Practical Paper

Loss of chlorine, chloramine or chlorine dioxide concentration following exposure to UV light

Jennie L. Rand and Graham A. Gagnon

ABSTRACT

In a field study conducted previously in Pinellas County, Florida, implementing UV treatment following chemical disinfection hindered control of HPC bacteria and resulted in higher counts in most samples. It was believed that free chlorine and monochloramine were either decaying in the presence of UV light or that they were absorbing UV irradiation. These occurrences would both lead to a decrease in available disinfection and in turn lead to increased bacteria counts.
A bench-scale study was conducted to further investigate interactions between UV light and chemical residuals in drinking water. Three separate water sources (surface water, blended water and deionized water) were treated with chlorine, monochloramine or chlorine dioxide at different concentrations, then exposed to low-pressure UV light. It was confirmed that chemical disinfectants decay when samples are exposed to UV light. Specifically, for deionized water free chlorine was lowered to approximately 95% of initial concentration following UV treatment.
In contrast, free chlorine was decreased to 89% and 84%, on average, in the tested groundwater and surface water, respectively. A similar range in decreased disinfectant concentration was also observed for chlorine dioxide and chloramines. However, no significant absorption of UV irradiation by chemical disinfectants was observed. These results provide greater insight into the confounding effects between chlorine-based disinfectants and UV light, which may be important for utilities or institutions that are considering UV treatment of previously disinfected water.

Key words | chloramines, chlorine, chlorine dioxide, disinfection, UV disinfection

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INTRODUCTION

Previous studies have shown synergistic benefits with sequential disinfection (Li *et al.* 2004; Koivunen & Heinonen-Tanski 2005; Dykstra *et al.* 2007), considering synergy as when the 'efficiency of combined disinfection method is greater than the efficiency achieved when summing the effects of individual disinfectants' (Koivunen & Heinonen-Tanski 2005). A potential concern related to the implementation of UV irradiation in a treatment process is the interaction between UV light and chemical disinfection. Some studies have shown that free chlorine (Cl_2) or monochloramine

(NH_2Cl) in water exerts demand on the UV light through absorbance of UV irradiation, and conversely that the UV light destroys the chemical disinfectants reducing the available residual for inactivation of microbial cells. Ormeci *et al.* (2005) found that, although UV absorbance of free chlorine and monochloramine was relatively small, it may alter the effectiveness of UV light towards targeted microorganisms. This study also found that chlorine and monochloramine in potable water decay steadily in the presence of UV light, especially chlorine in poorer water quality.

A study was conducted in Pinellas County, Florida, to investigate the potential for enhanced disinfection due to the implementation of UV light following treatment with chlorine or monochloramine (Rand & Gagnon 2007, this issue). Annular reactors (ARs) were used to simulate drinking water distribution systems with varying treatments including Cl_2, NH_2Cl, Cl_2 followed by UV light, and NH_2Cl followed by UV light. The results showed that those ARs additionally treated with UV light had higher suspended and biofilm heterotrophic (HPC) bacteria levels. Considering the results of the Pinellas County study, it was important to determine whether UV light decreased chemical residual thereby allowing higher bacteria levels in the streams additionally treated with UV. Findings could be beneficial for implementing UV light in a treatment process, especially where UV disinfection is used for water entering a distribution system. The focus of this study was to further investigate the interactions between chlorine, monochloramine or chlorine dioxide (ClO_2) and UV light in various types of water. Specifically, the goal was to determine the extent of free Cl_2, NH_2Cl and ClO_2 decay in the presence of UV light, and the potential for these chemicals to absorb UV light.

METHODS AND MATERIALS

Experimental design

A bench-scale experiment was designed to further investigate interactions between UV light and chlorine-based disinfectants. This included the decay of these chlorine-based disinfectants in the presence of UV light in addition to their potential absorbance of UV irradiation. Water was collected from three sources: groundwater from Pinellas County, surface water from Halifax, Nova Scotia, and deionized water (DI). A sample of each water source was dosed with a disinfectant to achieve a desired concentration. DI water samples were dosed with chlorine, monochloramine and chlorine dioxide and had resulting concentrations of between approximately 0.20 and 5.00 mg l^{-1}. Samples from Pinellas County had existing free chlorine (0.45 mg l^{-1} Cl_2) or monochloramine (3.10 mg l^{-1} NH_2Cl). The chlorinated water samples were analysed with no additional dosage as well as at residuals of between approximately 0.50 and 5.00 mg l^{-1} free chlorine. The sample pre-treated with monochloramine was also analysed with no additional chemical added as well as approximate concentrations of 0.40, 1.00 and 5.00 mg l^{-1} monochloramine. Finally, the surface water sample from Halifax was dosed with chlorine, monochloramine or chlorine dioxide with resulting concentrations of between approximately 0.20 and 5.0 mg l^{-1}.

