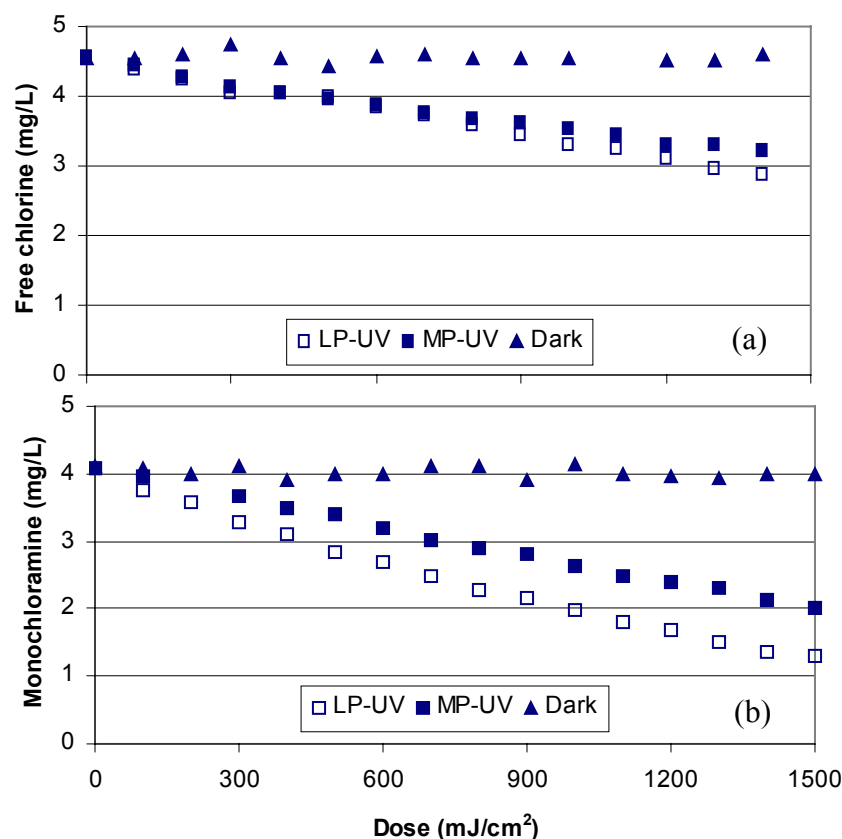


Figure 1. The decay of (a) free chlorine and (b) monochloramine in deionized (DI) water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light

Organic and inorganic matter present in treated water may be involved in a variety of chemical and photochemical reactions in the presence of chlorine. Possible reactions include: chlorine decay in natural waters due to reactions with organic (amino acids and proteins) and inorganic (ammonia, nitrites, nitrates) nitrogen; chlorine reacting with ammonia and organic nitrogen to form chloramines and organochloramines respectively; chlorine reactions with inorganic ions, such as Fe and S, contribute to the chlorine decay as well. The rapid decrease in free chlorine in the control sample (dark, Figure 2) is attributed to the chlorine demand of the water sample. The free chlorine decay rates in treated water are presented in Table 1. Decay rates in treated water under monochromatic ($K = -0.0038 \text{ mg.cm}^2/\text{mJ.L}$) and polychromatic ($K = -0.0056 \text{ mg.cm}^2/\text{mJ.L}$) UV light were much higher compared to the decay rates in deionized water ($K = -0.0012 \text{ mg.cm}^2/\text{mJ.L}$ and $K = -0.0009 \text{ mg.cm}^2/\text{mJ.L}$). Natural water contains various organic and inorganic species, including humic substances, algae, and suspended particles, that can have a substantial influence on the photolysis of chlorine (Nowell and Hoigne, 1992a; Nowell and Hoigne, 1992b). Presence of these constituents changes the reaction rates of direct and indirect photolysis by absorbing, scattering, and attenuating UV light. UV light is primarily absorbed by dissolved organic matter and organic particles in water (Schwarzenbach et al., 1993). Absorbance of light by organic constituents may enhance

the rate of indirect photolysis and initiate a series of reactions that eventually consume chlorine. On the other hand, organic and inorganic matter in water may scatter and attenuate UV light and decrease the rate of direct photolysis. Miller and Zepp (1979) have demonstrated that suspended sediments can change the photolysis rates through scattering and light attenuation. Sorbed species on particles may also alter the rate of the photochemical reactions (Miller and Zepp, 1979b) since a compound in sorbed state may behave differently than its dissolved state. Overall, the increase due to the indirect photolysis rate is likely to be more significant than the decrease due to the direct photolysis rate which explains the higher decay rates observed in treated water.

