Characterization of unknown iodinated disinfection byproducts during chlorination/chloramination using ultrahigh resolution mass spectrometry

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HIGHLIGHTS

• The formulas of 206 iodinated DBPs in chloraminated drinking water were proposed.
• More than 68% of the I-DBPs might have aromatic or polycyclic aromatic structures.
• Precursors with high aromaticity is preferential to form iodinated DBPs.

GRAPHICAL ABSTRACT

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Abstract

Iodinated disinfection byproducts (I-DBPs), formed from the reaction of disinfectant(s) with organic matter in the presence of iodide in raw water, have recently been focused because of their more cytotoxic and genotoxic properties than their chlorinated or brominated analogues. To date, only a few I-DBPs in drinking water have been identified. In this study, C18 solid phase extraction coupled with electrospray ionization ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) was used to characterize unknown I-DBPs in chloraminated/chlorinated water spiked with iodide and humic substances. In total, 178 formulas for one-iodine-containing products, 13 formulas for two-iodine-containing products, and 15 formulas for one-chlorine and one-iodine-containing products were detected in the chloraminated water sample, while only 9 formulas for one-iodine-containing products and 6 formulas for one-chlorine and one-iodine-containing products were found in the chlorinated water sample. Most I-DBPs have corresponding chlorine-containing analogues with identical CHO compositions. As indicated by the modified aromaticity index (AImod), in the C18 extracts, more than 68% of the I-DBPs have aromatic structures or polycyclic aromatic structures. This result demonstrates that the use of chloramination as an alternative disinfection method may lead to the formation of more aromatic I-DBPs.
1. Introduction

Formation of iodinated disinfection byproducts (I-DBPs) including iodine containing trihalomethanes (THMs) and iodinated acetic acids during disinfection of drinking water has recently caused wide attention because they exhibit greatly increased toxicological effects compared to their chlorinated and brominated analogues (Plewa et al., 2004; Gemeli et al., 2006; Richardson et al., 2007; Plewa et al., 2008; Richardson et al., 2008). Mammalian cell assay has shown that iodoacetic acid is 3 and 288 times more cytotoxic, and 2 and 47 times more genotoxic than bromoacetic acid and chloroacetic acid, respectively (Plewa et al., 2004). Most recently, it has been reported that I-DBPs present significantly higher developmental toxicity and growth inhibition than their brominated or chlorinated DBP analogues (Yang and Zhang, 2013; Liu and Zhang, 2014). Yang et al. (2014) investigated toxic impact of bromide and iodide on drinking water disinfection and found that both cytotoxicity and genotoxicity were correlated with total organic iodine (TOI), but not to total organic chlorine (TOC). Therefore, the potential health impacts of the I-DBPs could not be neglected.

Richardson et al. (2006) surveyed over 100 distribution systems and found the presence of I-THMs in one plant with a concentration as high as 25 μg/L. At the same time, five iodinated acids, including iodoacetic acid, bromoiodoacetic acid, 3-bromo-3-iodopropenoic acid, and 2-iodo-3-methylbutenedioic acid, have been identified in drinking water disinfected with chloramine during a nationwide DBP occurrence study in the U.S. (Plewa et al., 2004; Krasner et al., 2006). These iodinated acids were also found in most drinking water samples in a 23-city DBPs occurrence study conducted in the U.S. and Canada, and the maximum concentration for iodoacetic acid was 1.7 μg/L (Richardson et al., 2008).

Several studies have investigated the formation and occurrence of I-DBPs during chlorination and chloramination, a substitution of chlorination to reduce the formation of the regulated THMs and haloacetic acids (HAAs), of iodide containing water samples (Karpel Vel Leitner et al., 2003; Kim et al., 2006a, 2006b; Hertkorn et al., 2008). It is thus anticipated that the ESI FT-ICR MS method could also be suitable for identifying the molecular formulas of unknown I-DBPs.

The main objective of this study was to characterize unknown I-DBPs in chlorinated/chloraminated water spiked with iodide and humic substances by using ESI FT-ICR MS. In addition, the species pattern of unknown I-DBPs was compared with that of Cl-DBPs formed during chlorination or chloramination to reveal the effect of different disinfectants on the formation of I-DBPs.

2. Materials and methods

2.1. Materials

Suwannee River fulvic acid (SRFA) was obtained from the International Humic Substances Society. Methanol (LC-MS grade) was purchased from Merck (Darmstadt, Germany). Formic acid (95%) was purchased from Acros. Sodium hypochlorite solution (analytical grade, Sinopharm Chemical Reagent, Beijing) was diluted and used to prepare free chlorine. Ammonium chloride (p.a. grade) was obtained from Sinopharm Chemical Reagent (Beijing). Ultrapure water with a resistivity of 18.2 MΩ-cm⁻¹ was obtained from a Milli-Q purification system (Millipore, USA).

