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Effects of UV irradiation and UV/chlorine co-exposure on natural organic matter in water

Wei Liu, Zaili Zhang, Xin Yang, Yiyue Xu, Yongmei Liang *

School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China

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ABSTRACT

The effects of co-exposure to ultraviolet (UV) irradiation (with either low- or medium-pressure UV lamps) and free chlorine (chloramine) at practical relevant conditions on changes in natural organic matter (NOM) properties were investigated using four waters. The changes were characterized using the specific disinfection by-product formation potential (SDBPFP), specific total organic halogen formation potential (STOXFP), differential UV absorbance (ΔUVA), and size-exclusion chromatography (SEC). The results for exposure to UV irradiation alone and for samples with no exposure were also obtained. The SDBPFPs in all UV-irradiated NOM waters observed were higher than those of non-irradiated samples. UV irradiation led to increases in STOXFPs as a result of chlorination, but no changes, or only small decreases, from chloramination. UV irradiation alone led to positive ΔUVA spectra of the four NOM waters; co-exposure to UV and chlorine gave larger negative ΔUVA spectra than those obtained by chlorine exposure alone. No obvious changes in SEC results were observed for samples only irradiated with UV light; co-exposure gave no detectable changes in the abundances of small fractions for exposure to chlorine only. Both UV photooxidation and photocatalytic oxidation appear to affect the reactivity of the NOM toward subsequent chlorination, and the magnitude of the changes is generally greater for medium-pressure lamps than for low-pressure lamps. These results suggest that applying UV disinfection technology to a particular source may not always be disinfection by-product-problem-free, and the interactions between UV light, chlorine, and NOM may need to be considered.

1. Introduction

Ultraviolet (UV) technology is of increasing interest, and is considered to be cost-effective as an additional inactivation measure in chlorination or chloramination of water utilities to meet the requirements of microbial pathogen control in the Long-Term 2 Enhanced Surface Water Treatment Rule (Kashinkunti et al., 2004). Sequential disinfection schemes using UV irradiation and chlorination are also expected to minimize disinfection by-product (DBP) formation in water because lower chlorine dosages can be used in such processes for long-term residual protection in distribution systems.

Both low- and medium-pressure UV irradiation are very effective in the inactivation of *Cryptosporidium parvum* (Bukhari et al., 1999; Clancy et al., 2000; Craik et al., 2001). UV irradiation at wavelengths from 200 to 400 nm inactivates pathogens by causing changes in the genome DNA or other intracellular molecules, such as proteins and enzymes, with unsaturated bonds. Organic materials, e.g., natural organic matter (NOM) in the water, are also able to absorb UV light from the whole UV wavelength range of 200–400 nm. Absorption of photons by NOM molecules in natural water may lead to direct photochemical changes in the molecules. NOM degradation by photooxidation with UV light has been studied as a process for removing NOM under conditions of long exposure times (hours) and/or high intensities (Dahlén et al., 1996; Corin et al., 1996; Frimmel, 1998). Generally, high-molecular-weight organic matter in NOM is decomposed to low-molecular-weight organic acids by UV irradiation and then further mineralized to CO_2 (Corin et al., 1996). It has been shown that the high-molecular-weight organic components of NOM become more aliphatic in character, because more carboxyl and carbonyl carbon atoms appeared after UV irradiation (Kulovaara et al., 1996). Low-molecular-weight carboxylic acids such as oxalic, formic and acetic acids (Dahlén et al., 1996) and low-molecular-weight keto acids and aldehydes (Corin et al., 1996) have also been identified in UV-irradiated natural waters. Preferential degradation of higher-molecular-weight chromophores by UV irradiation and increases in low-molecular-weight chromophores have also been shown using size-exclusion chromatography (SEC; Naffrechoux et al., 2003; Thomson et al., 2004). Furthermore, changes in very hydrophobic components of NOM to hydrophilic materials after UV irradiation have been proven using fractionation methods (Buchanan et al., 2005). These smaller organic compounds enrich the availability of microbial substrates and then enhance bacterial growth (Corin et al., 1998; Buchanan et al.,

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* Corresponding author. Tel./fax: +86 20 39332690.
E-mail address: liangym@mail.sysu.edu.cn (Y. Liang).

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2004). It should be noted that these phenomena were observed at UV irradiation doses higher than 200 mJ/cm^2.

Because of safety concerns with respect to drinking water disinfection, variations in DBP formation in UV-irradiated waters have been studied. Some researchers have reported insignificant increases in DBP formation when pre- or post-UV irradiation is combined with existing chlorination methods (Kashinkunti et al., 2004). In our previous studies, although the results varied largely among different waters, statistically significant enhancements of chloroform, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and CNCl formation as a result of additional UV irradiation were observed in most cases compared with chlorination or chloramination on their own (Liu et al., 2006). In view of these incompatible results, it is of great importance to understand how NOM changes as a result of UV irradiation, and how the changes relate to DBP formation during the secondary disinfection stage.

Few studies on the effects of UV irradiation alone of NOM at doses for normal disinfection have been reported. UV irradiation (254 nm) reduced (Lehtola et al., 2003) or insignificantly increased (Shaw et al., 2000) the assimilable organic carbon concentration of several natural water sources. Electrospray ionization mass spectrometry (ESI-MS) has been used to study changes in NOM on UV irradiation, and the results showed that UV irradiation of extracted organic matter induced obvious changes in the mass spectra (Magnuson et al., 2002). Other researchers have also reported that UV disinfection caused shifts from large NOM molecules to small ones (Lehtola et al., 2003).

