Molecular characterization of transformation and halogenation of natural organic matter during the UV/chlorine AOP using FT-ICR mass spectrometry

Xiaoxue Ruan¹, Yingying Xiang², Chii Shang²,³, Shuangshuang Cheng¹, Jingfu Liu⁴, Zhineng Hao⁴,*, Xin Yang¹,*

¹ School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510275, China
² Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China
³ Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, The Hong Kong University of Science and Technology, Hong Kong, China
⁴ State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ABSTRACT

UV/chlorine process, as an emerging advanced oxidation process (AOP), was effective for removing micro-pollutants via various reactive radicals, but it also led to the changes of natural organic matter (NOM) and formation of disinfection byproducts (DBPs). By using negative ion electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS), the transformation of Suwannee River NOM (SRNOM) and the formation of chlorinated DBPs (Cl-DBPs) in the UV/chlorine AOP and subsequent post-chlorination were tracked and compared with dark chlorination. In comparison to dark chlorination, the involvement of ClO−, Cl−, and HO• in the UV/chlorine AOP promoted the transformation of NOM by removing the compounds owning higher aromaticity (AIaromat) value and DBE (double-bond equivalence)/C ratio and causing the decrease in the proportion of aromatic compounds. Meanwhile, more compounds which contained only C, H, O, N atoms (CHON) were observed after the UV/chlorine AOP compared with dark chlorination via photolysis of organic chloramines or radical reactions. A total of 833 compounds contained C, H, O, Cl atoms (CHOCl) were observed after the UV/chlorine AOP, higher than 789 CHOCl compounds in dark chlorination, and one-chlorine-containing components were the dominant species. The different products from chlorine substitution reactions (SR) and addition reactions (AR) suggested that SR often occurred in the precursors owning higher H/C ratio and AR often occurred in the precursors owning higher aromaticity. Post-chlorination further caused the cleavages of NOM structures into small molecular weight compounds, removed CHON compounds and enhanced the formation of Cl-DBPs. The results provide information about NOM transformation and Cl-DBPs formation at molecular levels in the UV/chlorine AOP.

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* Corresponding authors.
E-mails: znhao@rcees.ac.cn (Z. Hao), yangx36@mail.sysu.edu.cn (X. Yang).
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**Introduction**

UV irradiation and chlorination are widely used disinfection methods in water treatment and wastewater treatment. In recent years, the combined use of both methods has developed as an UV/chlorine advanced oxidation process (AOP), which attracts lots of research interests and has become an alternative to UV/H$_2$O$_2$ AOP (Sichel et al., 2011; Guo et al., 2017; Gao et al., 2020). Free chlorine photolysis under UV irradiation generates reactive oxidants, including hydroxyl radicals (HO$^\cdot$), reactive chlorine species (RCS, e.g., Cl$^\cdot$, ClO$^-\cdot$ and ClO$^\cdot$) (Eqs. (1)-(4) (Anastasio and Matthew, 2006; Jayson et al., 1973; Watts et al., 2007).

\[
\text{HOCl/OCl}^- \xrightarrow{hv} \text{HO}^\cdot/\text{O}^\cdot^- + \text{Cl}^\cdot \quad (1)
\]

\[
\text{Cl}^\cdot + \text{Cl}^- \rightarrow \text{Cl}_2^\cdot^- \quad (2)
\]

\[
\text{HOCl/OCl}^- + \text{HO}^\cdot \rightarrow \text{H}_2\text{O}/\text{HO}^- + \text{OCI}^\cdot \quad (3)
\]

\[
\text{HOCl/OCl}^- + \text{Cl}^\cdot \rightarrow \text{HCl/Cl}^- + \text{OCl}^\cdot \quad (4)
\]

By taking advantage of the reactive oxidants (i.e., HO$^\cdot$ and RCS), the UV/chlorine AOP has the superior antimicrobial ability and is highly effective in eliminating a variety of organic micropollutants, such as pharmaceuticals, personal care products, and petroleum compounds (Guo et al., 2017; Xiang et al., 2016; Wu et al., 2016; Wang et al., 2016; Qin et al., 2014; Yang et al., 2016; Pan et al., 2017). For example, HO$^\cdot$ produced in the UV/chlorine AOP effectively inactivates UV resistant microorganism-bacteriophage MS2 by damaging its viral genome (Rattanakul et al., 2017). Extensive studies have shown that the removal of micropollutants through the UV/chlorine AOP is more effective than oxidation by free chlorine and UV irradiation alone, and often more effective than UV/H$_2$O$_2$ AOP at acidic to neutral pHs (Wang et al., 2015a; Sun et al., 2016; Wang et al., 2016; Li et al., 2017).

Despite the benefits of the UV/chlorine AOP, the formation of more disinfection byproducts (DBPs) is often observed in comparison to dark chlorination. For example, increases in haloacetic acids, chloral hydrate, and absorbable organic halogen are observed during the UV/chlorination of natural organic matter (NOM) (Wang et al., 2017a). Trichloronitromethane formation is found to increase up to 15-fold under the UV/chlorine AOP with amine as precursors in comparison to chlorination alone. In addition, radical involved oxidation and photochemical enhanced chlorination reactions may cause the changes of DBP precursors (Deng et al., 2014). Consequently, the changes of precursors will also change the DBP formation during post-chlorination process (Dotson et al., 2010; Sun et al., 2019; Chu et al., 2014). Therefore, it is essential to improve understanding about how the precursors of chlorinated DBPs change under the UV/chlorine AOP.