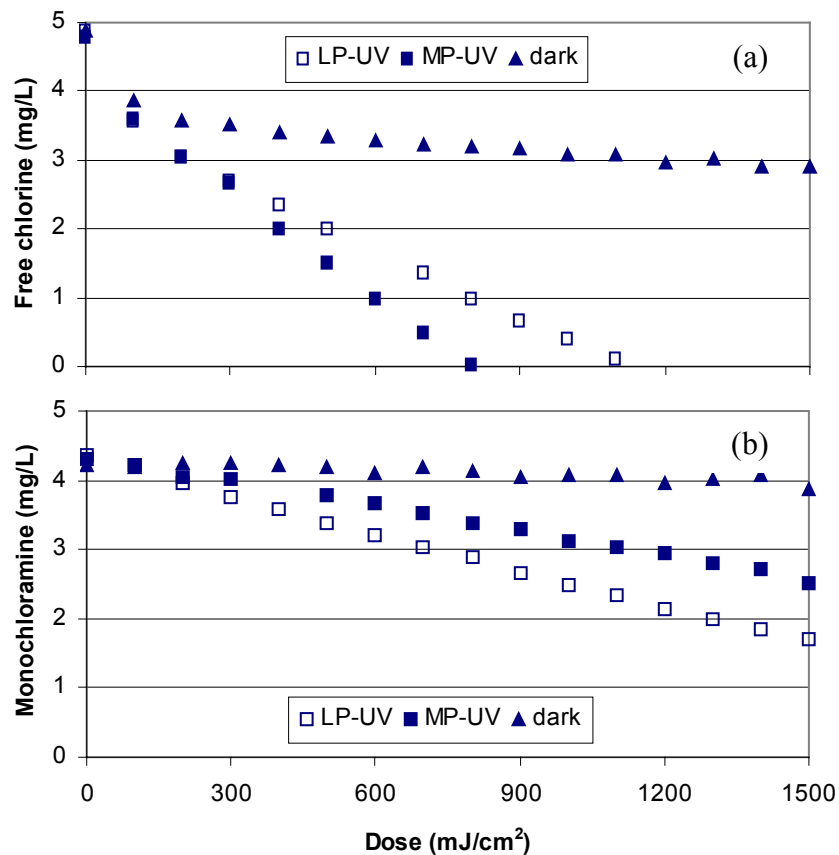


Figure 2. The decay of (a) free chlorine and (b) monochloramine in treated water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light

Table 1.
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
DI	Free chlorine	K= -0.0012	K= -0.0009	K= -0.00003
	Monochloramine	K= -0.0018	K= -0.0012	K= -0.00006
Treated	Free chlorine	K= -0.0038	K= -0.0056	K= -0.0008
	Monochloramine	K= -0.0018	K= -0.0012	K= -0.0002
Raw	Free chlorine	K= -0.0068	K= -0.0084	K= -0.0015
	Monochloramine	K= -0.0017	K= -0.0011	K= -0.0003

* Unit of decay coefficient K is $\text{mg}\cdot\text{cm}^2/\text{mJ}\cdot\text{L}$

Presence of natural organic matter in water accelerates the decay of monochloramine as well. Vikesland et al. (1998) reported that natural organic matter directly reacts with monochloramine by redox and substitution reactions, and the role of organic matter as an acid catalyst is negligible. This might explain the slightly higher rates of monochloramine decay in the dark in treated and raw water compared to deionized water. As in the case with chlorine, UV irradiation also increased the rate of monochloramine decay. However, unlike chlorine, monochloramine decay rate did not show a significant change between treated and raw water samples under UV exposure. As illustrated in Table 1, monochloramine decay coefficient was approximately $-0.0002 \text{ mg}\cdot\text{cm}^2/\text{mJ}\cdot\text{L}$ in the dark, $-0.0018 \text{ mg}\cdot\text{cm}^2/\text{mJ}\cdot\text{L}$ under monochromatic UV, and $-0.0012 \text{ mg}\cdot\text{cm}^2/\text{mJ}\cdot\text{L}$ under polychromatic UV regardless of the organic and inorganic content of the water. This is as expected because monochloramine is relatively stable compared to free chlorine.

