



# Role of NOM molecular size on iodo-trihalomethane formation during chlorination and chloramination



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## ABSTRACT

Natural organic matter (NOM) is the major precursor for the generation of disinfection byproducts (DBPs) during disinfection, but the role of the NOM molecular size on the formation of iodinated DBPs (I-DBPs) is still unclear. The objective of this study was to evaluate the function of the NOM molecular size on the formation of iodo-trihalomethane (I-THMs) during chlorination and chloramination. Humic acid was adopted as the NOM matrix and fractionated into four molecular weight (MW) groups. Various parameters, including iodide, bromide, NOM concentrations, pH, and pre-chlorination time, were investigated for each MW fraction. During chlorination, high MW fractions (i.e., MW > 100 K Da and 50 K < MW < K00 K Da) produced more I-THMs compared with small MW fractions (i.e., MW < 3 K Da and 3 K < MW < 50 K Da). With the increase in the I<sup>-</sup> or NOM concentration, the formation of I-THMs increased for small MW fractions, while a slight reduction occurred for high MW fractions during chlorination. Higher pH resulted in more I-THM formation for small MW fractions, while the opposite was true for high MW fractions during chlorination. Compared to small MW fractions, bromide was relatively more reactive with high MW fractions in the formation of I-THMs during chlorination. During chloramination, the I-THM yields decreased with the increasing NOM concentration for high MW fractions. The concentration of bromine-containing I-THMs decreased with increasing pH for all MW fractions during chloramination. Additionally, with the prolongation of pre-chlorination time, the total amount of I-THMs decreased remarkably for MWs higher than 3 K Da, while a slight change for MW lower than 3 K Da occurred during chloramination. The results from this study suggest that the molecular weight of the NOM plays an important role in the formation of I-THMs during chlorination and chloramination.

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## 1. Introduction

Chemical disinfectants are widely used in drinking water treatments to inactivate pathogens, including ozone (O<sub>3</sub>), chlorine dioxide (ClO<sub>2</sub>), chlorine (Cl<sub>2</sub>), and chloramine (NH<sub>2</sub>Cl). However, the reaction between disinfectants and natural organic matter leads to the formation of hazardous disinfection byproducts, including trihalomethanes (THMs), haloacetic acid (HAAs), halogen acetonitrile (HANs), halogenated ketones (HKs) and so on

(Richardson et al., 2012; Bond et al., 2011).

Recently, iodinated disinfection byproducts (I-DBPs) have been detected in many water treatment plant effluents and laboratory studies (Cancho et al., 2000; Richardson et al., 2003; Plewa et al., 2004; Hebert et al., 2010). Consequently, I-DBPs have become a focus of attention in drinking water treatment. Previous studies have suggested that I-DBPs are among the most genotoxic and cytotoxic DBPs identified in drinking water (Plewa et al., 2008). Moreover, the iodo-trihalomethanes (I-THMs), such as iodoform (CHI<sub>3</sub>), generated during the oxidative disinfection of iodide-containing drinking water can cause taste and odor problems. Over the past 20 years, the formation of various I-THMs have been intensively studied during disinfection, including iodoform (CHI<sub>3</sub>), chlorodiiodomethane (CHClI<sub>2</sub>), bromodiiodomethane (CHBrI<sub>2</sub>),

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dichloriodomethane ( $\text{CHCl}_2\text{I}$ ), dibromiodomethane ( $\text{CHBr}_2\text{I}$ ), and bromochloriodomethane ( $\text{CHBrClI}$ ) (Krasner et al., 2006; Hua et al., 2006). In general,  $\text{CHCl}_2\text{I}$  is the most abundant I-THM during chlorination while  $\text{CHI}_3$  would be the major product at higher iodide concentrations. Moreover, the increase in iodide concentration in the raw water could lead to the enhanced formation of I-THMs during disinfection (Zhang et al., 2015; Hua and Reckhow, 2007a).

In addition to the commonly used chlorine, chloramine is another widely used disinfectant in drinking water treatments. Considerable numbers of water utilities in the U.S. have switched from chlorination to chloramination because  $\text{NH}_2\text{Cl}$  can form less classical THMs and HAAs (Seidel et al., 2005). Unfortunately, the use of  $\text{NH}_2\text{Cl}$  as a disinfectant might result in the formation of more nitrogenated disinfection byproducts (N-DBPs) and I-DBPs (Plewa et al., 2004; Hong et al., 2007; Richardson et al., 2000). Normally, the iodide present in raw water could react with chloramine to form hypiodous acid (HOI), which then reacts with natural organic matter (NOM), resulting in the formation of I-DBPs. In contrast with chlorine, chloramine was not able to further oxidize HOI to iodate, a nontoxic and stable form of iodine in drinking water (Bürgi et al., 2001; Bichsel and Von Gunten, 1999). Various strategies have been developed to minimize the formation of I-DBPs during chloramination. One option is the application of pre-chlorination followed by chloramination, in which chlorine is followed by an ammonia addition to form  $\text{NH}_2\text{Cl}$  (Joo and Mitch, 2007; Choi and Valentine, 2002). This approach has been demonstrated to remarkably reduce the formation of I-DBPs during chloramination because the iodide would be directly oxidized to iodate by HOCl in pre-chlorination (Allard et al., 2015; Jones et al., 2011).

