

Fluorescence characteristics of natural organic matter in water under sequential exposure to UV irradiation/chlor(am)ination

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ABSTRACT

The organic matter in International Humic Substances Society Natural Organic Matter (IHSS NOM) water exposed to ultraviolet (UV) irradiation and chlor(am)ine sequentially under practically relevant conditions was characterized based on fluorescence spectra. IHSS NOM water exposed to UV irradiation or chlor(am)ine alone was also evaluated. Both chlor(am)ine alone and UV/chlor(am)ine exposure showed similar chlor(am)ine demand and fluorescence spectra. UV irradiation and UV/chlorine exposure diminished the fluorescence intensity of IHSS NOM water, while UV/chloramine exposure resulted in increased fluorescence intensity. When compared with the results obtained following chlor(am)ination alone, IHSS NOM water showed decreased chlorine decay and increased chloramine decay after UV irradiation/chlor(am)ination. Additionally, IHSS NOM water exposed to UV/chloramine and chloramine showed less disinfection by-product (DBP) formation than water subjected to UV/chlorine and chlorine. Overall, these findings indicate that UV irradiation degrades NOM molecules to low-molecular-weight fractions, facilitating the subsequent reaction with chlor(am)ine. However, chlorine and chloramine play different roles in the reaction. Chlorine degradation and substitution dominates the process of UV/chlorine exposure, while chloramine substitution is the major reaction during UV/chloramine exposure.

Key words | chlor(am)ination, natural organic matter, sequential disinfection, UV

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INTRODUCTION

Chlorine is the chemical oxidant most commonly used worldwide for drinking water disinfection (Deborde & von Gunten 2008); however, its use has been decreasing, mainly because of the formation of toxic, mutagenic and carcinogenic disinfection by-products (DBPs) and residual chlorine during the disinfection process (Ates *et al.* 2007). Moreover, chlorination has low efficiency against viruses, bacterial spores and protozoan cysts (Korich *et al.* 1990).

Ultraviolet (UV) irradiation is a promising alternative to free chlorine as a primary disinfectant because of its ability to inactivate *Cryptosporidium parvum* without producing DBPs at common disinfection doses (Liu *et al.* 2002). However, owing to a lack of residual activity and the possible repair of UV-damaged microorganisms, UV irradiation

cannot be used as a stand-alone disinfectant (Hassen *et al.* 2000). Accordingly, combined use of UV and chlor(am)ine to maintain lasting residual activity and disinfection effects has been studied. The combination of UV irradiation as a primary disinfectant and free chlorine or monochloramine as a secondary disinfectant (sequential disinfection) has been shown to prevent subsequent microbial regrowth and produce a synergetic disinfection effect (Shang *et al.* 2007).

DBPs are formed when natural organic matter (NOM) in water reacts with a disinfectant (White *et al.* 2003). The most common DBPs include trihalomethanes (THM) and haloacetic acids (HAA). Humic substances (HS) are commonly found in natural waters, including humic acids (HA), fulvic acids (FA) and humins, which have different characteristics.

The effects on NOM water and the dominate reaction during the sequential exposure of UV/chlor(am)ine have rarely been reported. Wang *et al.* (2011) reported that the sequential disinfection of UV and chlorine effectively controlled photoreactivation and minimized the concentration of chlorine, decreasing the genotoxicity of treated wastewater. Liu *et al.* (2006) reported that monochloramine could be a better secondary disinfectant owing to its much smaller DBP formation and lower decay rate. Therefore, the present study was conducted to investigate how NOM transforms during the sequential exposure to UV/chlor(am)ine and elucidate the mechanism of the reaction. International Humic Substances Society (IHSS) NOM waters were used in this study, and chlor(am)ine was used as the disinfectant. Changes in NOM during the disinfection process were identified by three-dimensional excitation-emission matrix fluorescence spectroscopy (3D-EEM). The residual chlor(am)ine concentration, which was characterized by decay chlor(am)ine kinetics curves, was also investigated.

