



# Characterization of brominated disinfection byproducts formed during chloramination of fulvic acid in the presence of bromide

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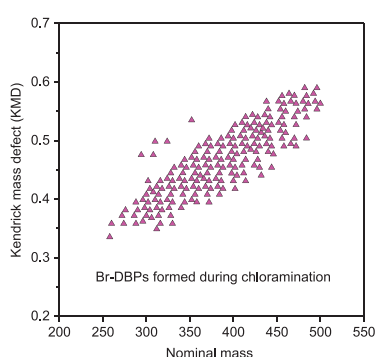
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## HIGHLIGHTS

- 198 formulae of Br-DBPs were detected in chloraminated artificial drinking water.
- Precursor molecules with high O/C and low H/C were more reactive toward chloramine.
- Precursor molecules with high  $\overline{\text{O}}\text{Sc}$  and high DBE/C were preferred to form Br-DBPs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To date, study on the speciation of brominated disinfection byproducts (Br-DBPs), which have higher cytotoxicity and genotoxicity than their analogous chlorinated DBPs (Cl-DBPs), formed in chloramination is still limited. In this study, the previous unknown Br-DBPs formed during chloramination of artificial drinking water were explored with electrospray ionization ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). In total, 193 formulae of one bromine containing Br-DBPs and 5 formulae of two bromine containing Br-DBPs were detected in the chloraminated artificial drinking water sample. Compared to Br-DBPs formed in chlorination, Br-DBPs formed in chloramination have relatively high O/C ratio for the same nominal molecular mass. More than 63% of the Br-DBPs formed during chloramination can be classified as aromatic molecules or polycyclic aromatic molecules, according to their modified aromaticity index (Almod). Further investigation on the change of precursor SRFA molecules during chloramination showed that SRFA molecules with high O/C ratio and low H/C ratio were more reactive and decreased significantly in relative abundance during chloramination. Precursor SRFA molecules with high degree of oxidation and high unsaturation were preferred to form Br-DBPs during chloramination. The results reported in this study provide valuable information on Br-DBPs formed during chloramination and may help us in minimizing DBPs during chloramination.

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## 1. Introduction

Bromide is a natural constituent in source water globally. In fresh water, concentrations of bromide ion generally range from trace

amounts to about 500 µg/L (WHO, 2009). During drinking water disinfection, such as chlorination or chloramination, bromide ion can be quickly oxidized to hypobromous acid (HOBr) or bromochloramine (NHBrCl) and monobromamine (NH<sub>2</sub>Br), which will react with dissolved organic matter (DOM) present in water to form brominated disinfection byproducts (Br-DBPs) (Cowman and Singer, 1996; Kristiana et al., 2009; Symons et al., 1993; Zhai et al., 2014; Zhang et al., 2000). Results from in vitro toxicity assays have shown that Br-DBPs have higher cytotoxicity and genotoxicity than their analogous chlorinated DBPs (Cl-DBPs) (Echigo et al., 2004; Plewa et al., 2002; Richardson et al., 2007). For example, cytotoxicity of bromoacetic acid is approximately 20 and 90 times higher than that of chloroacetic acid in *Salmonella typhimurium* strain TA100 and Chinese hamster ovary cells, respectively (Richardson et al., 2007). Genotoxicity of bromoacetic acid is approximately 200 and 25 times higher than that of chloroacetic acid in *Salmonella typhimurium* strain TA100 and Chinese hamster ovary cells, respectively (Richardson et al., 2007). Hence, Br-DBPs have attracted much more attention.

On the other hand, in order to minimize the formation of trihalomethanes and haloacetic acids, which are regulated in many countries, there has been an increasing interest in replacing chlorination with chloramination (Bougeard et al., 2010). Although the amount of total organic bromine (TOBr) formed during chloramination was only about 31% of that formed during chlorination, about 86% of the TOBr formed during chloramination was unknown, which is higher than that formed during chlorination (40%) (Zhang et al., 2000). Results from epidemiological studies showed that unknown halogenated DBPs may contribute a large part to the increased risk of bladder cancer resulting from exposure to DBPs (Bull et al., 2001). Thus further exploration of the unknown Br-DBPs formed during chloramination is needed to better understand the connection between exposure to Br-DBPs and the possible health effect.

Several methods have been used in exploring the unknown Br-DBPs formed during chlorination or chloramination (Richardson et al., 2007; Richardson, 1998; Zhai and Zhang, 2011; Zhai et al., 2014; Zhang et al., 2014). Gas chromatography-mass spectrometry (GC-MS) is a widely used method for identify Br-DBPs (Richardson et al., 2007; Richardson, 1998). However polar or highly polar Br-DBPs, which may be the most abundant portion of the entire Br-DBPs pool, are not amenable to be detected by the GC-MS method. Recently, two promising electrospray ionization mass spectrometry approach have been developed for the characterization of unknown Br-DBPs (Zhai and Zhang, 2011; Zhai et al., 2014; Zhang et al., 2014). One approach is the precursor ion scan (PIS) method, which selectively detects Br-DBPs by performing precursor ion scans of *m/z* 79 and 81 with electrospray ionization-tandem mass spectrometry (ESI-MS/MS) (Zhai and Zhang, 2011; Zhai et al., 2014). By using the PIS method, Zhai and colleagues have identified many polar Br-DBPs in artificial drinking water samples (Zhai and Zhang, 2011; Zhai et al., 2014). The other approach is based on ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), which provides a mass accuracy of <1 ppm, enabling the determination of molecular formulae of Br-DBPs by exact mass and isotopic pattern of <sup>79</sup>Br and <sup>81</sup>Br (Gonsior et al., 2015; Zhang et al., 2014). This method has been successfully used to detecting unknown polar Br-DBPs in artificial drinking water (Zhang et al., 2014) and electrochemically disinfected ballast water (Gonsior et al., 2015).