The characteristics of waters used in this study are illustrated in Table 2. In raw water, which contained more organic and inorganic matter compared to the first two samples, the chlorine degradation was fastest (Figure 3a). The free chlorine exhibited an exponential decay in the dark as was the case with treated water, however the decay rate was faster. Polychromatic UV was again more effective than monochromatic UV light in the degradation of free chlorine. The chlorine concentration in the sample dropped to 0 mg/L following doses of $400 \text{ mJ}/\text{cm}^2$ with polychromatic UV, and $700 \text{ mJ}/\text{cm}^2$ with monochromatic UV irradiation. Monochromatic UV 254 nm light, on the other hand, was more effective for the degradation of monochloramine (Figure 3b). The decay rates of monochloramine in raw water under monochromatic and polychromatic UV light were very similar to the decay rates of monochloramine in treated water.

Table 2.
Water quality characteristics of waters used in the study

Sample	pH	Turbidity (NTU)	TOC (ppm)	IC (ppm)
DI	6.48	0.10	0.25	0.79
Treated Water	7.00	2.44	3.33	0.83
Raw Water	7.13	9.61	5.86	0.86

The absorbance spectra of free chlorine and monochloramine are illustrated in Figure 4a and 4b respectively. The absorption maximum of free chlorine is somewhere around 290 nm which falls in the range of polychromatic UV light from the medium pressure UV lamp output. The absorption maximum of monochloramine, on the other hand, is approximately 246 nm, close to the low pressure UV lamp output at 254 nm, therefore when decay rates are based on delivered UV energy, monochromatic UV 254 irradiation proves more effective than polychromatic UV light in the photochemical degradation of monochloramine. The UV absorbance spectra of deionized, treated and raw water samples dosed at 5 mg/L free chlorine or monochloramine are presented in Figure 4a and b. Free chlorine absorbance maximum at approximately 290 nm was most visible in deionized water, and gradually decreased in the filtered and raw water. However, the absorbance spectra peak of monochloramine at approximately 246 nm did not change noticeably between the 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 increases. Absorbance spectra of monochloramine, in contrast, does not seem to be affected by the organic and inorganic matter content, and indicating that the rate of monochloramine decay is not influenced as much by water quality parameter changes.

Table 3 and Table 4 illustrate the effect of chlorine and monochloramine UV absorbance respectively, on average monochromatic UV irradiance in a batch completely mixed sample with depth of 1 cm. The initial dosed chlorine or monochloramine concentration was 5 mg/L. Addition of chlorine and monochloramine increases the UV absorbance of the water samples slightly, and therefore decreases the average UV 254nm irradiance received by the water body. However, 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. This is likely due to chlorine oxidizing the organic matter present in the raw water sample.

