Study on Transformation of Natural Organic Matter in Source Water during Chlorination and Its Chlorinated Products using Ultrahigh Resolution Mass Spectrometry

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S *Supporting Information*

ABSTRACT: Natural organic matter (NOM) can affect the performance of water treatment processes, and serves as a main precursor for the formation of disinfection byproduct (DBPs) during chlorination. To minimize such undesirable effects, a better understanding of its structural information and reactivity toward chlorine is necessary. In this study, electrospray ionization coupled to Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) was used to study the molecular composition of NOM in source water. More than four thousand NOM components were resolved in the sample. NOM molecules with a low degree of oxidation (low O/C ratio) were found to be more reactive toward chlorine than those with high O/C ratio. Totally, 659 one-chlorine containing products and 348 two-chlorine containing products were detected in the chlorinated sample at a high confidence level. The chlorinated products can be arranged into series, which indicate they were originated from precursor compounds in series related by the replacement of CH_4 against oxygen. Of the 1007 chlorine-containing products observed in this study, only 7 molecular formulas can be found in previous studies, showing the distinct difference from previous studies. This study explored the reactivity of NOM toward chlorine on a molecular level, which was previously explained on the level of whole mixtures or fractions of NOM, and the identified chlorinated products may contribute to our knowledge of the unknown total organic halide (TOX).

Source water NOM before chlorination — Chlorination → Source water NOM after chlorination
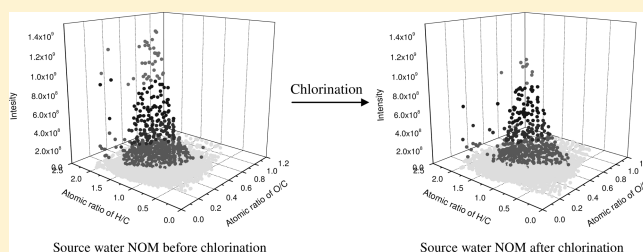
INTRODUCTION

Natural organic matter (NOM) is a heterogeneous mixture of complex organic matter, including humic substances (fulvic acid, humic acid, and humin), amino acids, lipids, amino sugars, proteins, and polysaccharides.[1] Major sources of NOM result from the degradation and exudation of organisms in the natural environment.[2] Because NOM can affect the solubility, bioavailability, and eventual fate of hydrophobic organic contaminants[3] and trace metals,[4] the properties of NOM are of great environmental interest. NOM has a strong implication with water supply. It may not only cause adverse aesthetic qualities such as color, taste, and odor, but also negatively affects the performance of water treatment processes including activated carbon adsorption, ozonation, and membrane filtration.[5] In water distribution systems, NOM may promote undesired microbial growth.[6] In addition, it can react with disinfectants such as chlorine to form a variety of harmful disinfection byproducts (DBPs) during disinfection of drinking water.[7−9]

Since Rook[7] observed that chlorine reacted with NOM in drinking water to produce trihalomethanes (THMs), consistent efforts have been made to study reactions between chlorine and NOM for better understanding the DBPs formation mechanisms. Two important groups of DBPs, THMs and haloacetic acids (HAAs), are regulated in many countries because of their suspected carcinogenicity and developmental and reproductive toxicity.[9,10] However, these compounds only contribute a small part to the increased risk of bladder cancer from consumption of chlorinated water revealed by epidemiological studies.[9,11,12] Although approximately 600−700 chlorinated DBPs in drinking water have been identified,[9] it is estimated that 50% of the total organic halide (TOX) in drinking water, being mainly incorporated into larger molecules of NOM, remains unidentified.

Because NOM may contain literally thousands of different chemical compositions, it is not realistic to characterize it on the basis of a thorough compilation of the individual compounds.[13] Researchers have found it more practical to characterize NOM according to operationally defined chemical

groups having similar properties. These groups are commonly isolated by methods which involve concentration and fractionation of bulk NOM. Bulk characteristics of different fractions of NOM have been effectively determined by numerous analytical techniques, such as elemental analysis (EA), ultraviolet/visible (UV/vis) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, fluorescence excitation/emission matrix (EEM) spectroscopy, and nuclear magnetic resonance (NMR).[14−19] Although these methods are useful in improving the understanding of the nature of NOM from various aquatic environments, they cannot provide structure information at molecular level. Recently, a very promising technique, electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), has emerged in the characterization of NOM from different water environments[20−23] as well as the biological[22] and photolytic[24] transformation of NOM. The ultrahigh resolution and mass accuracy of FT-ICR MS provides molecular masses accurate to within 1 ppm, which often enables the determination of molecular formulas by mass measurement alone.[20,25] The technique provides a tool with the power to examine individual molecules within NOM, which provides a chance not only to investigate the transformation, but also to identify the chlorinated products of NOM.