MATERIALS AND METHODS

UV irradiation systems

Collimated-beam UV apparatuses consisting of two low-pressure UV (LPUV) lamps (254 nm, UVP, Upland, CA, USA) were used to apply UV exposure (Liu *et al.* 2006). The UV lamps were turned on 30 min prior to the experiments to ensure constant radiation output. At the range in which the water samples were irradiated, the average UV intensity of collimated irradiation from the LPUV apparatus was 0.25 mW/cm^2 , as determined by a radiometer (DRC-100X, Spectronics, USA). The UV dosage (mJ/cm^2) was calculated as the product of the measured intensity and exposure time. A small glass dish (internal diameter 50 mm) containing the test solution (20 mL in volume and 8 mm in depth) was used to expose the water samples.

Reagents and water

Suwannee River NOM (RO isolation, Cat. 1R101N, from the IHSS, MN, USA) were dissolved into Maxima

Ultra Pure water to prepare NOM water samples. The NOM solutions were then passed through $0.45 \mu\text{m}$ cellulose acetate membrane filters and the filtrates were collected to make stock NOM solutions. The concentrations of NOM in the stock solutions were quantified by dissolved organic carbon (DOC) analysis using a total organic carbon (TOC) analyzer (Shimadzu TOC-5000A, Japan), after which they were freshly diluted to 3 mg/L as DOC using ultra pure water containing phosphate buffer ($\text{pH} = 7.5$, 0.05 M) to prepare the testing solutions.

A free chlorine stock solution (about 1 g/L as Cl_2) was freshly prepared before each test by diluting a 4.5% sodium hypochlorite (NaOCl) solution (Allied Signal, USA) with a chlorine-demand-free pH 7 phosphate buffer solution (0.05 M) to a concentration of approximately 1,200 mg/L. The stock solution was periodically standardized by the DPD/FAS method. The monochloramine solution was freshly prepared by combining an ammonia chloride (Riedel-de Haën, Germany) solution and a free chlorine stock solution at a chlorine-to-nitrogen mass ratio of 4:1. The solution was rapidly mixed for over 30 min prior to usage to ensure that free chlorine was completely converted to monochloramine.

Analytical methods

The concentrations of residual chlor(am)ine in the aqueous solutions were measured by the 4,500-Cl F DPD/FAS method (Standard Methods 1998).

Fluorescence 3D-EEM measurements were conducted using a Hitachi F-4500 fluorescence spectrometer that employed a xenon excitation source (150W), with excitation and emission slits set to a 10 nm band-pass and a scan speed of 1,200 nm/min. To obtain fluorescent 3D-EEMs, excitation wavelengths were incrementally increased from 250 to 400 nm in 5 nm steps and emission wavelengths were incrementally increased from 270 to 550 nm in 5 nm steps. To limit second-order Rayleigh scattering, a 290 nm cut off was used for all samples. All samples were diluted to a final DOC and pH of 1.5 mg/L and 7.5, respectively, with 0.01 M KCl.

According to Liu *et al.* (2006), concentrations of chloroform and HAA (only dichloroacetic acid (DCAA)

and trichloroacetic acid (TCAA in this experiment) in aqueous samples were measured using a gas chromatograph (Trace GC 2000, Thermo Finnigan, USA) equipped with an electronic capture detector (ECD) and a DB-5 ms fused silica capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness, J&W Scientific) according to USEPA methods 551 and 552 (USEPA 1990), respectively. The temperature program for THM detection was 35 °C for 5 min, followed by an increase to 70 °C at 10 °C/min, which was held for 8 min, then to 100 °C at 10 °C/min, which was held for 3 min. The temperature program for HAA detection was 35 °C for 10 min, followed by an increase to 70 °C at 5 °C/min, which was held for 10 min, then to 100 °C at 5 °C/min, which was maintained for 5 min, after which the temperature was increased to 135 °C at 5 °C/min, where it was held for 10 min. The concentrations of cyanogen chloride (CNCl) in the aqueous samples were determined by membrane introduction mass spectrometry (MIMS) method (Yang & Shang 2005).

Experimental procedures

Sequential exposure to UV radiation and chlor(am)ine was used in the study. The UV doses in the trials were 0, 20, and 60 mJ/cm², with exposure times of 0, 80, and 240 s, respectively.