Each sample was analysed for turbidity, UV transmittance (UVt) and disinfectant residual. The samples were then placed on a stirrer and exposed to UV light to achieve a dose of 100 mJ cm^{-2}. A control sample was also stirred for the same time to account for volatilization of the samples. Following exposure, the samples were re-measured for disinfectant residual and UVt to compare values pre- and post-UV treatment. Exposure to UV light was achieved by using a collimated beam apparatus. Dosages were achieved by following a method written by Bolton & Linden (2003) that attempts to standardize the determination of UV fluence.

Generation of disinfectants

Chlorine dioxide was generated onsite according to Method 4500-ClO_2 of *Standard Methods for the Examination of Water and Wastewater* (1998). The generator consists of a bench-top apparatus, in which a 25% sodium chlorite solution is slowly added to an 18N sulphuric acid solution, producing chlorine dioxide. The chlorine dioxide is purged from the mixture in a gas-washing bottle, and trapped in water surrounded by an ice bath. Off-gas from this bottle is directed to a potassium iodide trap to prevent the release of chlorine dioxide into the air. The resulting chlorine dioxide solution is approximately 2–7 g l^{-1}. The ClO_2 was diluted with de-ionized water as necessary in demand-free amber bottles as stock solution for the experiment.

Concentrated free chlorine was produced using a 12.5–16% solution of analytical grade sodium hypochlorite. Chlorine stock bottles were prepared in demand-free amber glass bottles containing de-ionized water, and used to attain desired concentrations for the experiment.

Monochloramine was generated by diluting 100 ml of phosphate buffer solution (PBS) in 900 ml of de-ionized water. The pH of this solution was adjusted to 9.4 using sodium hydroxide. Ammonium chloride (4 g) was dissolved in 500 ml of the diluted PBS. The remaining 500 ml PBS

solution was mixed with 18.7 ml of 12.5% analytical grade sodium hypochlorite. The chlorine stock was then added to the ammonium chloride solution while being continuously stirred with a stir bar and magnetic stir plate. This procedure produced a 1–l monochloramine stock solution of between 2,800 and 3,500 mgl^{-1}.

Sample analysis

Turbidity, UVt, pH and disinfectant concentration were measured for each sample before exposure to UV light, and disinfectant residual and UVt were also measured post-UV treatment. All sampling and testing protocols were carried out as described in *Standard Methods* (1998).

UVt was measured using an HF Scientific UVT-15 photometer with a 1-cm path length. Samples were analysed for turbidity using a HACH 2100P turbidimeter (HACH Company, Loveland, Colorado), and pH was measured using an ORION model 230A. Finally, chlorine and chlorine dioxide were measured using the DPD colorimetric method and a HACH DR/2100 spectrophotometer (HACH Company, Loveland, Colorado). Monochloramine was measured using a DPD ferrous titrimetric method (4500 D; *Standard Methods for Examination of Water and Wastewater* 2005).

UV collimated beam apparatus

The collimated beam apparatus consisted of a low pressure light that was encased. At the centre of the lamp, a UV-transparent window directed the light down a tunnel-like path, which was also encased, towards a stirrer. A Petri dish containing the sample was placed on the stirrer for the UV exposure. The UV dose was set at 100 mJ cm^{-2} using a method presented by Bolton & Linden (2003). A spreadsheet programmed by Bolton (2004) was used to determine exposure times in order to reach the objective UV dose. A reading from a radiometer at the centre of the stirrer was input into the spreadsheet, as well as the absorption coefficient of the sample, vertical distance from the surface of the lamp to the Petri dish, sample volume and desired fluence. Taking into consideration a reflection factor, a divergence factor and a Petri factor (irradiation at outer edge of Petri dish compared with centre), exposure times for various dosages were calculated and output with the spreadsheet.

Sample volumes were constant at 45 ml, and the radiometer reading and distance between the Petri dish and the lamp was also consistent throughout the experiment. Absorption coefficients did not change significantly between different disinfectant concentrations and were therefore kept constant for each water source for the purposes of the spreadsheet. However, the absorption coefficients varied between water sources and were adjusted accordingly for DI water, Halifax water and Pinellas water. Exposure times for each water source to obtain a 100 mJ cm^{-2} dose ranged from 8.42 minutes (DI water) up to 9.37 minutes (Halifax water).

RESULTS AND DISCUSSION

Water quality parameters were measured for each water source and the average values of this analysis are presented in Table 1. In general, the Halifax surface water had a slightly higher UV absorbance at 254 nm than the Pinellas water. However, the total organic carbon (TOC) concentrations in both sources were statistically similar at the 95% level of confidence.