The aim of the present study was to characterize the polar Br-DBPs formed during chloramination using FT-ICR MS. The difference in the species patterns of polar Br-DBPs between chloramination and chlorination was compared to reveal the different effect of chloramination and chlorination on the formation of polar Br-DBPs. In addition, the change of the molecular composition of the precursor fulvic acid upon chloramination was investigated to better understand the reactivity of Br-DBP precursors.

## 2. Materials and methods

### 2.1. Chemicals

Suwannee River fulvic acid (SRFA, 2S101F) was obtained from the International Humic Substances Society (IHSS). Methanol (LC-MS grade) and hydrochloric acid (p.a. grade) were supplied by Merck (Darmstadt, Germany). Ammonium chloride (GR grade) and hypochlorite sodium solution (analytical grade) were purchased from Sinopharm Chemical Reagent (Beijing, China). Ultrapure water (18.2 MΩ·cm) was purified using a Milli-Q water purification system. Free chlorine stock solution was prepared by diluting the sodium hypochlorite solution with ultrapure water. Monochloramine stock solution was prepared fresh daily by dissolving ammonium chloride in ultrapure water, followed by slow addition of sodium hypochlorite solution to obtain a chlorine to ammonium mole ratio of 0.8:1.0. Free chlorine and monochloramine were measured by the DPD (*N,N*-diethyl-*p*-phenylenediamine) colorimetric method 4500-Cl G (APHA et al., 1998).

### 2.2. Preparation of artificial drinking water samples

Artificial drinking water samples were prepared by dissolving 3.0 mg/L SRFA (as C), 2.0 mg/L NaBr (as Br<sup>-</sup>), and 90.0 mg/L NaHCO<sub>3</sub> in ultrapure water as described previously (Zhai and Zhang, 2011). Water samples were chloraminated in one liter amber glass bottles sealed with PTFE lined caps at 20 °C in darkness. The initial monochloramine dose was 5.0 mg/L as Cl<sub>2</sub>. Immediately after monochloramine addition, the pH of the samples were adjusted to 7.5 with hydrochloric acid. The reaction was stopped after 5 days by addition of excess Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

Water samples were pretreated using solid phase extraction (SPE) as described previously (Zhang et al., 2014). Briefly, the pH of the water sample was adjusted to 2.0 with hydrochloric acid, then the water sample was pumped through a Sep-pak C18 SPE column (1 g, 6 mL, Waters) at a flow rate of ~5 mL/min. The column was conditioned with 12 mL of methanol and 12 mL of acidified (pH 2) water. After sample loading, the SPE column was rinsed with 20 mL of ultrapure water and eluted with 20 mL of methanol.

### 2.3. FT-ICR MS analysis

The FT-ICR MS analyses were carried out on a Bruker apex ultra Fourier transform mass spectrometer equipped with a 9.4 T superconducting magnet as described previously (Zhang et al., 2014). Briefly, C18 extract was infused into the ESI source at a flow rate of 3 µL/min using a KD Scientific syringe pump. The negative ESI source parameters were as follows: emitter voltage is 4.0 kV, capillary column introduce voltage is 4.5 kV, and capillary column end voltage is -320 V. The acquired mass range was from *m/z* 150 to *m/z* 800. The data size was 4 M words, and each spectrum was recorded by co-added 256 scans.

### 2.4. FT-ICR MS data process

The FT-ICR mass spectrometer was externally calibrated with an aqueous solution of sodium formate. Acquired spectra were internally calibrated with a series of known DOM molecules according to previous study (Zhang et al., 2012a, 2012b). After internal calibration, the mass accuracy within 0.5 ppm was achieved. Molecular formulae were assigned for the *m/z* peaks (signal to noise ratio, S/N > 6) limited to the following elements compositions: 0-100<sup>12</sup>C, 0-200<sup>1</sup>H, 0-3<sup>14</sup>N, 0-30<sup>16</sup>O, 0-2<sup>32</sup>S, 0-3<sup>35</sup>Cl, and 0-3<sup>79</sup>Br. All assigned molecular formulae must meet criteria as described previously to ensure the assigned formulae can at least chemically exist (Zhang et al., 2014). It should be noted that since the focus of the present study was on characterization of polar Br-DBPs formed during chloramination, further data analysis was only performed for molecular formulae containing C, H, O, and Br and the precursor molecules containing C, H, O.

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