NOM is a heterogeneous mixture of complex organic compounds and known as important DBP precursors during chlorination. Therefore, characterization of NOM and the formed DBPs during AOP at the molecular level is very important and useful. The common methods used for NOM compositional variation during AOP are mainly UV−vis (Korshin et al., 1999; Hur et al., 2006; Spencer et al., 2007; Li et al., 2009), fluorescence (Liu et al., 2007; Spencer et al., 2007; Baker et al., 2008; Hudson et al., 2008; Bieroza et al., 2009; Peiris et al., 2010), GC−MS (Parsi et al., 2007; Templier et al., 2005) and LC−MS (Reemtsma, 2005; Mawhinney et al., 2009). However, spectroscopic characterization can only provide bulk properties for NOM. The LC−MS and GC−MS techniques, which are also frequently used for DBPs analysis, are only suitable for compounds with different polarities, and the identification of compounds needs standard substances due to the low resolution and accuracy. Recent progress in Fourier transform ion cyclotron resonance mass spectrometry (FT−ICR MS) has made it own ultrahigh resolution and accuracy, and been widely used in characterization of NOM and the halogenated compounds (Wang et al., 2018; Hao et al., 2017, 2018a, 2018b, 2020; Lavonen et al., 2013; Varanasi et al., 2018; Zhang et al., 2012a; 2014; Wang et al., 2017b). However, most of the studies focus on the NOM and halogenated products in natural water process and traditional water treatment process especially for chlorine disinfection, and only a few investigated the changes of NOM and generation of halogenated DBPs during AOPs by FT−ICR MS (Stubbins et al., 2010; Varanasi et al., 2018; Lavonen et al., 2013; Zhang et al., 2012a, 2014). As for the UV/chlorine AOP, Varanasi et al. (2018) has explored the composition changes of Suwannee River fulvic acid during the UV/chlorine AOP by using ESI FT−ICR MS, and found a distinct transformation in the aliphatic components of NOM due to HO$^\cdot$ and proposed the reaction pathway between Cl$^\cdot$ and NOM in the UV/chlorine AOP. But they only focus a fraction of NOM and fail to reveal the production of Cl−DBPs in the UV/chlorine AOP. Therefore, it is essential to study the compositional transformation of NOM and production of Cl−DBPs during the UV/chlorine AOP at the molecular level by using FT−ICR MS.

This study thus aimed to explore the compositional changes of NOM and the formation of Cl−DBPs during the UV/chlorine AOP and subsequent post-chlorination treatment. Firstly, the molecular changes of NOM during the UV/chlorine AOP and dark chlorination were explored and compared. Secondly, the formation and distribution patterns of Cl−DBPs were acquired and compared for these processes. Finally, we evaluated the concentrations and changes of the formed Cl−DBPs expressed as total organic chlorine (TOCl) during the UV/chlorine AOP. This work is of significance in providing molecular-level insights into NOM composition changes and Cl−DBPs formation under the UV/chlorine AOP and post-chlorination treatment.

1. Materials and methods

1.1. Chemicals

Suwannee River NOM (SRNOM, Cat. NO. 2R101N) was obtained from the International Humic Substances Society. Its stock solution was prepared by dissolving SRNOM in ultrapure water and filtering through a 0.45 μm glass fiber membrane. Sodium bromide, sodium sulfate, hydrogen peroxide (H$_2$O$_2$) and methanol were obtained from Sigma-Aldrich (USA).
trobenezene (NB) and benzoic acid (BA) were purchased from Fisher Scientific (USA). A stock solution of free available chlorine was prepared by diluting 5% sodium hypochlorite (Sigma-Aldrich, USA) to 1000 mg/L as Cl₂.

1.2. Experimental procedures

UV exposure was carried out in a bench-scale UV irradiator equipped with a low-pressure Hg lamp (254 nm, GPH 212TS/4, 10 W, Heraeus) in a quartz tube. The UV irradiator was in the center of a 1 L cylindrical borosilicate glass reactor. The reaction solution was placed in the glass reactor and the temperature was maintained at 25 °C by using water circulation (Appendix A Fig. S1). The UV lamp was turned on for 15 min prior to the experiments to warm up the lamp. The UV photon flux (I₀) was 0.13 μE/sec determined by iodide/iodate chemical actinometry. The effective optical path length (L) was 2.43 cm measured by the photolysis kinetics of dilute H₂O₂ solution (Appendix A Fig. S2). The details for the measurement of UV photon flux and effective optical path length were provided in Appendix A Text S1. The average UV fluence rate (Ep) was 0.36 mW/cm² and was calculated via Appendix A Eq. (54).

To perform the UV/chlorine experiments, a 700 mL solution containing 3 mg C/L NOM and 10 mg/L free chlorine at pH 7.3 buffered with 5 mmol/L phosphate was exposed to UV irradiation. Chlorination alone experiments were conducted in the dark using the similar procedures as described above. The chlorine dosage was within the range of commonly used dose in full-scale tests of the UV/chlorine AOP in water treatment plants (Wang et al., 2015b; Wang et al., 2019). After 30 min of UV irradiation and chlorination, free chlorine concentration in the system was measured and supplemented to 10 mg/L as Cl₂ to proceed post-chlorination for 3 days. The long incubation of 3 days with a chlorine dosage of 10 mg/L was aimed at amplifying the formation of Cl⁻-DBPs to explore the DBP formation potential of NOM. The temperature during the post-chlorination was controlled at 25 ± 0.1 °C. A certain volume of solutions was sampled at the given interval for the analysis of residual chlorine and TOCl content, as well as the characterization of NOM and Cl-DBPs by FT-ICR MS. The residual oxidants in samples for TOCl, NOM and CI-DBPs analysis were quenched with excess amounts of Na₂SO₃. The quench step ensured the minimum effect of the residual oxidants on sample pre-treatment and analysis. The experiments were conducted in duplicate. Considering the little effects of UV irradiation and major roles of reactive species on NOM structural variation in 30 min, the UV alone + 3-d post chlorination was not investigated in this work.