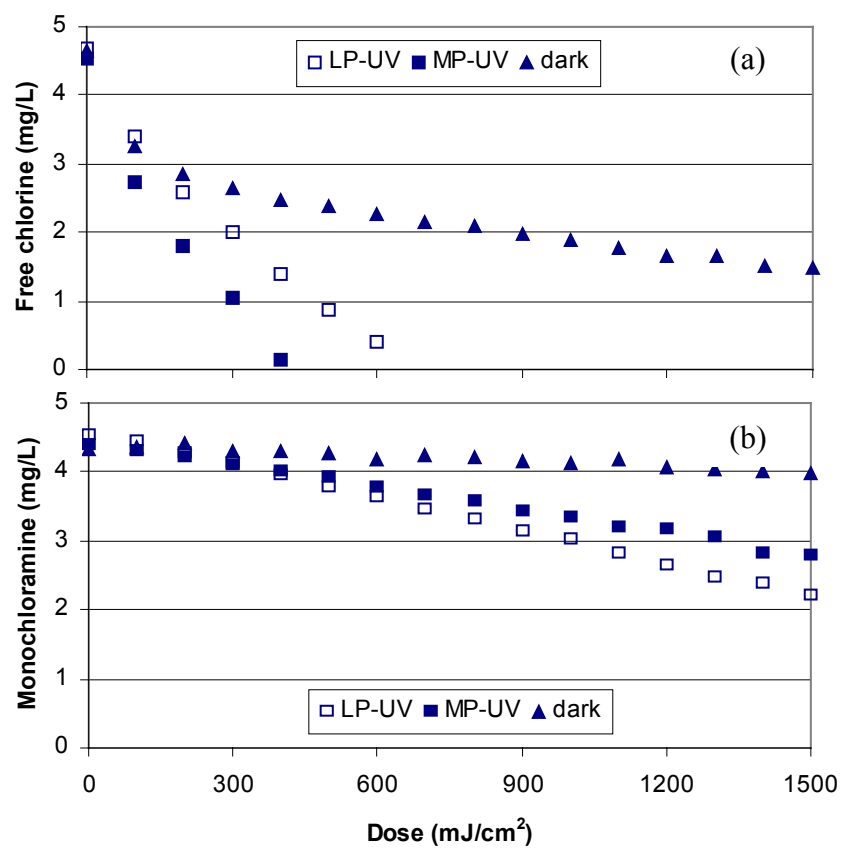


Figure 3. The decay of (a) free chlorine and (b) monochloramine in raw water after exposure to monochromatic 254 nm (LP-) and polychromatic (MP-) UV light

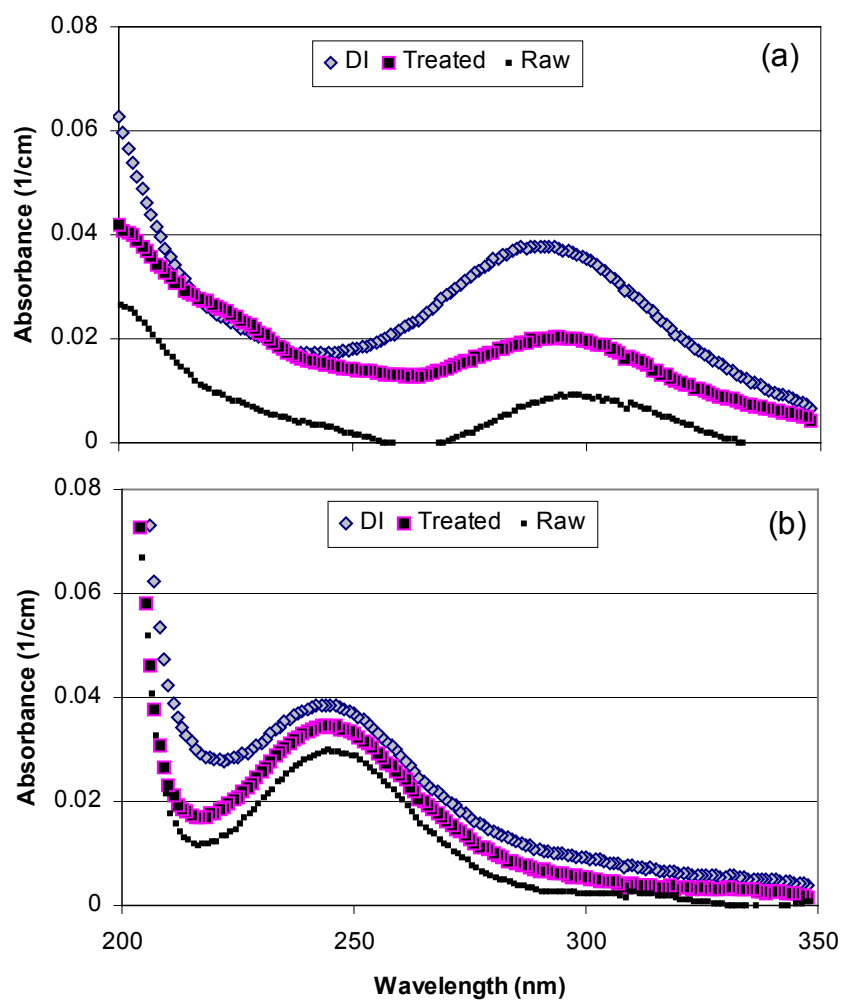


Figure 4. The absorbance spectra of (a) free chlorine and (b) monochloramine following a dose of 5 mg/L free chlorine or monochloramine into DI, treated, and raw waters.

Table 3.

The effect of chlorine UV absorbance on average LP- UV 254 nm irradiance in a 1 cm batch sample with an initial dose concentration of 5 mg/L.