In this study, the molecular composition of NOM from source water was characterized, and the transformation of individual NOM molecules during chlorination was revealed using ESI FT-ICR MS to better understand the nature of NOM in source water and the reactivity of individual NOM components toward chlorine. In addition, efforts were made to identify some chlorine-containing products after chlorination by accurate mass analysis using ESI FT-ICR MS data. To our knowledge, this is the first study exploring the mechanisms of chlorination of NOM and identifying new chlorinated DBPs using ESI FT-ICR MS.

■ EXPERIMENTAL SECTION

Samples and Preparation. Three source water samples were collected in May 2010 from different locations. The Taihe sample was collected from the intake of Taihe treatment plant whose source was the Qingcaosha Reservoir. The reservoir is located in the estuary of the Changjiang River, and is a major drinking water source for Shanghai City. The Huangpujiang sample was collected from the intake of Yangshupu treatment plant, whose source was the Huangpujiang river, another major drinking water source for Shanghai City. The Miyun sample was collected from the Miyun Reservoir, which is the largest reservoir in north China and is now the only drinking water source for Beijing City. Once collected, the samples were filtered through 0.45-μm Supor filter membranes (Pall, USA) and were stored in the dark at 4 °C until used.

The DOC concentration of the source water was 2.8 mg/L for Taihe sample, 3.9 mg/L for Huangpujiang sample, and 2.3 mg/L for Miyun sample. The chlorination experiment was based on an idea similar to the trihalomethane (THM) formation potential test.[26,27] Hypochlorite sodium solution was diluted and used to prepare free chlorine. Source water samples were chlorinated in sealed 1-L amber glass bottles at 20 °C in darkness. Samples (960 mL) were buffered at pH 7.2 (±0.2) with 20 mL of 0.5 M phosphate buffer. Twenty mL of a 1 mg/mL stock solution of hypochlorite sodium was added to achieve an initial Cl_2 concentration of 20 mg/L. The chlorine to carbon ratio was 7.1 for Taihe sample, 5.1 for Huangpujiang sample,

and 8.7 for Miyun sample. The chlorine dose was higher than that used in drinking water treatment plants to allow the NOM components to thoroughly react with chlorine. At the end of the chlorination, residual chlorine was measured by the DPD (N,N-diethyl-p-phenylenediamine) colorimetric method 4500-Cl G. The residual chlorine were 6 mg/L for Taihe sample, 4 mg/L for Huangpujiang sample, and 6.5 mg/L for Miyun sample. The reaction was halted after 7 days by the addition of excess $Na_2S_2O_3$.

Raw water samples and chlorinated water samples were acidified with hydrochloric acid (p.a. grade, J.T. Baker) to pH 2 and pumped through a Sep-pak C18 solid-phase extraction cartridge (1 g, 6 mL) (Waters, USA) at a flow rate of ∼5 mL/min. The cartridges were previously rinsed with methanol and acidified (pH 2) Milli-Q water. For complete removal of salt, the cartridges were rinsed with 20 mL of acidified Milli-Q water before elution. Immediately after extraction, NOM was eluted with 30 mL of LC-MS grade methanol (Merck, Germany). The eluted samples were freeze-dried and stored at −18 °C in the dark.

FT-ICR MS Analysis. The MS analyses were performed using a Bruker apex ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. NOM sample was dissolved in methanol solution and injected into the electrospray source at 180 μL/h using a syringe pump. The operating conditions for negative-ion formation consisted of a 4.0 kV emitter voltage, 4.5 kV capillary column introduce voltage, and −320 V capillary column end voltage. Ions accumulated in the ion source for 0.1 s in a hexapole. All of the ions passed through a single quadrupole, accumulated in an argon filled hexapole collision pool, in which ions accumulated for 1 s. The delay was set to 1.2 ms to transfer the ions from the collision pool to an ICR cell by electrostatic focusing of transfer optics. The mass range was set at m/z 150−1000. The data size was set to 4 M words, and time-domain data sets were coadded with 256 acquisitions.