To analyze the steady-state concentrations of active radical species in the UV/chlorine AOP, NB (0.2 μmol/L) and BA (0.2 μmol/L) were added to the solutions as probe compounds for HO· and Cl· detection, respectively. NB and BA were selected as the model compounds because of their high reactivity towards HO· and/or Cl· but inert to either chlorination or UV photolysis (Fang et al., 2014). The details about the two probe compounds and experiments were provided in Text S2. The concentrations of Cl₂⁻ and ClO⁻ were obtained by using Kinecus model provided in Table S1.

1.3. Sample pretreatment for FT-ICR MS analysis

The water samples for FT-ICR MS analysis were pretreated according to the general solid phase extraction procedures as described elsewhere (Dittmar et al., 2008). Briefly, the water samples were firstly acidified with hydrochloric acid to pH 2.0 to increase the extraction efficiency of NOM and Cl-DBPs (Lavonen et al., 2013; Hawkes et al., 2016; Dittmar et al., 2008; Li et al., 2015; Lv et al., 2016; Zhang et al., 2012a). The addition of hydrochloric acid would have little effect on the extraction of NOM and CI-DBPs due to the quenching of residual oxidants with excess Na₂SO₃. The PPL cartridges were rinsed with 12 mL methanol and 12 mL acidified ultrapure water (pH 2.0). The water samples were then pumped through the PPL cartridges at a flow rate of 3 – 5 mL/min. Immediately after extraction, the cartridge was firstly rinsed with 18 mL of acidified ultrapure water for complete removal of salt and then eluted with 10 mL methanol. The eluate was blow-dried with N₂ and stored at −18 °C in the dark. These dried samples were dissolved in 1 mL 50:50 methanol/water (V/V) before FT-ICR MS analysis. The DOC recoveries were 74 ± 7% and comparable with previous studies (Lavonen et al., 2013; Lv et al., 2016).

1.4. Analytical methods

The DOC concentrations were analyzed using a Shimadzu TOC-VPCH analyzer (Shimadzu, Japan). The concentrations of free chlorine were measured by DPD colorimetric method (APHA, 1998). The TOCl content was measured with activated carbon adsorption method with details provided in Appendix A Text S3. The spectrums of the samples after different treatment were recorded using a 1-cm quartz cell on a Shimadzu UV-2700 spectrophotometer.

Ultra-high-resolution mass spectra were acquired using a Bruker SolarXi FT-ICR MS equipped with a 15.0 T superconducting magnet in negative ionization mode. The ESI needle voltage was set to −3.8 kV. Four M 32-bit data points were recorded per broadband mass scan, and the mass range was set at m/z 153–1000 Da. The sample solution was continuously infused into the ESI unit using a syringe pump at a flow rate of 120 μL/hr. The injection syringe and lines were washed three times with 50:50 (V/V) methanol/water between each measurement to minimize cross-contamination and any sample carryover. Spectra were first externally calibrated with 10 mmol/L of sodium formate solution and then internally recalibrated with a known homologous series of NOM compounds.

1.5. Data analysis

Data Analysis 4.4 (Bruker Daltonics) software was used to assign molecular formulas to the peaks in FT-ICR MS spectrum with the S/N (signal-to-noise ratio) > 4 and mass error between the measured and the theoretical mass for a given chemical formula <1 ppm. The following element combinations of C₁₅H₁₀O₁₀N₄Cl₂O₃ were considered in the assignment of the molecular formulas with further restric-
tions of N rules, N/C = 0.5, 0.333 < H/C ≤ 2.25 and 0.1 < O/C ≤ 1.0 (Hao et al., 2017). The rules of the minimum number of N, P and S, 13C isotope analysis, homologous analysis based on –CH2 for formulas above 500 Da were collectively used further for one peak with several formulas assigned (Zhang et al., 2012b; Hao et al., 2017). Because of the low N content in SRNOM (1.27%), Cl-DBPs contained heteroatoms were not investigated, i.e. Cl-DBPs referred to compounds contain only C, H, O and Cl. According to the isotopic abundance ratio of Cl (35Cl: 37Cl = 3:1), the assigned Cl-DBPs were further validated manually with isotope simulation using the Data Analysis 4.4. O/C and H/C ratio indicated the different degrees of oxidation and saturation/aromaticity, and the combination of O/C and H/C ratio in van Krevelen diagram was used to identify or classify different compounds. Double-bond equivalence (DBE) values was used to evaluate the unsaturation degree of organic matter. The modified aromatic index (Al_mod) was used to estimate aromatic and condensed aromatic structures (Hao et al., 2017). As parallel experiments were conducted, only common formulas occurred both in parallel samples were selected as the final molecular formulas for the sample, which accounted for 76%–86%. The percentages were calculated by dividing the number of the common compounds presented in both parallel samples into the number of compounds of each sample, and then took the average, which reflected the reproducibility for the whole experiment stages. Although FT-ICR MS was not quantitative, since all the NOM samples were measured with the same procedures by FT-ICR MS, the acquired spectra should reflect similar systematic biases, and the intensity of the same molecules at different conditions can partly reflect the changes of identified molecules (Sleighter et al., 2008; Hao et al., 2018a). The relative intensity was equal to the intensity of each peak divided by the sum intensity of all peaks. The deviation of the relative intensity of the same formulas assigned in the duplicate samples was calculated to be < 30%. Therefore, only the difference of relative intensity for a peak in different samples > 30% can be thought to have a significant increase or decrease.