2.2. Simulated drinking water sample preparation

Simulated drinking water samples were prepared with ultrapure water containing 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃, and 200 μg/L potassium iodide as I⁻, according to Ding and Zhang (2009). A relatively high iodide concentration (200 μg/L) was used to amplify iodinated DBPs so that unknown iodinated DBPs could be detected and identified by the FTICR MS method. For chlorination, 1-L water samples were chlorinated in sealed 1-L amber glass bottles with a chlorine dose of 5.0 mg/L as Cl₂. For chloramination, 1-L water samples were chloraminated in sealed 1-L amber glass bottles with 5.0 mg/L monochloramine (as Cl₂). Monochloramine was prepared just before use by reacting ammonium chloride and sodium hypochlorite solutions in a chlorine-to-ammonia ratio of 0.8 mol/mol. All the samples were kept in darkness at 20 °C. The reaction was halted 5 days later by the addition of excess Na₂S₂O₃.

to determine whether there were any impurities in the reagents or any artifacts in the disinfection and subsequent pretreatment, SRFA control samples were generated by repeating the same procedure with samples of the aforementioned simulated water without chlorination or chloramination and chlorination/chloramination control samples were generated by repeating the same chlorination/chloramination procedure with simulated water samples without potassium iodide. Information of simulated drinking water sample composition and treatment applied are provided in Table 1.

2.3. Pretreatment of simulated drinking water samples

Procedures for water sample pretreatment were carried out according to previous studies (Zhang et al., 2012a). Briefly, 1-L water samples were adjusted to pH 2.0 with formic acid and pumped through a Sep-pak C₁₈ solid-phase extraction (SPE) cartridge (1 g, 6 mL, Waters, USA) at a flow rate of ~5 mL/min. The SPE cartridge was activated and
conditioned with methanol and acidified ultrapure water. For complete removal of inorganic ions, the cartridge was rinsed with 10 mL of acidified ultrapure water before elution. After extraction, the cartridge was dried under high-purity grade nitrogen gas and eluted with 10 mL of methanol. A concentration factor of 100 was achieved for water samples before further analysis.

2.4. FT-ICR MS

The ultra-high resolution mass spectrometry analyses were performed using a Bruker apex ultra 9.4 T FT-ICR MS interfaced with a custom-developed mass calculator (Zhang et al., 2009). The other 203 formulas of I-DBPs identified in this study were also found in the study by Ding and Zhang (2009). The other 203 formulas of I-DBPs are for the mass range of 150–800 using a sodium formate aqueous solution (Zhang et al., 2012a; Zhang et al., 2014). The acquired spectra were internally recalibrated with a known homologous series of the SRFA sample (Zhang et al., 2012a; Zhang et al., 2014). After internal calibration, mass accuracy of < 1 ppm was achieved. Molecular formulas were assigned from the m/z peaks by a custom-developed mass calculator program (Zhang et al., 2012a) limited to the following chemical elements: \(\text{C}^{12}, \text{O}^{16}, \text{N}^{14}, \text{Cl}^{35}, \text{Cl}^{37}, \text{Br}^{81}, \text{I}^{125} \text{I}^{127}\). All assigned formulas must meet the following criteria: (1) mass accuracy < 0.5 ppm; (2) the sum of H and halogen (Cl, I) atoms must be at least 1/3 the number of C atoms and cannot exceed 2C + N + 2; (3) the sum of H, halogen and N atoms must be even (the “nitrogen rule”); and (4) the number of N or O atoms cannot exceed the number of C atoms (Zhang et al., 2014). These criteria ensure that formulas were assigned at a high level of confidence and can at least chemically exist.

2.5. Limitations

In this study, solid phase extraction (SPE) was used to extract complex mixtures of DBPs, as pointed in previous studies (Zhang et al., 2012a; Zhang et al., 2014), only 18 extractable DBP molecules were analyzed by mass spectrometry. In addition, the mass range was set to m/z 150–800. Therefore, this study mainly characterized the C_{18} extractable DBP molecules and the detected formulas do not represent the entire pool of I-DBPs formed after chlorination/chloramination.