Solvent blanks and C18 extraction blanks were measured. Methanol blank analyses were performed to check whether the instrument was clean prior to analyzing the samples. Very few peaks overlapped between the C18 extraction blank and the sample mass spectra. Nonetheless, all peaks found in the blank were removed from the sample peak lists.

Mass Calibration and Data Analysis. The FT-ICR mass spectra were externally calibrated for a mass range of 150−1000 using a sodium formate aqueous solution and internally recalibrated with a known homologous series $C_8H_{10}O_4(CH_2)_n$, $C_{12}H_{14}O_6(CH_2)_n$, $C_{16}H_{18}O_8(CH_2)_n$, $C_{20}H_{22}O_{10}(CH_2)_n$ and $C_{24}H_{26}O_{12}(CH_2)_n$ ($n = 0-5$) of the NOM sample. The m/z values between 150 and 600 Da with relative abundance greater than 6 times the standard deviation of the baseline noise value were exported to a spreadsheet. Data analysis was performed using custom software.[28−30]

Molecular compositions of hydrocarbon homologues can be identified by their unique combination of nominal mass and Kendrick mass defect (KMD), and can be expressed as a general chemical formula, $C_cH_{2c+Z}X$, in which c is the carbon number, Z is referred to as the hydrogen deficiency index, and X denotes the constituent heteroatoms (O, N, S) in a hydrocarbon molecule.[29,30] For convenience, we can denote a given hydrocarbon "type" and "class" according to its Z and X components. For example, $C_cH_{2c-6}O_4$ is abbreviated as $-6O_4$, whereas $C_cH_{2c-29}NO$ is listed as $-29NO$. The Z value is directly related to the number of rings plus double bonds in the molecule. For example, the number of rings plus double bonds

in a molecule of chemical formula, $C_cH_hN_nO_o$, is $(c - h/2 + n/2 + 1)$. Each member of a given "type" series has the same Z-value (i.e., same number of rings plus double bonds), but may differ by multiples of 14.01565 in International Union of Pure and Applied Chemistry (IUPAC) mass (and by multiples of exact 14 in Kendrick mass) according to the number of CH_2 groups appended to the rings. Members of such a series can therefore be recognized from their identical Kendrick mass defects.

The program first converted the measured masses from the IUPAC mass scale to the Kendrick mass scale. Even and odd nominal Kendrick masses were then sorted, and the Kendrick mass defect was calculated. Molecular compositions of hydrocarbon homologues were identified by their unique combination of nominal mass and KMD. For an assigned class species, compound types with various double-bond equivalence (DBE) values were identified by the difference of integer multiples of H_2. The range of DBE values of 0–40 was allowed. Members of a homologous series differ by integer multiples of CH_2. Each homologous series was identified by the assigned single member, with an additional limit of KMD tolerance of ± 0.0010 (set by the user). Once all compounds have been sorted and all relationships based on the given "type" and "class" have been found, the program begins to assign elemental formulas. Molecular formulas were assigned to lower molecular weight members based solely on mass measurement to ± 1 ppm. Elemental compositions were assigned by a mass calculator program limited to molecular formulas consisting of up to 100 ^{12}C, 2 ^{13}C, 200 ^1H, 5 ^{14}N, 20 ^{16}O, 5 ^{32}S, and 1 ^{34}S atoms. If two (or more) elemental compositions were found within the mass tolerance of ± 1 ppm, one formula could usually be confirmed/eliminated unequivocally by the presence/absence of the corresponding nuclide containing one ^{13}C. Because members of a homologous series differ only by integer multiples of CH_2, assignment of a single member of such a series usually suffices to identify all higher-mass members.

To evaluate the reproducibility of the instrumental measurement, peak lists for each identified class species from triplicate samples were used to calculate the relative standard deviation (RSD) according to Parsons et al. and Soule et al.[31,32] The boxplots of RSDs for each molecular class are given in Supporting Information (SI Figure S1). RSDs were 4.1–11% for raw water sample and 3.2–16.6% for chlorinated water sample.