Cl-DBPs were grouped into two categories according to the reaction types, i.e. addition reaction (AR) and substitution reaction (SR) according to previous study (Hao et al., 2017). Briefly, the chlorine atom was first replaced with hydrogen to revert the molecule to the one that only contained C, H, and O and compared it with the NOM without treatment. If this formula could be found in NOM control sample, the Cl-containing formula was then proposed to be generated via SR pathway. For example, a Cl-DBP like C14H20O13Cl can be converted into C16H18O10 and then compared to NOM control sample. If C16H18O10 occurred in the control sample, C16H17O10Cl can be recognized as to be formed through SR. On the other hand, if C16H18O10 can be found in the NOM control sample, C16H17O10Cl possibly can be recognized as to be formed through HOCI addition (AR). Except AR or SR, other reaction types, such as oxidation, which were also existed in the UV/chlorine AOP, were not considered in this study because of the complex reaction mechanisms. It should be noted that, as some formulas have several isomers and underwent transformation during the UV/chlorine AOP, the DBPs classified by reaction type might not reflect their actual formation pathway.

2. Results and discussion

2.1. Steady-state concentrations of reactive radicals in the UV/chlorine AOP

Unlike dark chlorination, the UV/chlorine AOP involves radical reactions. During the UV/chlorine AOP, the steady-state concentrations of HO• ([HO•]ss) and Cl• ([Cl•]ss) were determined to be 4.95 × 10−14 mol/L and 3.89 × 10−15 mol/L, respectively. The steady-state concentrations of Cl2•− and ClO• were predicted to be 3.99 × 10−13 mol/L and 1.59 × 10−13 mol/L, respectively, based on Kinecus model (Table S1). The reaction rate constant of HO• with NOM was reported to be 2.5 × 104 (mg C/ L)−1 sec−1 (Fang et al., 2014). The reaction rate constants of Cl•, ClO• and Cl2•− with NOM were not experimentally determined, but were estimated to be 1.3 × 104 (mg C/ L)−1 sec−1 (Fang et al., 2014), 4.5 × 104 (mg C/ L)−1 sec−1 (Guo et al., 2017) and 500 (mg C/L)−1 sec−1 (Brigante et al., 2014; Lei et al., 2019), respectively. Based on the content of radicals and the reactivity with NOM, ClO•, and HO• seemed to be the major radicals leading to the transformation of NOM. Excess chlorine in the UV/chlorine AOP also can consume HO• and Cl•, which might cause more formation of ClO• (Fang et al., 2014). The radical reactions referred to NOM transformation will be discussed hereafter.

2.2. Transformation of NOM and formation of Cl-DBPs in the UV/chlorine AOP

The ultra-high-resolution mass spectra of NOM before and after treatment by the UV/chlorine AOP and the UV/chlorine AOP followed by post-chlorination were shown in Fig. 1. The close-up views of expanded mass spectra for the newly formed Cl-DBPs at the nominal mass m/z 337 were also presented. As shown in Fig. 1, some Cl-containing compounds, such as C12H20O6Cl− (m/z 336.94443) and C14H16O2Cl− (m/z 336.9566) were only detected after 30-min dark chlorination followed by 3-day post chlorination. In order to visualize the distribution and composition of NOM and Cl-DBPs, van Krevelen diagrams were constructed according to the O/C and H/C ratios of molecular formulas. The van Krevelen diagram for SRNOM was displayed in Appendix A Fig. S3, the distribution and composition of NOM was similar to that in previous research and suggested good reproducibility (Consior et al., 2011). The common elemental compositions observed in the 5 samples included compounds contained only C, H and O atoms (CHO), only C, H, O and S atoms (CHOS), only C, H, O, N and S atoms (CHONS), and only C, H, O and N atoms (CHON) (Appendix A Fig. S4). In the following section, the transformation of NOM and the formation of Cl-DBPs will be discussed in detail.

2.2.1. Differential UV absorbance changes of NOM in the UV/chlorine AOP

Although no obvious changes of the DOC concentrations of the two samples were observed (Appendix A Fig. S5), the obvious changes about the UV absorbance of NOM after the UV/chlorine AOP suggested the compositional transformation of NOM (Appendix A Fig. S6). Differential spectra of
NOM after the UV/chlorine AOP and dark chlorination treatment were shown in Figs. S6a and S6b. Overall, the peak intensity in the sample under 30-min UV/chlorine AOP was higher than that under 30-min dark chlorination treatment. A broad absorbance band from 250 to 300 nm with a maximum at approximately 272 nm was observed no matter in the UV/chlorine AOP or dark chlorination treatment, which was recognized as a signal for chlorination (Yan et al., 2014; Roccaro et al., 2009). The scale of the differential spectra slowly increased with increasing reaction time and a stronger peak intensity at 272 nm was observed after the UV/chlorine AOP than dark chlorination treatment. In fact, the formation of peak at 272 nm was contributed to the reaction between NOM chromophores and chlorine (Korshin et al., 2007), therefore the UV/chlorine AOP promoted this reaction mechanism and caused higher intensity of these peaks. Besides, the different reaction mechanisms, corresponding distinct reaction intermediates and final products might also contribute to the differences in spectral characteristics between the UV/chlorine AOP and dark chlorination.