A total of 100 mL (in 20 mL aliquots) of IHSS NOM solution diluted to a final pH of 7.5 was exposed to UV irradiation at the dosages listed above. Each water sample was mixed with chlorine or chloramine solutions at an initial concentration of 4.5 mg/L, and the reactions in the solutions were immediately quenched by the addition of excess sodium thiosulfate (1 mL, 10 g/L). Each mixed solution was then measured by the 4500-Cl F DPD/FAS method or 3D-EEM. To measure fluorescence during the sequential application of UV irradiation and chloramine, water samples exposed to UV radiation alone were also analyzed using the same procedures described above, without the addition of chlor(am)ine. All tests and measurements were duplicated and the figures presented below show the average values of each duplication. The error bars of each value indicate the range of the two measurements.

Data analysis

Chlor(am)ine decay kinetics

The chlorine decay curves fit the parallel first-order model, while the cubic polynomial model was most suitable for the chloramine decay curves in reused water, both of which have no significant relationship with conditions of water (Huang *et al.* 2009).

The parallel first-order model was as follows:

$$C(t) = C_0 \left[x e^{-k_1 t} + (1 - x) e^{-k_2 t} \right] \quad (1)$$

Koehler (1998) observed that initial chlorine decay is composed of a rapid initial decay and a second component that decays more slowly. In this model, $C(t)$ is the residual chlorine concentration at time t , C_0 is the initial chlorine concentration, x is the chlorine decay attributed to rapid reaction, k_1 is the first-order rate constant for rapid chlorine decay, and k_2 is the first-order rate constant for slow chlorine decay (Chiang *et al.* 2010). This model assumes that there are two kinds of constituents in water that react with chlorine: fast reacting components, which exert initial chlorine decay; and slow reacting components, which are responsible for long-term chlorine demand (Clark & Sivaganesan 2002).

The cubic polynomial model is as follows:

$$C(t) = at^3 + bt^2 + ct + C_0 \quad (2)$$

where $C(t)$ is the chloramine concentration at time t , C_0 is the initial chlorine concentration, and a , b , and c are constants.

Fluorescence spectra analysis

EEM peaks of NOM have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds (Chen *et al.* 2003). As previously reported (Leenheer & Croue 2003), peaks at different excitation/emission wavelengths (Ex/Em) are related to different organic components (Table 1).

Table 1 | Major fluorescent components in excitation/emission matrix

Range of excitation (nm)	Range of emission (nm)	Component type
220–250	280–300	Tyrosine-like
220–250	320–350	Tryptophan-like
280	350	Phenol-like
270–290	300–330	Soluble microbial byproduct-like
230–270	380–460	Fulvic acid-like
300–360	410–480	Humic acid-like

RESULTS AND DISCUSSION

Water samples exposed to UV irradiation alone

3D-EEM showed the excitation/emission wavelengths (Ex/Em) and fluorescence intensity of analyte. In the Ex/Em spectrum of IHSS NOM water (Figure 1), lower contour lines showed a higher fluorescence intensity than other contour lines. Two main peaks with higher fluorescence intensity appeared. The lower one surrounded by denser