RESULTS AND DISCUSSION

Molecular Characterization of NOM in Source Water. Figure 1 shows the representative FT-ICR mass spectrum of the C18 extracts of NOM (Taihe NOM) in source water. Typical mass spacing patterns such as 14.0156 Da for CH_2-groups and an increase of 36.4 mDa for the replacement of O by CH_4, as well as a strong predominance of odd over even mass ions were observed for Taihe NOM. This implies that Taihe NOM may be largely composed of molecules belonging to chemically related families, or homologous series, which have also been described by other researchers for various humic-rich NOM samples.[33−35] Figure 2 and Figure 3 show close-up views of expanded mass spectra at the nominal mass 301 and 300 of Taihe NOM obtained under the resolving power of >300 000, respectively. The high resolution and high mass accuracy of abundant peaks allow the assignment of a unique elemental composition to each peak in the mass spectrum.
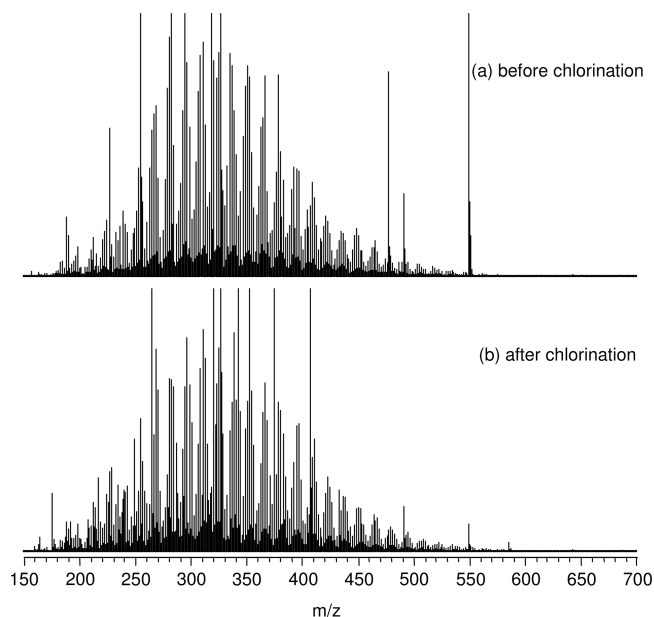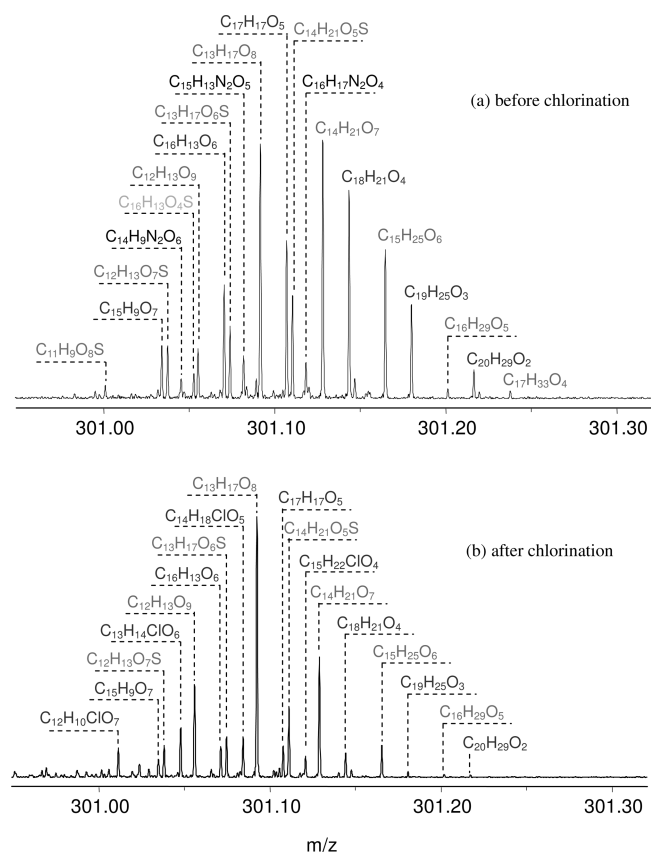

Figure 1. Broadband negative-ion ESI FT-ICR mass spectra of C18 extracts of Taihe source water NOM (a) before chlorination and (b) after chlorination.

Transformation of NOM. *Changes of C, H, O-Only Molecules.* Various C, H, O-only class species were identified in Taihe NOM before and after chlorination, including O_2–O_{14}. The major C, H, O-only class species identified were similar to

Figure 2. Negative-ion ESI FT-ICR mass spectra expanded at nominal mass 301 of C18 extracts of Taihe source water NOM (a) before chlorination and (b) after chlorination.