2.2.2. Changes of the molecular composition of NOM in the UV/chlorine AOP

Overall, the alterations of weighted average values of MW (i.e., 479 to 444), weighted average value of AI_{mod} (AI_{mod-w}) (i.e., 0.366 to 0.311) and weighted average value of DBE (DBE_w) (i.e., 11.89 to 10.07) of NOM after the UV/chlorine AOP were more significant than that after dark chlorination (Appendix A Table S2). The changes about the compositions of NOM during 30-min UV/chlorine AOP and dark chlorination treatment were analyzed more detailly from compositional change, mainly including the produced formulas (the formulas which produced after treatment), removed formulas (the formulas which belonged to NOM composition but disappeared after treatment), decreased and increased formulas after the UV/chlorine AOP compared to NOM sample (Fig. 2). It should be noted that Cl-DBPs were not included in these figures and will be discussed separately in the next section. In total, 1189 formulas were removed after the UV/chlorine AOP, occupying 25.8% of the total formulas (Appendix A Table S3), and 613 formulas were newly formed after the UV/chlorine AOP. In contrast, 1052 formulas were removed and 390 formulas were newly produced after dark chlorination treatment. The number of newly produced formulas after the UV/chlorine AOP was larger than that after dark chlorination. This meant that more complex reactions were conducted in the UV/chlorine AOP and promoted the transformation of NOM. Compared with the newly formed formulas after the UV/chlorine AOP, the removed formulas owned higher weighted average value of DBE/C (DBE/C_w) and AI_{mod} values (AI_{mod-w}), lower weighted average value of H/C (H/C_w) and weighted average value of O/C (O/C_w) (Appendix A Table S4). This meant the UV/chlorine AOP and the radicals could cause the ring opening and NOM compositional variation. Consequently, more unsaturated aliphatic and hydroxylated carboxylic acids would be produced in this process. One previous study has reported similar results that lignin can be oxidized by enzymatic hydroxyl radicals and resulted in ring opening (Higuchi et al., 2004). From Fig. 2a, it was found that many aliphatic compounds, saturated fatty and carbohydrates were produced and fewer aliphatic compounds were removed after the UV/chlorine AOP. In contrast, no obvious difference was observed for these compounds in dark chlorination treatment (Fig. 2c). The significantly lower AI_{mod-w} of the newly produced formulas also suggested the structural shifts from aromatic toward aliphatic constituents in NOM due to the UV/chlorine AOP (Table S4). This phenomenon indicated that radical-induced alterations of aromatic constituents in NOM might be one of the major formation pathways of the newly produced aliphatic compounds in NOM during the UV/chlorine AOP. In addition to the interactions be-
between NOM and HO’ or RCS, various reaction mechanisms existing in the UV/chlorine AOP also can contribute to the ring cleavage reaction. For example, reaction between NOM and free chlorine, and reaction between photons with NOM (Varanasi et al., 2018; Lei et al., 2019).

For the common formulas of NOM presented before and after the UV/chlorine AOP, the peak intensity changed significantly. Among these common compounds, the peak intensity of 27.51% of the compounds increased and the remaining 28.30% decreased after the UV/chlorine AOP. As shown in Fig. 2b and 2d, the difference of the H/C ratio between the formulas with decreased and increased peak intensity after the UV/chlorine AOP was more obvious compared to that after dark chlorination. And most of the formulas with increased peak intensity after the UV/chlorine AOP were highly unsaturated and phenolic compounds, which owned higher unsaturation. These comparisons indicated that the compounds with higher unsaturation (higher DBE/C ratio and AI_{mod} values) was susceptible to the reactions during the UV/chlorine AOP. This phenomenon might contribute to the cleavage of the aromatic ring or loss of aromaticity in the UV/chlorine AOP. In this way, more compounds which owned lower MW value could be produced and thus promoted the decrease of MW values. This effect was attributed to the chromophores and fluorophores (double bonds, aromatic groups and phenolic groups) being preferentially degraded by the UV/chlorine oxidation, particularly reactive groups with high electron donating capacity (Wang et al., 2017a). Besides, radicals produced during the UV/chlorine AOP can also react with different moieties of NOM and lead to the degradation and various transformation pathways for NOM (Zhao et al., 2011). For example, HO’ can induce NOM transformation produces small-molecular-weight organic compounds, such as aldehydes, ketones, alkenes and carboxylic acids (Westerhoff et al., 2009).

Fig. 2 - van Krevelen diagram showing the difference in NOM after treatment by (a)(b) 30-min UV/chlorine and (c)(d) 30-min dark chlorination. Note: produced-the spectra are not originally presented in NOM and appeared after treatment; removed-the spectra are originally presented in NOM and diminished after treatment; increased-relative intensity of the spectra increase after treatment; decreased-relative intensity of the spectra decrease after treatment. Five groups in this diagram are classified based on the AI_{mod} and H/C value: group 1 represents polycyclic aromatics (AI_{mod} > 0.66), group 2 represents polyphenols (0.66 ≥ AI > 0.50), group 3 represents highly unsaturated and phenolic compounds (AI_{mod} ≤ 0.50 and H/C < 1.5), group 4 represents aliphatic compounds (2.0 ≥ H/C ≥ 1.5), and group 5 represents saturated fatty and carbohydrates (H/C > 2.0) (Hao et al., 2017).
2.2.3. A closer look on the changes of CHO and CHON compounds of NOM in the UV/chlorine AOP