Previous studies have shown the NOM content and type to have a significant influence on the formation of THMs during disinfection. A strong correlation was found between the initial THM formation potential and the UV absorbance of NOM during disinfection (Gallard and von Gunten, 2002), where the initial THM formation potential was defined as the fast reacting THM precursors formed within the first hours of reaction time. On the contrary, Hua et al. (2015) reported that no significant relationship was observed between the specific ultraviolet absorbance at 254 nm ( $\text{SUVA}_{254}$ ) of the NOM and THM formation. Lin et al. (2014) reported that hydrophobic NOM with molecular weight (MW) lower than 1 K Da contributed the most to the formation of C-DBPs after chlorination, whereas for chloramination, hydrophilic NOM with MW < 1 K Da contributed the most to the formation of C-DBPs. Another work also indicated that the smallest MW fraction had the highest yield coefficient of THMs (Gang et al., 2003). Nevertheless, several recent work obtained the different results. Farre et al. (2013) reported that large MW fractions with rich humic portion formed more DBPs, while low MW fractions yielded more brominated DBPs. Han et al. (2015) chlorinated secondary effluent of a sewage treatment plant and concluded that MW < 1 K Da produced less THMs than high MW fractions. Hua et al. (2015) evaluated three geographically and chemically distinct natural waters (Waco, Winnipeg and Repentigny waters) for chlorination, and found that NOM with MW < 0.5 K Da generated less THMs while high MW produced more THMs for Repentigny water.

Very few studies have been conducted to evaluate the function of NOM molecular size on the formation of I-DBPs, especially for the I-THMs during disinfection. The study by Hua and Reckhow (2007a) indicated that hydrophilic NOM precursors with low MW could result in the formation of more  $\text{CHI}_3$  during chloramination, but only two MW groups (MW > 3 K Da and MW < 3 K Da) of NOM precursors were investigated. A wider range of molecular size would be considered to gain deeper insight about the mechanisms of I-THM formation during disinfection. Additionally, Lin et al.

(2014) found after chlorination most of the I-DBPs came from MW fractions > 10 K Da and < 1 K Da in the Huangpu and Yangtze rivers respectively, whereas after chloramination the MW < 1 K Da fraction was the major source in both rivers. So far there was lack of sufficient and clear information about the relationship between NOM molecular size and I-THM formation during disinfection.

Therefore, the primary aim of this study was to clarify the influence of the molecular weight of NOM precursors on the formation of I-THMs during chlorination and chloramination. Humic acid was adopted as the NOM matrix and fractionated into four MW groups as follows: < 3 K Da, 3 K–50 K Da, 50 K–100 K Da, and > 100 K Da. Four key factors for I-THM formation were investigated at various MW fractions, including the bromide, iodide and NOM concentrations and solution pH. Subsequently, the influence of pre-chlorination time on the formation of I-THMs for each MW fraction during chloramination was evaluated in this study.

## 2. Materials and methods

### 2.1. Chemicals

Five I-THM standards, including  $\text{CHCl}_2\text{I}$  ( $\geq 95\%$ ),  $\text{CHBrClI}$  ( $\geq 95\%$ ),  $\text{CHBr}_2\text{I}$ , 90–95% and  $\text{CHBrI}_2$  (90–95%), were obtained from Can-Syn Chem. Corp. (Canada) while  $\text{CHI}_3$  (99%) was purchased from Sigma-Aldrich (USA). Other chemicals were purchased from Sino-pharm Chemical Reagent Co., Ltd. (China). All of the solutions were prepared with ultra-pure water produced using a Milli-Q water purification system (Millipore, USA).

### 2.2. Molecular size fractionation

The diluted humic acid solution (Aldrich, USA) was initially filtered through 0.45  $\mu\text{m}$  cellulose acetate membranes (Anpel Co. Ltd, China) and then fractionated into different molecular sizes using a series of polyethersulfone ultrafiltration (UF) membranes with MW cut-offs of 3 K, 50 K, and 100 K Da (Millipore, USA). The fractionation experiment was conducted in a 400 mL stirring cell (Amicon 8400, Millipore Corp., USA) under a constant nitrogen gas pressure of 0.1 Mpa (Lin et al., 2000).

### 2.3. Disinfection experiments

All disinfection experiments were conducted in duplicate under headspace-free conditions at room temperature in the dark. A 50 mL solution was initially prepared in glass amber vials containing a desired concentration of  $\text{I}^-$  and  $\text{Br}^-$  as well as a 5 mM phosphate buffer (pH at 7.0). Then, a small volume of disinfectant stock solution (chlorine or chloramine) was spiked to the bottom of the glass amber vials to achieve the desired concentration. After that, the amber vials stirred vigorously on magnetic stir plates for 5 min and then capped for a 24-h reaction. Four key factors, including the iodide, NOM and bromide concentrations and solution pH, were tested to evaluate the I-THM formation for different MW fractions during chlorination and chloramination, and the experimental setup is summarized in Table S1 in the supporting information (SI). In addition, in order to clarify the function of excessive chlorine for each MW fraction, we also investigated the effect of initial chlorine concentration on the formation and speciation of I-THMs, and its concentration was changed from 1 to 8 mg/L with 2 mg/L DOC (dissolved organic carbon), 5  $\mu\text{M}$   $\text{I}^-$  and 10  $\mu\text{M}$   $\text{Br}^-$  at pH 7.0. The different pH values in run 4 were adjusted using an HCl or NaOH solution. The chloramine was freshly prepared in advance according to a previous study (Hua and Reckhow, 2007a).

Subsequently, the effect of pre-chlorination time on I-THM

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