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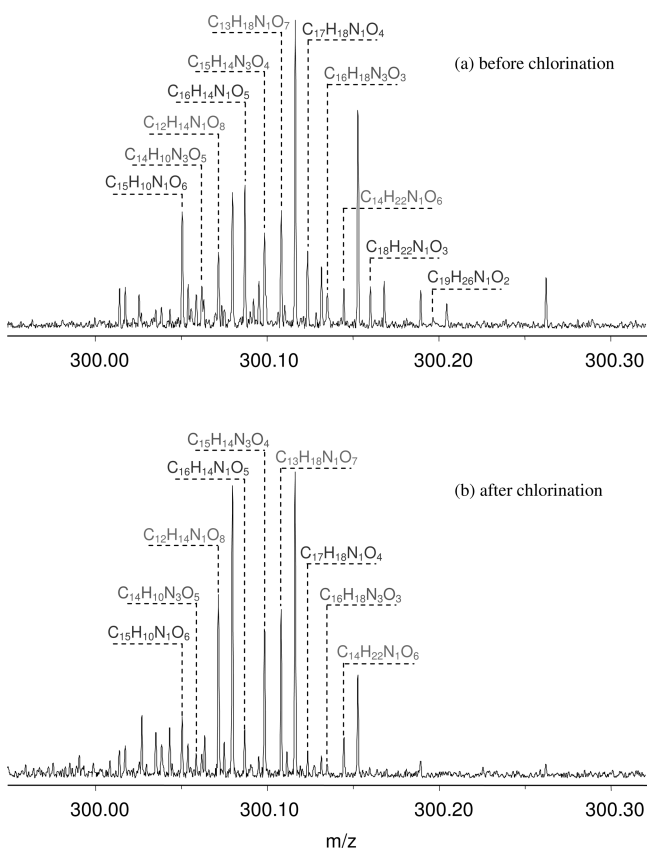dx.doi.org/10.1021/es203587q | Environ. Sci. Technol. 2012, 46, 4396–4402

Figure 3. Negative-ion ESI FT-ICR mass spectra expanded at nominal mass 300 of C18 extracts of Taihe source water NOM (a) before chlorination and (b) after chlorination.

those found in other river NOM samples.[20,33−35,37−39] Figure S2 shows the class analysis for Taihe NOM before and after chlorination. Although ESI FT-ICR MS is not a quantitative technique for the analysis of NOM due to absence of standard samples, many studies have demonstrated that comparison of relative peak intensities of molecules in ESI FT-ICR MS spectra of different samples analyzed under the same instrumental conditions can be used in a semiquantitative way to differentiate between similar types of compounds at the molecular level.[34−36,40] Comparisons of relative peak intensities of NOM before and after chlorination are also useful to evaluate the reactivity of individual NOM molecules toward chlorine. In this study, relative abundance is defined as the magnitude of each peak divided by the sum of the magnitudes of all identified peaks (excluding the isotopic peaks) in the mass spectrum. Same class species of C, H, O-only compounds are observed in Taihe NOM before and after chlorination, but with the intensity maxima shifting from O_7 class before chlorination to O_8 class after chlorination. Detailed carbon number range and DBE range for each class before chlorination and after chlorination are given in SI Table S1.

The expanded mass spectra at the nominal mass 301 of Taihe NOM before and after chlorination, which typifies the observed trends over the full mass spectral range, are exemplarily shown in Figure 2a and b, respectively. It is clear that the majority of peaks result from C, H, O-only compounds in Taihe NOM before chlorination. The C, H, O-only compounds can be arranged into series, which are related by the replacement of CH_4 against oxygen. Two C, H, O-only series (series 1: $C_{12}H_{13}O_9$, $C_{13}H_{17}O_8$, $C_{14}H_{21}O_7$, $C_{15}H_{25}O_6$, $C_{16}H_{29}O_5$,