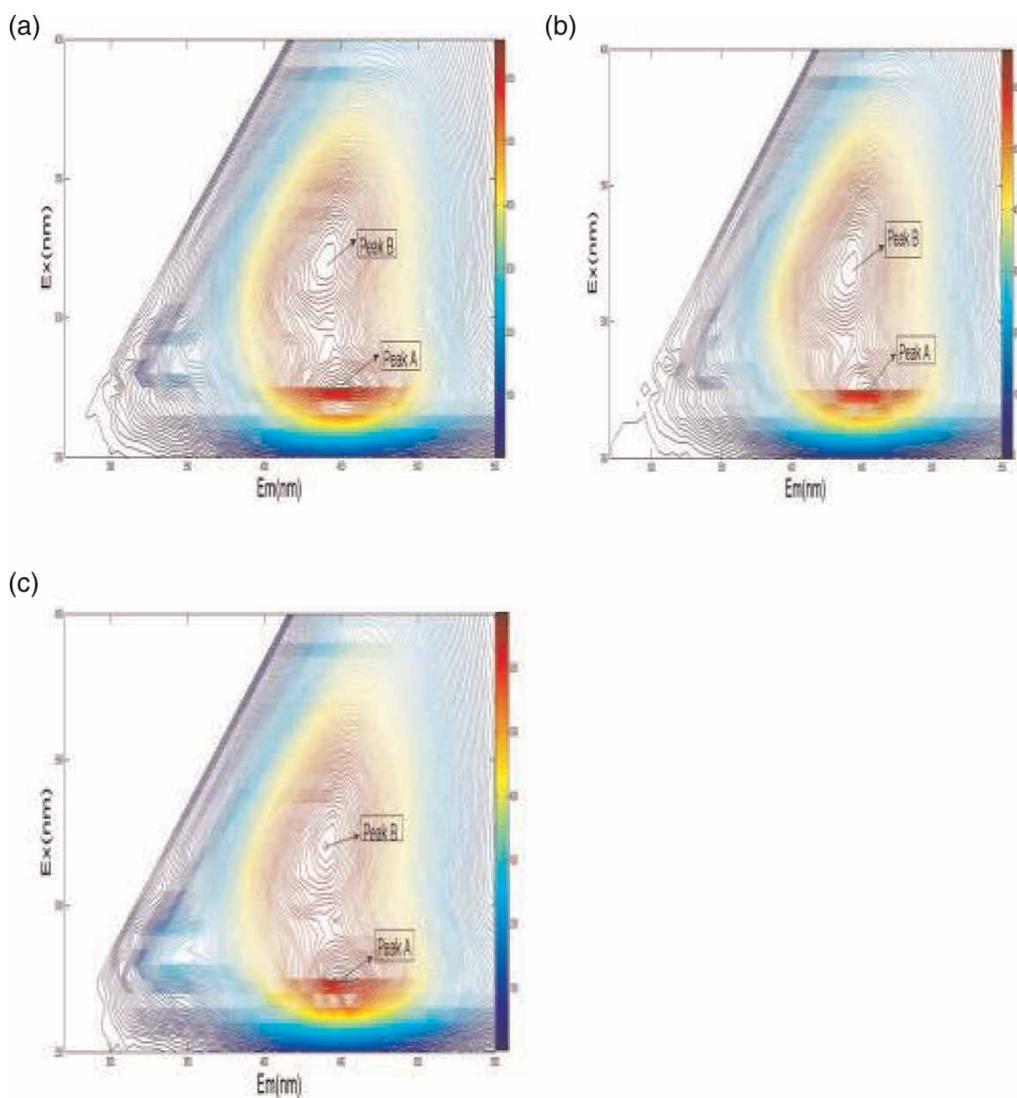


Figure 1 | Ex/Em spectrum of peak A and peak B in IHSS NOM water after exposure to UV irradiation alone (pH = 7.5, DOC = 3 mg/L). (a) 0 mJ/cm², (b) 20 mJ/cm², (c) 60 mJ/cm².

contour lines was defined as peak A, and the upper one was defined as peak B (Figure 1).

Evaluation of the Ex/Em spectrum of IHSS NOM water exposed to UV irradiation alone (Figure 1) revealed that peak A was located at the excitation/emission wavelengths (Ex/Em) of 275/450 nm for all UV dosages, while peak B was observed at the Ex/Em wavelengths of 325/450 nm for 0 mJ/cm² and 320/440 nm for both 20 and 60 mJ/cm². Peak A was related to FA-like organics and peak B corresponded to HA-like organics (Table 1).

The shift in emission maximum is caused by a reduction in the degree of the π -electron system, such as a decrease in the number of aromatic rings, reduction in conjugated bonds in a chain structure, or conversion of a linear ring system to a non-linear system (Coble 1996; Świetlik & Sikorska 2004). Additionally, Senesi (1990) reported that the shift could also be caused by elimination of carbonyl, hydroxyl and amine functional groups. According to Ex/Em spectrum of IHSS NOM water exposed to UV irradiation alone (Figure 1), UV irradiation shifted the fluorescence maxima toward shorter wavelengths for peak B, but induced no changes in peak A. Thus, UV irradiation may lead to the degradation of aromatic rings and removal of some functional groups in HA (peak B).