Since the CHOS and CHONS compounds were rarely detected in NOM (Appendix A Fig. S4), herein we only concerned the changes of CHO and CHON compounds before and after the UV/chlorine AOP or dark chlorination treatment. Amine is an important functional group of CHON compounds, the detected CHON compounds having protein-like and aromatic structures might contain a certain number of amine-containing compounds (Kim et al., 2003; Hertkomr et al., 2006). The number of CHO compounds decreased obviously both after the UV/chlorine AOP or dark chlorination treatment (Appendix A Fig. S4). For the compounds containing the same number of O, the shift of carbon number from high to low and decrease of DBE value after the UV/chlorine AOP were observed. The compounds only containing C, H and eight O atoms (O8 compounds) were chosen as an example because of its abundant existence in NOM (Appendix A Fig. S7). From Appendix A Fig. S7, the O8 compounds in NOM control sample had DBE values of 4 – 14 and carbon numbers of 11–26. After the UV/chlorine AOP, the O8 compounds had DBE values of 4 – 13 and carbon numbers of 10–25 (Appendix A Fig. S7b). In contrast, the O8 compounds had DBE values of 4 – 14 and carbon numbers of 10–26 after dark chlorination treatment. In addition, the O8 compounds after the UV/chlorine AOP owned lower DBE/Cw ratio and Almod-w value compared with the O8 compounds after dark chlorination treatment (Appendix A Table S5). Zhang et al. (2012a) put forward that the compounds with high carbon number (low O/C ratio) were more reactive toward chlorine than those with a low carbon number within the same oxygen class, and this shift contributed the decrease of DBE (Zhang et al., 2012a). In our study, this tendency was greatly promoted under the UV/chlorine AOP. It indicated that there existed more other reaction mechanisms about the compounds with high carbon number in the UV/chlorine process. Firstly, UV irradiation might destroy some chemical bonds of NOM, such as C–C double bonds in olefins, and can open the ring of some compounds. Besides, free radicals which produced in the UV/chlorine AOP can be involved in these reactions, for example, HO• and RCS seem to react quickly with some aliphatic chains with larger molecules (e.g., more than 20 carbon atoms) (Varanasi et al., 2018), which can also cause the decrease of carbon numbers. The cleavage of bonds due to UV irradiation and reaction with radicals leads to a reduction in the number of C atoms and the decrease of DBE values.

After the UV/chlorine AOP or dark chlorination treatment, the number of CHON compounds decreased compared with NOM sample (Appendix A Fig. S8). Therefore, CHON compounds in NOM can be transformed no matter under the UV/chlorine or dark chlorination treatment. The reaction between chlorine and dissolved organic nitrogen (DON) can cause the formation of various disinfection byproducts (Chang et al., 2011) and induce the decrease of CHON compounds of NOM. Meanwhile, the sample treated by the UV/chlorine AOP owned the higher number and proportion of CHON compounds compared with the sample treated by dark chlorination treatment. And the removed CHON formulas after the UV/chlorine AOP owned higher DBE/Cw and Almod-w value compared with that after dark chlorination treatment (Appendix A Table S4). In order to further explore the transformation of CHON compounds during the UV/chlorine AOP, the N2Ox compounds, which were stable and difficult to be removed in the drinking water treatment plant (Raeke et al., 2017), were chosen as examples (Appendix A Fig. S9). The results showed that the N2Ox compounds in the UV/chlorine treated sample were more abundant compared to that in dark chlorination treated sample. In NOM control sample, N2O12, N2O13 and N2O14 were the most abundant species and DBE values in these species were in the range of 9–16. After the UV/chlorine AOP, N2O12, N2O11 and N2O12 became the most abundant species and the DBE values in these species were in the range of 7–12. Comparably, N2O11 and N2O12 were the most abundant species from dark chlorination and the range of DBE values was 8–12. Considering the 30-min reaction time in this study, free chlorine primary reacts with some amines, amino acids and aromatic compounds (Deborde et al., 2008). For example, amino acids, one of the CHON species, can react with chlorine and generate organic chloramines quickly, then the organic chloramines can decay under UV irradiation by destroying N–Cl bond (Varanasi et al., 2018). The break of this bond made the organic chloramines lose Cl atom and become CHON compounds again, which might be nitrogenous DBPs (Weng et al., 2012; 2013). Except for the above reactions, HO• and RCS can react with heterocycles inert to free chlorine, and promote the transformation of N-containing compounds in NOM under the UV/chlorine AOP. For example, caffeine and carbamazepine, which are not degraded during chlorination alone, but can be effectively reduced from the reaction with ClO• radical (Guo et al., 2017; Pan et al., 2017). These phenomena indicated that HO• and RCS were very reactive toward molecules bearing nitrogen containing groups, though we don’t know whether the reactions directly occur towards nitrogen group. In natural waters, DON is composed of 0.5%–10% of NOM and can be the precursors of N-DBPs, some N-DBPs such as haloacetonitriles are known to be more genotoxic than those without nitrogen (Karanfil et al., 2008; Lee et al., 2007; Westerhoff and Maah, 2002; Plewa et al., 2008; Muellner et al., 2007). Our results clearly showed the significant difference of CHON change in the UV/chlorine AOP, which improved our understanding about CHON change in this process and would be helpful to evaluate the formation potential of N-DBPs. It should be noted that negative ionization mode has been reported to be unfavorable for CHON detection due to ion suppression (Carvalho et al., 2017), our results might not fully present the change of CHON compounds during the UV/chlorine AOP, future study need to combine with analysis results in positive ionization mode to explore CHON alteration and N-DBPs formation.