Sample	A₂₅₄	%T₂₅₄	I avg. mW/cm²	Δ I avg. (%)
DI	0.0133	96.98	0.4260	-0.68
DI with chlorine	0.0190	95.72	0.4192	
Treated	0.0117	97.34	0.4277	-0.25
Treated with chlorine	0.0137	96.89	0.4252	
Raw	0.0095	97.84	0.4302	1.02
Raw with chlorine	0.0006	99.86	0.4404	

Table 4.

The effect of monochloramine UV absorbance on average LP- UV 254 nm irradiance in a 1 cm batch sample with an initial dose concentration of 5 mg/L.

Sample	A₂₅₄	%T₂₅₄	I avg. mW/cm²	Δ I avg. (%)
DI	0.0133	96.98	0.4260	-2.25
DI with monochloramine	0.0341	92.45	0.4035	
Treated	0.0117	97.34	0.4277	-1.99
Treated with monochloramine	0.0302	93.28	0.4078	
Raw	0.0095	97.84	0.4302	-1.77
Raw with monochloramine	0.0257	94.25	0.4125	

Conclusions

1- Chlorine and monochloramine in water decay steadily when exposed to monochromatic and polychromatic UV light. However, total decay of chlorine and monochloramine are relatively small in the UV dose range that is generally applied for disinfection (15-130 mJ/cm²).

2- The decay rate of free chlorine under monochromatic and polychromatic UV light is closely related to the water quality. The decay rate of chlorine increases with increased concentrations of organic and inorganic matter in water.

3- In contrast, the decay rate of monochloramine under monochromatic and polychromatic UV light does not seem to be affected significantly by the water quality. The decay rate remains same under exposure to a given UV light source regardless of the organic and inorganic matter concentration in water.

4- Monochromatic UV light is more effective in degrading monochloramine, and polychromatic UV light is more effective in degrading free chlorine.

5- The UV absorbance of free chlorine and monochloramine are relatively small and their presence is unlikely to significantly influence the effectiveness of UV disinfection or the delivery of UV light to the targeted microorganisms at typical UV doses applied for disinfection.

REFERENCES

- APHA, American Public Health Association, American Water Works Association, and the Water Environment Federation (1995) *Standard Methods for the Examination of Water and Wastewater*. 19th Ed., Washington, D.C.
- Buxton, G. V., and Subhani, M. S. (1972) Radiation chemistry and photochemistry of oxychlorine ions – II. Photodecomposition of aqueous solutions of hypochlorite ions. *Trans. Faraday. Soc.*, **68**, 958-969.
- LeChevallier, M. W., Cawthon, C. D., and Lee, R. G. (1988) Inactivation of Biofilm Bacteria. *Appl. Environ. Microbiol.*, **54**(10), 2492-2499.
- Miller, G. C., and Zepp, R. G. (1979a) Photoreactivity of aquatic pollutants sorbed on suspended sediments. *Environ. Sci. Technol.*, **13**, 853-860.
- Miller, G. C., and Zepp, R. G. (1979b) Effect of suspended sediments on photolysis rates of dissolved pollutants. *Wat. Res.*, **13**, 459-543.
- Molina, M. J., Ishiwata, T., and Molina, L. T. (1980) Production of OH radical from photolysis of HOCl at 307-309 nm. *J. Phys. Chem.*, **84**, 821-826.
- Nowell, L. H., and Hoigne, J. (1992a) Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths – I. Degradation kinetics. *Wat. Res.*, **26**(5), 593-598.
- Nowell, L. H., and Hoigne, J. (1992b) Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths – II. Hydroxyl radical production. *Wat. Res.*, **26**(5), 599-605.
- Oliver, B. G., and Carey, J. H. (1977) Photochemical production of chlorinated organics in aqueous solutions containing chlorine. *Envr. Sci. Technol.*, **19**, 1206-1213.
- Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) *Environmental Organic Chemistry*, Wiley, New York, N.Y., USA.
- Vikesland, P. J., Ozekin, K., and Valentine, R. L. (1998) Effect of natural organic matter on monochloramine decomposition: Pathway Elucidation through the use of mass and redox balances. *Environ. Sci. Technol.*, **32**(10), 1409-1416.
- White, G. C. (1999) *Handbook of chlorination and alternative disinfectants*, Wiley, New York, N.Y., USA.