Figure 2 showed the fluorescence intensity of IHSS NOM water after exposure to various types of UV irradiation. UV irradiation alone led to a reduction in the fluorescence intensity of both peak A and peak B. High-molecular-weight chromophores in HA may be decomposed to low-molecular-weight ones following UV irradiation (Uyguner & Bekbolet 2005). Preferential degradation of higher-molecular-weight chromophores by UV irradiation and increases in low-molecular-weight chromophores have previously been demonstrated using size-exclusion chromatography (SEC) (Thomson *et al.* 2004; Liu *et al.* 2012).

The effects of NOM exposed to UV irradiation alone for normal disinfection have been reported in many studies. After UV irradiation, humus macromolecules adsorb photons, resulting in photochemical transformations (Corin *et al.* 1996; Uyguner & Bekbolet 2005). A few low-molecular-weight organic carboxylic acids such as oxalic, succinic, formic and acetic acids have been identified and quantified as photodegradation products (Corin *et al.* 1996). Therefore, it is assumed that HS in NOM water, especially HA,

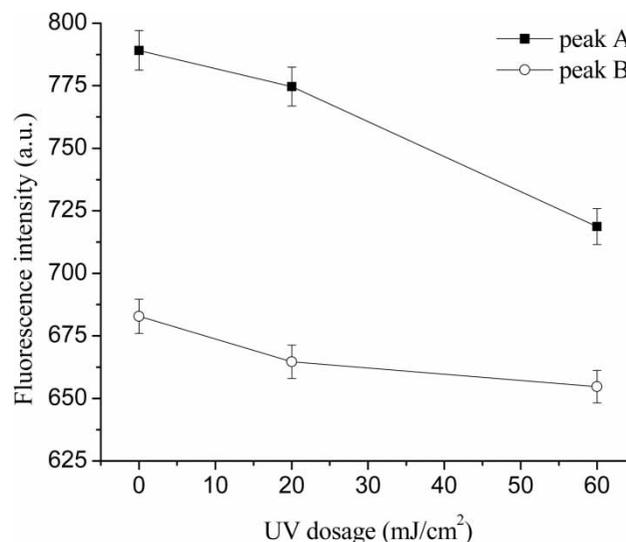


Figure 2 | Fluorescence intensity of peak A and peak B in IHSS NOM water after exposure to UV irradiation alone (pH = 7.5, DOC = 3 mg/L).

adsorbed photons and were primarily degraded into low-molecular-weight organic acids under UV irradiation.

IHSS NOM water exposed to UV/chlorine sequentially

Peak A was located at Ex/Em wavelengths of 270–285/430–455 nm, while peak B was observed at Ex/Em wavelengths of 315–325/430–450 nm. Peak A was related to FA-like organics and peak B corresponded to HA-like organics (Table 1). Since the shifts in Ex/Em wavelengths were uncertain and were all within the range of the certain organic compounds, the characteristics of the fluorescence spectra were neglected here.

The fluorescence intensity of peaks A and B followed a similar pattern (Figure 3). The fluorescence intensity showed a substantial decrease during the rapid chlorine decay stage. Electron-withdrawing substituents ($-\text{NO}_2$, $-\text{COOH}$, $-\text{CHO}$, $-\text{N}=\text{N}-$) and halogen substituents of benzene rings usually have weaker fluorescence intensity (Li 2007). Moreover, depletion of aromatic rings can lead to decreased fluorescence intensity (Uyguner & Bekbolet 2005). Consequently, it is reasonable to assume that free chlorine reacts with activated aromatics via electrophilic substitution reactions, leading to subsequent ring opening followed by further fragmentation, which can be attributed to decreased fluorescence intensity during the rapid chlorine decay stage.