In practice, UV irradiation before or after chlorination is technically feasible in water-treatment processes. In the latter case, the water is simultaneously exposed to UV irradiation and chlorination during the first disinfection stage. The impacts of co-exposure processes on NOM may be different from those of UV irradiation alone. However, changes in NOM after co-exposure processes have not been reported in the literature.

NOM is complex in structure, composition, and functional groups. The correlations between differential spectroscopy and total organic halogen (TOX) or DBP formation in chlorinated waters have been revealed (Korshin et al., 1999; Li et al., 2000; Korshin et al., 2002). Differential UV absorbance (ΔUVA) spectra can provide more information about NOM changes than UVA at a single wavelength can (Li et al., 2000; Korshin et al., 2007). The molecular weight and its distribution are important factors in NOM characterization, and they can also affect the DBP formation potential to a certain degree (Amy et al., 1987).

The goal of the current study is to investigate the effects of UV irradiation alone and of chlorine/chloramine co-exposure on NOM properties at practical relevant conditions for disinfection. Three sources of isolated NOM and one river water were selected in this study. The NOM changes were characterized by the specific disinfection by-products formation potential (SDBPFP), specific total organic halogen formation potential (STOXFP), ΔUVA, and SEC. The results for non-UV-irradiated water samples were also obtained for comparison.

2. Materials and methods

2.1. UV irradiation systems

Collimated-beam UV apparatuses consisting of either two low-pressure UV (LPUV) lamps (254 nm, UVP, Upland, CA, USA) or one medium-pressure UV (MPUV) lamp (220–580 nm, UVV-5, Hanovia, Slough, UK) were used to perform UV exposure (Liu et al., 2006). At the point of the irradiating vessels, the average UV intensity from the LPUV and from the MPUV apparatus was 0.2 mW/cm^2. The MPUV apparatus was calibrated by biodosimetry with coliphage MS2 (Linden and Darby, 1997). The UV dose (mJ/cm^2) was calculated as the product of the measured intensity and exposure time. A small glass dish (ID 30 mm) containing the test solution (7 mL in volume and 10 mm in depth) was used for carrying out the exposure.

2.2. Solutions and chemicals

Aldrich humic acid (Cat. H1675-2, Aldrich, St Louis, MO, USA), Suwannee River Humic Acid Standard II (Cat. 2S101H), and Suwannee River NOM (RO isolation, Cat. 1R101N, IHSS) were used to prepare NOM waters (Liu et al., 2006). Raw river water from the Yau Kom Tau water treatment facility in Hong Kong was collected from the inlet point of the water treatment system. The quality parameters of the river water were pH = 6.81, turbidity = 1 NTU, color = 16 CU, DOC = 2.2 mg C/L, and alkalinity = 30 mg/L $CaCO_3$. The characteristic parameters, including UV_{254}, SUVA, SDBPFP, STOXFP, and number-averaged (M_n), and weight-averaged (M_w) molecular weights of the four waters are illustrated in Table 1. Free chlorine and chloramine solutions were prepared according to methods used for previous tests (Liu et al., 2006).

2.3. Analytical methods

The concentrations of four species of THMs and nine species of HAAs in aqueous samples were measured using chromatography, according to USEPA methods 551 and 552 (USEPA, 1990), respectively.

TOXFPs of water samples were measured using a TOX analyzer (Model TOX-100, Mitsubishi Chemical Corp., Tokyo, Japan). The TOX analyzer consisted of an automatic boat controller, automatic quick furnace (AQF-100), gas absorption unit (GA-100), and online ion-chromatography system (ICS-90, Dionex, Sunnyvale, CA, USA). An IonPac analytical column (AS9-HC, Dionex) was used to monitor chloride and bromide ions, using 9 mM Na_2CO_3 solution as the eluent. Prepacked GAC columns were obtained from A1-Envirotech (organic halogen impurity < 0.3 μg/column, Germany). Water samples were acidified to pH 2 with nitric acid, diluted to 100 mL, and then adsorbed by two consecutive GAC columns through a TOX sample preparator (Mitsubishi Chemical Corp., Tokyo, Japan). Organic halogens were then washed out using 5 mL of potassium nitrate solution (5 g/L as NO_3^-) and the sample was then subjected to automatic combustion and IC measurements.

Table 1
NOM characteristics and DBPFP for different sources.

	$SUVA_{254}$ (L/mg-m)	E_{465}/E_{665}	SDBPFP (chlorination) (μg DBP/mg C)	SDBPFP (chloramination) (μg DBP/mg C)	STOXFP (chlorination) (μg TOX/mg C)	STOXFP (chloramination) (μg TOX/mg C)	M_n (Daltons)	M_w (Daltons)	TOC (mg/L)
Aldrich humic acid	7.9	2.63	66	17	199	49	2842	4370	5
Suwannee River humic acid	5.4	5.58	69	17	274	69	3559	6485	5
Suwannee River NOM	3.9	3.89	62	14	241	62	3307	5298	5
River water	3.1	5.61	74	14	258	139	1870	2600	2.2

Note: formation potential time was 14 days.