2.2.4. The formation of Cl-DBPs in the UV/chlorine AOP

Fig. 3 showed the distribution and the number of Cl-DBPs in the UV/chlorine AOP and dark chlorination treatment. A total of 833 peaks were assigned as Cl-DBPs in the UV/chlorine AOP, including 333 one-chlorine-containing compounds (Cl-DBPs-1Cl), 273 two-chlorine-containing compounds (Cl-DBPs-2Cl), 172 three-chlorine-containing compounds (Cl-DBPs-3Cl) and 55 four or five-chlorine-containing compounds (Cl-DBPs-4Cl or Cl-DBPs-5Cl). Cl-DBPs-1Cl were the dominant Cl-DBPs in the UV/chlorine AOP. Comparably, a total of 789 Cl-DBPs
Fig. 3 – van Krevelen diagram of chlorinated compounds identified after treatment by (a-d) 30-min UV/chlorine and (e-h) 30-min dark chlorination. (a)(e) one-chlorine containing components; (b)(f) two-chlorine containing components; (c)(g) three-chlorine containing components and (d)(h) four-chlorine containing components. Color bar represents the relative intensity of the formula.
were measured in dark chlorination, with 267 Cl-DBPs-1Cl, 315 Cl-DBPs-2Cl, 176 Cl-DBPs-3Cl and 31 Cl-DBPs-4Cl compounds. Cl-DBPs-2Cl were the dominant Cl-DBPs during dark chlorination treatment. Generally, more Cl-DBPs were generated during the UV/chlorine AOP compared with dark chlorination treatment. This was proved by the consumption of free chlorine and TOCl content in the two process within 30 min (Fig. 4 and Appendix A Fig. S10), which more free chlorine was consumed in the UV/chlorine AOP than that in dark chlorination treatment. The free chlorine in the UV/chlorine AOP not only reacts with NOM and leads to the formation of Cl-DBPs, but also decays to produce special radicals under UV irradiation, such as Cl\(^{-}\) or ClO\(^{2-}\), which would participate in the formation of Cl-DBPs. Meanwhile, according to the TOCl content, more Cl-DBPs were produced in the sample treated by the UV/chlorine AOP (12 \(\mu\)mol/L) than the sample treated by dark chlorination (7 \(\mu\)mol/L, Fig. 4a). There were 449 Cl-DBPs existed both in the UV/chlorine AOP and dark chlorination, the peak intensity of these Cl-DBPs was generally higher in the UV/chlorine AOP than that in dark chlorination treatment (Fig. 3). As listed in Appendix A Table S6, the Cl-DBPs presented in the UV/chlorine AOP had higher H/C and O/Cw value, lower A\(_{1\text{mod-w}}\) and DBE/Cw value than those presented in dark chlorination treatment. This can be partially explained by the different precursors in NOM in the UV/chlorine AOP or dark chlorination treatment.

To test this hypothesis, the Cl-DBPs and the corresponding precursors of these Cl-DBPs from the UV/chlorine AOP or dark chlorination treatment were tracked. Generally, free chlorine and RCS react with NOM to produce Cl-DBPs mainly via AR or SR (Minakata et al., 2017). Therefore, we compared the Cl-DBPs generated through SR or AR during the UV/chlorine AOP and dark chlorination treatment (Fig. 5a and 5b), and there was an obvious difference in the distribution and composition between these products. This was the same with distribution of the precursors (Fig. 5c and 5d). From Fig. 5, no matter after the UV/chlorine AOP or dark chlorination treatment, the AR precursors owned lower H/C ratio compared with the SR precursors, which indicated the higher aromaticity of AR precursors. The types of precursors can be determined roughly based on their distribution area in van Krevelen diagram. From Fig. 5c, the O/C ratio range of SR precursors after the UV/chlorine AOP was from 0.3 to 0.5, and the corresponding H/C ratio range was mainly from 0.8 to 1.5. The O/C ratio range of AR precursors after the UV/chlorine AOP was from 0.25 to 0.75 and H/C ratio range was from 0.4 to 1.4. In contrast, the O/C ratio range of SR precursors after dark chlorination was from 0.3 to 0.85, and the corresponding H/C ratio range was mainly from 0.6 to 1.6. The O/C ratio range of AR precursors after dark chlorination was mainly from 0.2 to 0.7 and H/C ratio range was from 0.4 to 1.4, respectively (Fig. 5d). This indicated that the characteristics of AR and SR precursors after the UV/chlorine AOP were different from that after dark chlorination. Most of the SR precursors after the UV/chlorine AOP were highly unsaturated and phenolic compounds. AR precursors in the UV/chlorine AOP included condensed polycyclic aromatics, polyphenols, highly unsaturated and phenolic compounds. As for dark chlorination, SR precursors in this process mainly included aliphatic compounds, polyphenols, highly unsaturated and phenolic compounds. AR precursors in this process mainly included condensed polycyclic aromatics, polyphenols, highly unsaturated and phenolic compounds. In fact, the biggest difference between the UV/chlorine AOP and dark chlorination treatment mainly arose from the generation of free radicals (especially RCS) in the UV/chlorine AOP. Regarding RCS, Cl\(^{-}\) can react with compounds such as substituted benzenes to form Cl-adduct compounds, and can undergo H abstraction for phenols, alcohols and carboxylic functional groups (Minakata et al., 2017; Lei et al., 2019). Meanwhile, Cl\(^{-}\) is selective and has higher reactivity than HO\(^{-}\) towards certain organics, such as benzoic acid, chlorobenzene, and phenol (Minakata et al., 2017). The reactions of ClO\(^{2-}\) are not well understood and preliminary results show the electron transfer pathways (Kong et al., 2018). Therefore, the reactions of RCS with NOM can lead to various Cl-DBPs. On the other hand, the reactions of HO\(^{-}\) and RCS change the NOM properties, which can result in different reaction patterns with free chlorine. HO\(^{-}\) and Cl\(^{-}\) can attack to the aromatic rings to produce phenolic structures, which then make it susceptible to be attacked by free chlorine. For example, benzoic acid, which is resistant to dark chlorination, can generate Cl-DBPs upon the UV/chlorine AOP (Zhao et al., 2011). On the contrary, for some precursors reactive toward free chlorine, they may also react with HO\(^{-}\) and RCS and be transformed to products without chlorine (Minakata et al., 2017).