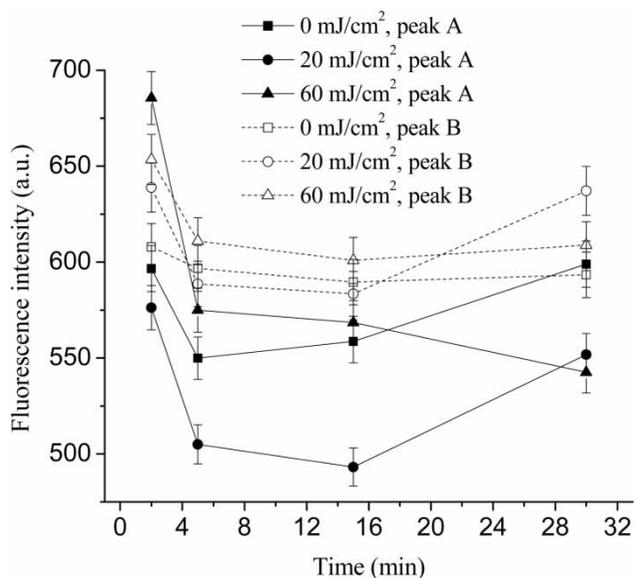


Figure 3 | Relationship between fluorescence intensity of peak A and peak B under sequential exposure to UV irradiation/chlor(am)ination (pH = 7.5, DOC = 3 mg/L).

These assumptions are consistent with previous findings (Thomson *et al.* 2004). The hydroxyl and phenols groups on the aromatic rings are in the ortho/para-direction, resulting in chlorination of the aromatic ring by stepwise 2, 4, 6-substitution followed by ring cleavage leading to chloroform formation (Duirk *et al.* 2012).

The correlation coefficients (R^2) of the chlorine decay curves of IHSS NOM water indicated a good fit with the parallel first-order model (Figure 4). The rapid drop with

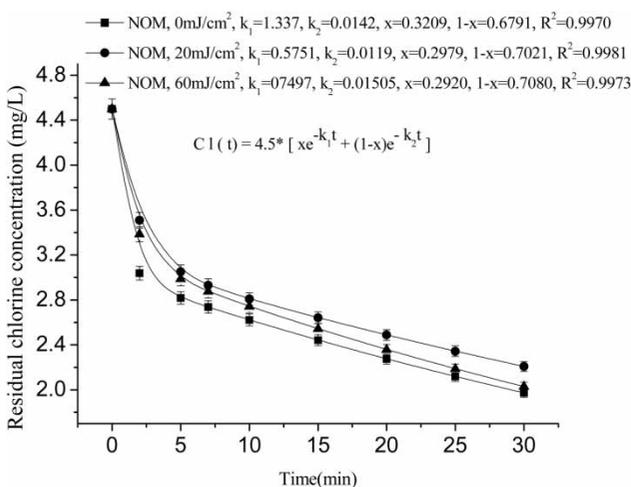


Figure 4 | Chlorine decay curves in UV-irradiated IHSS NOM waters (pH = 7.5, DOC = 3 mg/L).

sharp slope was identified to be the rapid decay stage, and the second section was the slow decay stage. The rapid chlorine decay rate k_1 was reduced after UV irradiation, indicating that UV irradiation could slow down the chlorine decay in the rapid decay stage. The hydroxyl substituent groups (OH, O⁻) on the aromatic rings influence the rate of chlorine substitution by changing the charge density of the aromatic rings, leading to a faster reaction rate of hypochlorous acid with phenolate (O⁻) species than neutral phenol species (Duirk *et al.* 2012).

The residual chlorine concentrations $C(t)$ after UV irradiation were larger than those of samples not subjected to UV irradiation, suggesting that UV irradiation could lessen the chlorine decay. According to Thomson *et al.* (2004), both UV irradiation and chlorination cause degradation of aromatic rings. Some chlorine demand is exerted via oxidative reactions that do not covalently bind chlorine into reaction products (Christman *et al.* 1983). Therefore, chlorine demand for substitution and oxidation decreases as the concentration of HS decreases after UV irradiation. That is to say, chlorine decay is reduced after UV irradiation.