Disinfectant residuals

On average water samples were exposed to chemical disinfectants for 10 minutes prior to being measured for initial concentration values followed by exposure to UV light. For each disinfectant and concentration, control samples were conducted to account for the loss of chemical disinfectant through stirring in the absence of exposure to UV light. The difference between final concentration in the

Table 1 │ Source water quality

Water source	pH	Absorption coefficient (cm^{-1})[*]	TOC (mg l^{-1})	Average turbidity (NTU)
Deionized water	8.05	0.001	0.30	< 0.10
Halifax	7.42	0.125	3.65	0.82
Florida (Cl$_2$)	7.87	0.091	3.70	0.81
Florida (NH$_2$Cl)	7.83	0.036	3.85	0.29

[*]UV absorbance was quantified at 254 nm

final test sample and the control sample was used for calculating the effects of UV treatment. Thus the results indicate the loss of chemical residual concentration due to UV light exclusively. The average reduction in chlorine control samples for DI water was $0.0 \pm 0.0 \, \text{mgl}^{-1}$, $0.11 \pm 0.06 \, \text{mgl}^{-1}$ for Halifax surface water and $0.12 \pm 0.16 \, \text{mgl}^{-1}$ for Florida water. Monochloramine was reduced in DI water on average by $0.13 \pm 0.13 \, \text{mgl}^{-1}$, $0.0 \pm 0.0 \, \text{mgl}^{-1}$ in surface water and $0.09 \pm 0.06 \, \text{mgl}^{-1}$ in Florida water. Chlorine dioxide proved to be a much more volatile chemical and control samples were reduced on average by $1.35 \pm 0.29 \, \text{mgl}^{-1}$ in Halifax and DI water sources.

Chlorine was decreased in every type of water source and at every residual concentration. Figure 1 shows the line of equivalence at which the amount of chlorine dosed (i.e. initial Cl_2 concentration) would equal the chlorine concentration following UV treatment (or final Cl_2 concentration). For deionized water the slope of this line was 0.95, and for the two experimental waters the slopes were 0.89 (Pinellas) and 0.84 (Halifax). These data show that, for Halifax, for $1 \, \text{mgl}^{-1}$ of chlorine prior to UV treatment it would be anticipated that $0.84 \, \text{mgl}^{-1}$ would be present following the UV treatment. At high Cl_2 concentrations this factor would not be expected to be significant issue (e.g. greater than $2 \, \text{mgl}^{-1}$). However at lower concentrations (e.g. less than $0.5 \, \text{mgl}^{-1}$) a loss of 10–15% may be of greater
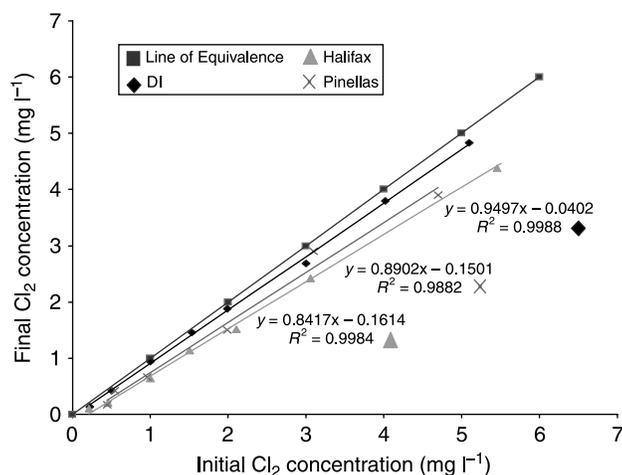
significance, especially for utilities that are aiming to maintain a residual chemical concentration.

These data correspond to findings by Ormeci et al. (2005) where higher reductions of chlorine were seen in waters of poorer quality (high turbidity and TOC). In this study, DI water had the lowest turbidity and TOC, while Cl_2 Pinellas water had higher turbidity and Halifax water had the highest (Table 1). The Cl_2 Pinellas water had an existing free chlorine concentration of $0.45 \, \text{mgl}^{-1}$. No change in Cl_2 concentration occurred in the control stirred sample, and the sample exposed to UV light while stirred had a decrease in free chlorine to $0.17 \, \text{mgl}^{-1}$, which corresponded to a 62.2% decrease.