2.3. Molecular transformation of NOM and formation of Cl-DBPs in the UV/chlorine AOP followed by post-chlorination

After 3-d post-chlorination, further decreases in the number of CHO and CHON compounds were observed compared to 30-min UV/chlorine AOP alone (Appendix A Fig. S4). For the CHO compounds, O\(_8\) compound was taken as an example, the sample after post-chlorination owned lower DBE values and carbon number compared to that in the UV/chlorine AOP (Appendix A Fig. S7). From Appendix A Fig. S7, the O\(_8\) compounds after the UV/chlorine AOP had DBE values of 4–13 and carbon numbers of 10–25. After the UV/chlorine AOP followed by post-chlorination, the O\(_8\)
compounds had DBE values of 4–12 and carbon numbers of 10–24. In contrast, the Q$_3$ compounds had DBE values of 4–14 and carbon numbers of 10–26 after dark chlorination followed by post-chlorination, which had no obvious difference compared to the sample treated by 30-min dark chlorination treatment. These phenomena were further proof for the effect of the UV/chlorine AOP on chemical bond break. As for CHON compounds, compared to the 650 CHON compounds identified in 30-min UV/chlorine AOP, 348 CHON compounds were detected after 3-d post-chlorination (Appendix A Fig. S8). It indicated that chlorine can react with some specific CHON compounds of NOM. Add of excess chlorine at the beginning of post-chlorination stage can completely transform these CHON compounds into N-DBPs. Therefore, the number and proportion of CHON compounds further decreased after post-chlorination process compared with 30-min UV/chlorine process. Besides, the number and proportion of CHON compounds in the sample treated by 30-min UV/chlorine AOP followed by 3-d post-chlorination were less than those in the sample treated by 30-min dark chlorination followed by 3-d post-chlorination. This phenomenon might be explained as follows. Firstly, less CHON compounds were removed in 30-min UV/chlorine pretreatment compared with that in 30-min dark chlorination pretreatment. These CHON compounds were left until the post-chlorination stage and react with excess chlorine. Secondly, the UV/chlorine AOP might change the molecular composition of NOM and promoted the production of special CHON compounds which were reactive towards chlorine. These newly generated CHON compounds during the UV/chlorine AOP could also participate in the reactions with chlorine during the post-chlorination process and caused the decline of number and proportion of CHON compounds. Finally, during post-chlorination, some structures might undergo oxidation by free chlorine and hydrolysis to release ammonia or chloramines. For example, for the typical reactions of N-chloro–amino acids, the oxidation by free chlorine generates imines, which would then undergo hydrolysis to form aldehydes with ammonia release (How et al., 2017). Therefore, prolonging reaction time in post-chlorination could cleave the NOM structures into small molecular weight compounds, and further lead to the decrease of CHON compounds.

Regarding Cl-DBPs formation in the post-chlorination process, the UV/chlorine AOP followed by post-chlorination generated the highest number of Cl-DBPs (1461 compounds),
compared to the UV/chlorine AOP alone (833 compounds) or post-chlorination without the UV/chlorine pretreatment (1295 compounds). Supplement of free chlorine in the post-chlorination treatment can lead to the formation of more Cl-DBPs. CI-DBPs-2Cl were the most abundant Cl-DBPs after post-chlorination treatment, this was different from the dominance of Cl-DBPs-1Cl in the UV/chlorine pretreatment (Appendix A Fig. S11). Clearly, free chlorine in 3-d post-chlorination period underwent further SR to produce more chlorine-containing components. This indicated that the UV/chlorine pretreatment can change the structures of NOM and produce the precursors reactive towards free chlorine.

3. Conclusions

This study explored the changes of molecular composition of NOM and Cl-DBPs produced in the UV/chlorine AOP and subsequent post-chlorination via ESI FT-ICR MS. The radicals involved in the UV/chlorine AOP (e.g., ClO’, Cl’, and HO’) and UV irradiation caused great difference in NOM composition and Cl-DBPs formation. The UV/chlorine AOP promoted the transformation of NOM by improving the removal of compounds owning higher DBE/C ratio and Al_mog values, and caused more cleavage of the aromatic ring or more loss of aromaticity than dark chlorination. Nitrogen bearing components had significant changes in the UV/chlorine AOP, which deserves further attention and evaluation as it can be related with the formation of nitrogenous DBPs. More chlorine-containing DBPs were observed in the UV/chlorine AOP than dark chlorination. The differentiation of chlorine SR and AR suggested different precursors in the UV/chlorine AOP and dark chlorination. The precursors of Cl-DBPs under the UV/chlorine AOP owned higher aromaticity compared to dark chlorination. Post-chlorination further caused the cleavages of NOM structures into small molecular weight compounds and enhanced the formation of Cl-DBPs.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.08.028.

REFERENCES