IHSS NOM water exposed to UV/chloramine sequentially

Ex/Em characteristics were similar to that mentioned above. Peak A was located at 275–285/430–455 nm while peak B was observed at 315–325/430–450 nm.

Fluorescence intensity generally tends to be enhanced with time (Figure 5). Additionally, electron-donating groups (-OH, -NH₂, -OR, -NR₂) substituted for aromatic rings can generally increase fluorescence intensity (Li 2007), and the decay of chloramine released ammonia for subsequent nitrification (Sung *et al.* 2005). Thus, chloramine exposure may generate more -NH₂ substituent groups, resulting in enhanced fluorescence intensity.

The correlation coefficients (R^2) of the chloramine decay curves of IHSS NOM water were greater than 0.96, which fit the cubic polynomial model well (Figure 6). There are no obvious rapid and slow decay stages for chloramine. When compared with a , b and c of 0 mJ/cm² UV dosage, chloramine decay with UV dosage of 60 mJ/cm² was accelerated, and the extent of chloramine decay was enhanced after UV irradiation. As discussed above, UV irradiation decomposes

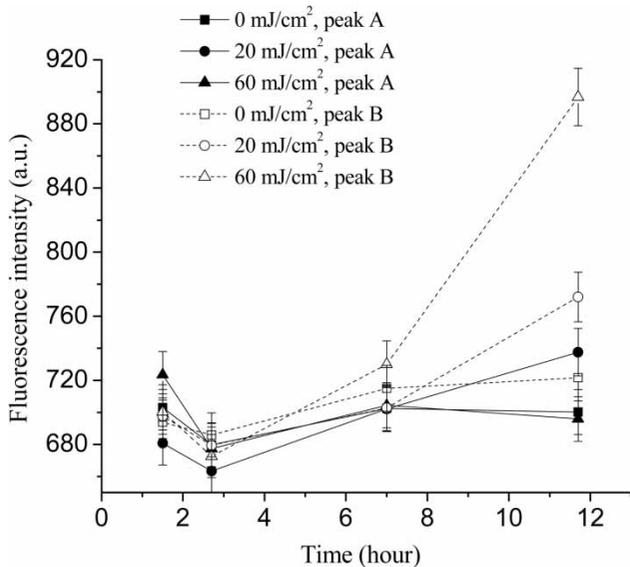


Figure 5 | Relationship between fluorescence intensity of peak A and peak B under sequential exposure to UV irradiation/chlor(am)ination (pH = 7.5, DOC = 3 mg/L).

high-molecular-weight HS, and more ammonia was released for subsequent reaction (Sung et al. 2005). Thus, more chloramine is consumed for substitution, which accounts for the extension of chloramine decay after UV irradiation.

HOCl is the main effective constituent of chloramine disinfection. However, as a disinfectant, chloramine releases lower quantities of HOCl than chlorine, and chloramine

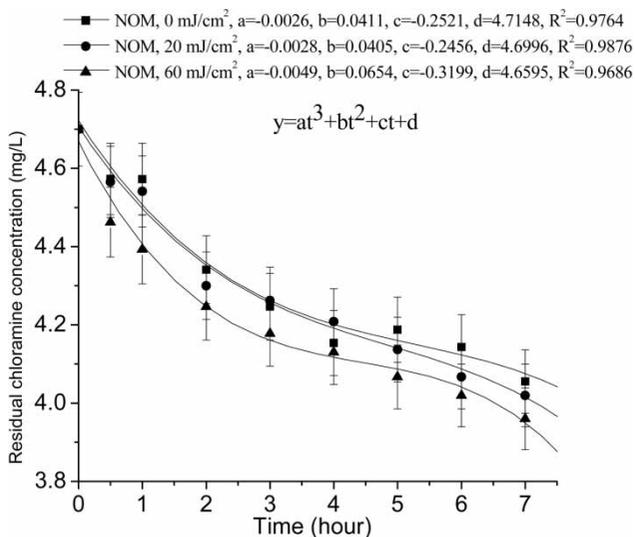


Figure 6 | Chloramine decay curves in UV-irradiated IHSS NOM water (pH = 7.5, DOC = 3 mg/L).

disinfection reduces the generation of THM and HAA significantly (82.8 and 68.7%, respectively) from organic matter with a Ku molecular weight of less than 10 (Gao et al. 2009). The effect of chloramination is weakened somewhat as the organic molecular weight increases (Gao et al. 2009). Therefore, it is assumed that chloramine exposure primarily leads to substitution of reactive sites other than ring-opening oxidation.