$C_{17}H_{33}O_4$; series 2: $C_{15}H_9O_7$, $C_{16}H_{13}O_6$, $C_{17}H_{17}O_5$, $C_{18}H_{21}O_4$, $C_{19}H_{25}O_3$, $C_{20}H_{29}O_2$) were observed in Figure 2a. According to the different molecular formulas of these C, H, O-only compounds, it is reasonable to expect that these compounds have different reactivity during chlorination. By comparing the relative signal intensities of these C, H, O-only compounds before and after chlorination (Figure 2a and b), it was found that some compounds reacted faster than others, some were completely removed, and some remained. After chlorination the relative signal intensities of $C_{16}H_{13}O_6$ (O/C 0.38), $C_{17}H_{17}O_5$ (O/C 0.29), $C_{18}H_{21}O_4$ (O/C 0.22), and $C_{19}H_{25}O_3$ (O/C 0.16) of series 2 decreased dramatically compared to those of $C_{12}H_{13}O_9$ (O/C 0.75), $C_{13}H_{17}O_8$ (O/C 0.62), $C_{14}H_{21}O_7$ (O/C 0.5), and $C_{15}H_{25}O_6$ (O/C 0.4) of series 1, suggesting that compounds with low degree of oxidation are more reactive toward free chlorine. Such trend in reactivity was also observed in compounds in series 1. After chlorination, the relative signal intensities of $C_{12}H_{13}O_9$ and $C_{13}H_{17}O_8$ of series 1 increased while the relative signal intensities of $C_{14}H_{21}O_7$, $C_{15}H_{25}O_6$, and $C_{16}H_{29}O_5$ decreased, and $C_{17}H_{33}O_4$ was completely removed, indicating that the reactivity increased with decreasing degree of oxidation from $C_{12}H_{13}O_9$ to $C_{17}H_{33}O_4$ (Figure 2b).These findings correspond to expectation when thermodynamics are considered, because oxidation of the least oxidized molecule provides the largest gain in energy. This is in agreement with a previous study[40] which showed that within an isobaric group, NOM molecules with a low degree of oxidation were preferentially oxidized by ozone, leaving the molecules with higher H/C values behind.

It should be noted that, in this study, C18 solid-phase extraction (SPE) was used to isolate and concentrate the NOM samples and for desalting because the ESI FT-ICR MS analysis requires a very low salt content of the samples. Because chlorination of NOM may produce both chlorinated and oxygenated products with higher polarity than precursor compounds,[41] a portion of the oxidized NOM may be too polar to be efficiently extracted by C18 SPE method. Thus, this study mainly evaluated the reactivity of the C18 extractable NOM molecules, and the extent of oxidation visible from the extract may not fully reflect the extent of oxidation of the source water NOM. In addition, during the ESI process, ion suppression and/or signal enhancement caused by the newly formed chlorine-containing compounds may affect the resulting mass spectrum and the relative peak abundances to some extent.

Detailed molecular composition analyses of the C,H,O-only class species in Taihe NOM before and after chlorination were carried out by plotting the relative abundance maps of DBE as a function of carbon number. For example, Figure 4 shows the relative abundance maps for the O_8 class species. The O_8 class species in Taihe NOM before chlorination have DBE values of 3−15 and carbon numbers of 10−30. The most abundant O_8 class species exhibit DBE 4−12 with carbon numbers 12−24. After chlorination, the O_8 class species had DBE values of 4−14 and carbon numbers of 9−28. The most abundant O_8 class species range from DBE 4−11 and carbon numbers 11−22. It is noteworthy that, after chlorination, the relative abundances of O_8 class species shifted from high carbon number to low carbon number, and from high DBE to low DBE. Similar transformation trends were also observed for O_4−O_7 and O_9−O_{14} class species, as shown in SI Figures S3−S12. These observations of NOM transformation during chlorination at molecular level suggest that NOM molecules with a high
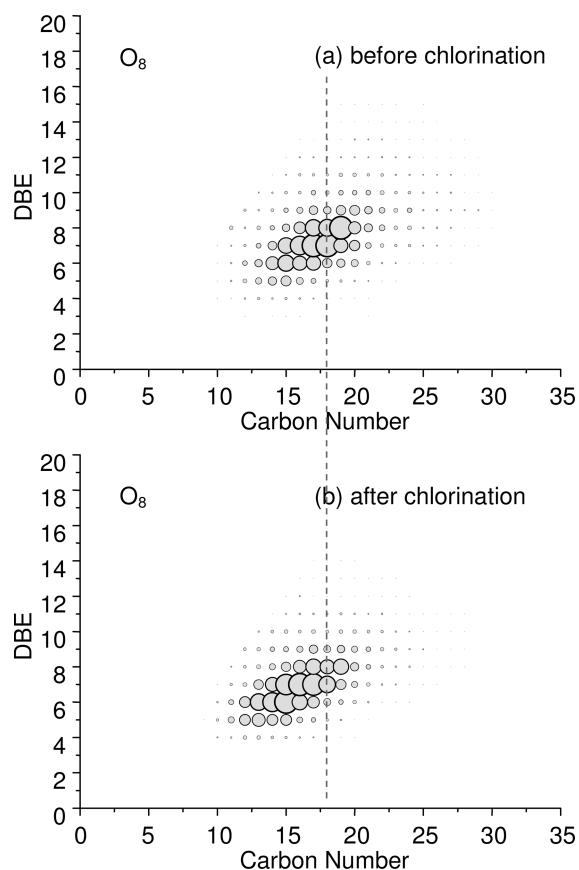
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Figure 4. Plots of DBE versus the carbon number for the O_8 C, H, O-only class species in Taihe NOM (a) before chlorination and (b) after chlorination.