Monochloramine did not show as large reductions as chlorine did. However concentrations were reduced in every water source. Similar plots were created for monochloramine and linear regression equations were obtained for each water source (Table 2). The demand of NH_2Cl in DI water was statistically similar to demand in Pinellas water although Pinellas water had higher turbidity ($0.29 \, \text{mg} \, \text{l}^{-1}$). Monochloramine concentration in DI water after UV exposure was approximately 90% of initial concentration and 92% in Pinellas water. The demand for monochloramine was statistically highest in the Halifax water, such that the final NH_2Cl concentration was 81% of initial concentration. Ormeci et al. (2005) demonstrated that water quality did not play a large role in the decay of NH_2Cl due to UV exposure, and these results also indicate NH_2Cl may not be as dependent on water quality as Cl_2. The Pinellas water had an existing NH_2Cl concentration of $3.10 \, \text{mg} \, \text{l}^{-1}$. The control sample decreased to $3.0 \, \text{mgl}^{-1}$ after being stirred, and the UV-exposed sample showed an even larger reduction to $2.80 \, \text{mgl}^{-1}$, which corresponded to a 6.5% reduction.

Only DI water and the surface water sources were treated with chlorine dioxide because the Pinellas samples contained either NH_2Cl or Cl_2. For the ClO_2 data, it was found that there was minimal, if any, loss of ClO_2 in DI water due to UV exposure in comparison with control samples. However ClO_2 is a much more volatile compound that was decreased by an average of 70% in control samples of DI water in this study. Halifax water demonstrated a loss of ClO_2 concentration following exposure to UV light and factoring the loss to volatilization. In particular the final ClO_2 concentration was approximately 82% of initial concentration.

Figure 1 │ Final chlorine concentration (post-UV light) versus initial chlorine concentration (pre-UV light).

Table 2 | Regression line equations for chlorine, monochloramine and chlorine dioxide in all water sources

Disinfectant	Halifax water		DI water		Pinellas water (Cl_2)		Pinellas water (NH_2Cl)	
	Regression line	R^2	Regression line	R^2	Regression line	R^2	Regression line	R^2
Cl_2	$y = 0.8417x - 0.1614$	0.9984	$y = 0.9497x - 00402$	0.9988	$y = 0.8902x - 0.1501$	0.9882		
NH_2Cl	$y = 0.8125x + 0.1500$	0.9999	$y = 0.9047x + 0.0025$	0.9996			$y = 0.9246x + 0.0087$	0.9998
ClO_2	$y = 0.8204x - 0.0093$	0.9999	$y = 1.0217x - 0.1156$	0.9998				

Ultraviolet light transmission

Less significant changes in UVt were observed compared with the reduction of disinfectant residual. However, there was an increase of UVt in each sample for each disinfectant type. Chlorinated samples on average showed an increase of 0.4% in DI water, 1.4% in surface water and 1.5% in Pinellas water. Samples containing monochloramine showed an increase in UVt for surface water (1.0%) and Pinellas water (0.5%), but none in DI water. Chlorine dioxide samples showed an increase in UVt for both surface water (1.3%) and DI (0.7%). As with disinfectant residual, less change was observed in higher quality sources. DI water on average had a smaller increase in UVt for each type of disinfectant compared with Pinellas and Halifax water sources. These results conflict with Ormeci *et al.* (2005) who found that UV absorbance (UVa) was increased due to the addition of chlorine or monochloramine, indicating these disinfectants absorbed UV light. This would suggest that there would be a decrease in the irradiation delivered to the water, thereby losing effectiveness of UV treatment. However, in both studies, the changes in UVa/UVt reported were very small (generally less than 2.5% with Cl_2 or NH_2Cl) and thus the impact of Cl_2 or NH_2Cl on UV absorbance is suspected to be subtle in practice. Thus, in agreement with the Ormeci *et al.* (2005) conclusions, it is recommended that a site-specific assessment be conducted to quantify the slight change in UV absorbance that is due to the presence of Cl_2 or NH_2Cl.

CONCLUSIONS

This bench-scale laboratory study confirmed the degradation of chlorine-based disinfectants with low-pressure UV treatment, where varying concentrations of chlorine, monochloramine and chlorine dioxide decayed with exposure to UV light. It was observed that chlorine concentration could be decreased in the range of 5–15% following UV treatment. Monochloramine and chlorine dioxide also showed decay at varying initial concentrations in different water sources. In addition, chlorine residual decreased by a higher percentage in poorer quality water, as was previously found by Ormeci *et al.* (2005). ClO_2 also had more significant decay in poorer quality water but this result was not as apparent with NH_2Cl. Decay of

residual concentration could lead to increased bacteria counts in water when UV treatment follows chemical disinfection.

The results from this study show it would be very important to consider the placement of UV light in the treatment train process. For instance, if implemented as water entered or within a distribution system, there is potential that the UV light could degrade the residual concentration, leaving the distribution system susceptible to breaches in the system and/or bacteria regrowth.

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