DBP formation

The formation of DBPs, including chloroform, DCAA, TCAA, and CNCl, after sequential exposure of IHSS NOM water samples to solely chlor(am)ine and UV/chlor(am)ine were tested (Figure 7; Liu et al. 2006). On the whole, DBP formation was increased to a certain degree comparing the results of UV/chlor(am)ine (shaded bars) with solely chlor(am)ine (black bars). UV irradiation does not appear to generate DBPs, and only small quantities of aldehydes have been detected in UV-irradiated wastewater samples at doses up to 200 mJ/cm² (Linden et al. 1998). Therefore, the increments of DBPs after UV/chlor(am)ine may due to the oxidation of UV irradiation which led to degradation of NOM molecules and then facilitated subsequent reaction of chlor(am)ine with NOM molecules.

Moreover, IHSS NOM waters exposed to UV/chloramine and chloramine showed less DBP formation than those exposed to UV/chlorine and chlorine, and the formation of

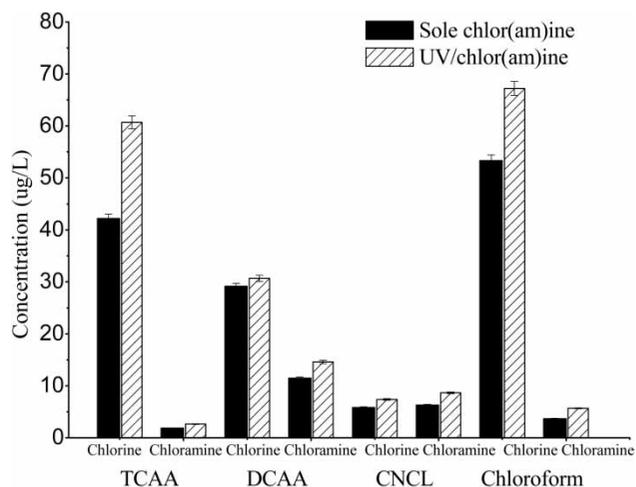


Figure 7 | Chloroform, DCAA, TCAA and CNCl formation in IHSS NOM water exposed to solely chlor(am)ine and UV/chlor(am)ine (pH = 7, DOC = 5 mg/L, UV dosage = 60 mJ/cm²).

TCAA and chloroform was drastically diminished in the UV/chloramine and chloramine trials. These findings indicate that chlorine substitution and degradation of NOM molecules was much greater than that of chloramine, and generated more completely oxidized products such as chloroform.

CONCLUSIONS

UV irradiation led to a decrease in the fluorescence intensity of IHSS NOM water samples. The subsequent chlorination and chloramination resulted in weakened and strengthened fluorescence intensity, respectively. Investigation of the residual chlor(am)ine concentration revealed that UV irradiation decreased chlorine decay and increased chloramine decay. UV irradiation also resulted in increased DBP formation. Degradation of NOM molecules after UV irradiation facilitated the reaction of chlor(am)ine with NOM molecules, resulting in the formation of DBPs. UV irradiation facilitates degradation of HS, leading to less chlorine demand for degradation.

Conversely, UV irradiation exposes more active sites to chloramine substitution, enriching chloramine demand for substitution. Both UV irradiation and chlorination could degrade high-molecular-weight aromatic HS, but chloramination mainly played a substitution role. In summary, UV treatments play the same role in UV/chlorine and UV/chloramine processes, both of which degraded high-molecular-weight NOM. Moreover, it is also proposed that chlorine degradation and substitution dominates the process of UV/chlorine disinfection, while chloramine substitution is the major reaction occurring during the UV/chloramine disinfection process.

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