carbon number (low O/C ratio) are more reactive toward chlorine than those with a low carbon number within the same oxygen class. The shift toward lower DBE may be a consequence of the shift from high carbon number to low carbon number, considering that less C means less DBE if DBE/C is constant.

The transformation trends of NOM components in Huangpujiang sample and Miyun sample were very similar to that of Taihe sample as exemplarily shown in SI Figures S13 and S14, respectively.

Changes of Nitrogenous Molecules. Elemental composition of nitrogen-containing compounds can be identified by accurate mass and Kendrick analysis. Eight one-nitrogen class species, $N_1O_3–N_1O_{10}$, nine two-nitrogen class species, $N_2O_3–N_2O_{11}$, and three three-nitrogen class species, $N_3O_3–N_3O_5$, were identified in Taihe NOM. A characteristic mass difference of 11.2 mDa was observed in the mass spectra of many odd mass ions which may be due to the replacement of CO by N_2 between molecules consisting only C, H, and O and those with two nitrogen atoms (Figure 2). The same distance between pairs of signals was also observed for even mass ions, between ions containing one and three nitrogen atoms (Figure 3). As shown in Figure 2, molecules containing two nitrogen atoms were almost completely removed after chlorination. Two one-nitrogen containing series and one three-nitrogen containing series were observed in Figure 3. Similar with the C, H, O-only compounds, the influence of the molecular composition on the reactivity toward chlorine was also observed for the nitrogenous compounds (Figure 3a and b). For example, the one nitrogen-

containing series ($C_{15}H_{11}NO_6$, $C_{16}H_{15}NO_5$, $C_{17}H_{19}NO_4$) with relatively low O/C value was also more reactive than another one nitrogen-containing series ($C_{12}H_{15}NO_8$, $C_{13}H_{19}NO_7$, $C_{14}H_{23}NO_6$) with relatively high O/C value.

UV spectroscopy and stoichiometry studies have suggested that nitrogen in NOM might play a significant role in the chlorine consumption reaction.[16,27] In this study, we investigated the intensity distribution of the nitrogen class species before and after chlorination (SI Figure S2). Before chlorination, N_1O_6 class species was the most abundant nitrogen class species in Taihe NOM, followed by other nitrogen class species as shown in SI Table S1. N_1O_7 became the most abundant nitrogen class species, while the N_1O_3 and N_3O_3 class species were not observed after chlorination. Compared to those before chlorination, relative intensity became more average among each nitrogen class species after chlorination. Thus, we identified the reaction of nitrogen containing chemicals during chlorination. Solid state ^{15}N NMR spectra of aquatic NOM has shown that nitrogens primarily exist in amide/aminoquinone structures and heterocyclic nitrogen structures.[42] Previous studies with small nitrogenous molecules have shown that the amide/aminoquinone group is more reactive than the heterocyclic nitrogenous group during chlorination.[43] However, it is still not clear whether the reaction sites were located at the nitrogenous groups since detailed structure information on the functional groups of the nitrogenous compounds is not available.

Changes of Sulfur Molecules. Several one-sulfur molecules ($O_4S–O_{11}S$) were also identified in Taihe NOM with an intensity of approximately 1/3 of the C, H, O-only compounds (Figure 2). The intensity distribution of the sulfur class species before and after chlorination can be observed in SI Figure S2. Before chlorination, O_6S class species was the most abundant sulfur class species in Taihe NOM, followed by other sulfur class species. After chlorination, O_5S became the most abundant sulfur class species, followed by other sulfur class species as shown in SI Figure S2 and Table S1.

Chlorinated Products. Due to its ultrahigh resolution capacity, the FT-ICR MS spectra also allow determination of chlorination products that occur at exact masses not detected before chlorination. Clear signals of molecular ions for newly formed products were obtained in the mass spectra at almost every odd m/z value and even m/z value. Figure 5 exemplarily showed some newly formed molecules at m/z 323. Some of the newly formed molecules also have a characteristic mass difference of 36.4 mDa for the replacement of O by CH_4, suggesting they may be yielded from homologous series of parent NOM compounds. However, molecular formulas of these newly formed compounds cannot be identified by accurate mass calculation using only C, H, O, N and S, suggesting that the newly formed products may contain other atoms, such as chlorine. Accurate mass analysis using C, H, O, N, S, and Cl was performed. Many of the new peaks formed after chlorination were assigned to be chlorine-containing formulas by accurate mass analysis and isotopic pattern matching as exemplified by the four chlorine-containing peaks ($C_{11}H_9Cl_2O_7^-$, $C_{12}H_{13}Cl_2O_6^-$, $C_{14}H_8ClO_7^-$, and $C_{15}H_{12}ClO_8^-$) at m/z 323 in Figure 5. Isotopic peaks of the newly formed chlorine containing compounds could be observed at corresponding odd and even m/z. In this work, with the powerful ESI FT-ICR MS technique, 8629 newly formed peaks ($S/N > 6$) were detected after chlorination. Of these peaks, 659 peaks containing one chlorine and 348 peaks containing two
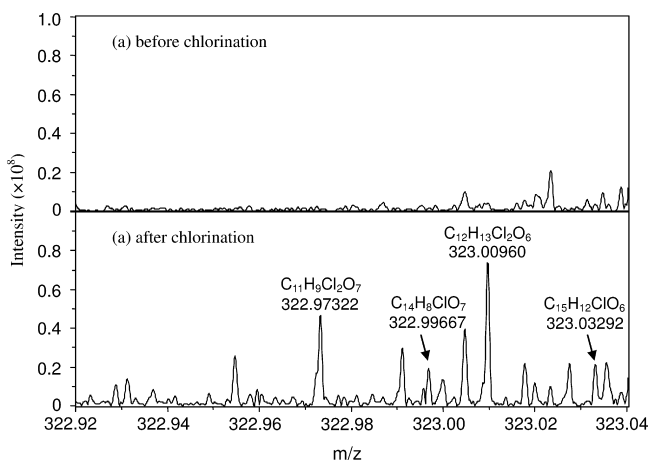
Figure 5. Exemplary negative-ion ESI FT-ICR mass spectra for newly formed chlorine-containing products at nominal mass 323 (a) before chlorination (b) after chlorination of Taihe NOM.

chlorines were assigned at a high level of confidence by accurate mass analysis and Kendrick analysis. The other 7622 newly formed peaks contain two parts: (1) isotopic peaks of newly formed chlorine containing products and (2) peaks whose formulas could not be assigned. It should be noted that no nitrogenous chlorine-containing products could be identified at odd or even m/z, probably because the abundance of the nitrogenous precursor molecules was relatively low. Detailed molecular formula data for these chlorine-containing compounds are listed in SI Table S2 (also available as a spreadsheet file in SI for download).

Chlorinated products as a result of the reaction of the disinfectant chlorine with NOM in raw water have been intensively studied over the past 30 years, yet only about 50% of the TOX formed during chlorination has been chemically identified to individual species.[8,44,45] Richardson compiled a review on drinking water DBPs in which she listed approximately 600 chlorination DBPs, among which 217 compounds contain at least one chlorine atom, and almost all of them were identified by gas chromatography/mass spectrometry (GC/MS) or derivatization-GC/MS.[9,10] However, even with derivatization, GC/MS generally is not amenable to the detection of highly polar compounds. The chlorine-containing products detected in this study fall in a molecular mass range from 150 to 500 Da, and may be rich in carboxylic and phenolic groups. Of the 1007 chlorine-containing products observed in this study, only 7 molecular formulas can be found in Richardson's list of 217 chlorine-containing DBPs (SI Table S3), showing the distinct difference from the previous studies. As exemplarily shown in SI Figures S13 and S14, the same chlorine-containing products were also found in chlorinated Huangpujing sample and Miyun sample, respectively. Although it is still difficult to obtain structural information of these new chlorine-containing products, our results demonstrate that ESI FT-ICR MS is a powerful tool for the detection of the electrospray ionizable chlorine-containing compounds in a complex mixture. Further work with chromatographic preseparation and MS/MS fragmentation is needed to provide more structure information on the chlorine-containing products.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures and table as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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