3. Results and discussion

3.1. Detection of unknown I-DBPs

Fig. 1 exemplarily shows the detection of unknown Cl-DBPs and I-DBPs at the nominal mass m/z 403 in simulated drinking water samples after chlorination and chloramination. Newly formed one-iodine-containing DBPs and two iodine-containing DBPs were clearly observed in the mass spectrum of the SRFA+I+NH₂Cl sample (Fig. 1e). The I-DBPs were observed at almost every odd nominal mass from m/z 247–499 in the SRFA+I+NH₂Cl sample, and occasionally observed in the SRFA+I+NaClO sample. The very high mass accuracy (< 0.5 ppm) in combination with ultrahigh resolution of the FT-ICR MS allowed us to assign exact molecular formulas for the newly formed I-DBPs. In total, molecular formulas of 178 peaks containing one iodine, 13 peaks containing two iodine and 15 peaks containing one chlorine and one iodine were identified in the SRFA+I+NH₂Cl sample, while only 9 peaks containing one iodine and 6 peaks containing one chlorine and one iodine were identified in the SRFA+I+NaClO sample. All of the iodine-containing formulas detected in the SRFA+I+NaClO sample were also found in the SRFA+I+NH₂Cl sample.

Recently, Ding and Zhang (2009) have developed the precursor ion scan (PIS) method using electrospray ionization-triple quadrupole mass spectrometry (ESI-tqMS) for fast selective detection of polar/highly polar iodinated DBPs, and characterized 17 polar/highly polar I-DBPs in chloraminated simulated drinking water. Only 3 formulas of I-DBPs identified in this study were also found in the study by Ding and Zhang (2009). The other 203 formulas of I-DBPs are for the first time reported.

3.2. Pattern of I-DBPs

Molecular formulas of I-DBPs can be analyzed using Kendrick plot with z* value, in which homologous series of molecules could be easily identified. The z* (Eq. (1)) value has been shown to be a useful parameter for presorting homologous series of fulvic acids (Hsu et al., 1992; Stenson et al., 2003; Reemtsma and These, 2005). In Eq. (1), the modulus is the remainder of the division of nominal mass (NM) by 14. Presorting based on z* ensures that molecules assigned to the same homologous series (differing only in the number of \(\text{CH}_2\) groups) differ from each other in mass by 14 Da, because molecules that differ from each other by multiples of 14 will have the same \(z^*\) value. Fig. 2 shows the Kendrick plot of formulas of I-DBPs detected in the SRFA+I+NH₂Cl sample. Similar to previous findings for Cl-DBPs and Br-DBPs, the iodine-containing formulas can be sorted out into homologous series, suggesting they may arise from homologous series of parent NOM components.

\[
z^* = \text{modulus}([\text{NM}]/14) - 14
\]  

(1)

The van Krevelen diagram is another widely used tool for visualizing FT-ICR MS data (van Krevelen, 1950; Schmidt et al., 2009; Ohno et al., 2010). In a van Krevelen diagram, individual molecular formulas are plotted based on their elemental ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C). The specific H/C and O/C ratios for each molecular formula align and fall at a certain point on the diagram, allowing evaluation of relative hydrogen deficiency or oxygen deficiency of the molecular formulas. Fig. 3 shows the van Krevelen diagram of the I-DBPs detected in the SRFA+I+NH₂Cl sample. The H/C ratios of these iodinated DBPs were lower than 1.2. The relatively low H/C ratios suggest relatively high degree of unsaturation and the presence of aromatic structures in the molecules of I-DBPs. A modified aromaticity index (\(A_{\text{mod}}\)), which is a suitable parameter for the identification of aromatic and polycyclic structures in NOM from ultra-high resolution mass spectrometry data, was calculated from the molecular formulas according to Koch and Dittmar (2006) to estimate the fraction of aromatic

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Table 1

| Sample name                  | Components                                      | Disinfection          | SPE     |
|------------------------------|-------------------------------------------------|-----------------------|---------|
| SRFA control                 | 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃, and 200 μg/L potassium iodide as I⁻ | Not applied           |         |
| SRFA+NaClO                   | 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃            | Chlorination          | Applied |
| SRFA+NH₄Cl                   | 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃            | Chlorination          | Applied |
| SRFA+I+NaClO                 | 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃, and 200 μg/L potassium iodide as I⁻ | Chlorination          | Applied |
| SRFA+I+NH₄Cl                 | 3.0 mg/L SRFA as C, 90.0 mg/L NaHCO₃, and 200 μg/L potassium iodide as I⁻ | Chlorination          | Applied |
Fig. 1. Negative-ion ESI FT-ICR mass spectra for iodine-containing products at nominal mass 403. (a) SRFA control sample, (b) SRFA+NaClO sample, (c) SRFA+NH2Cl sample, (d) SRFA+I+NaClO sample, and (e) SRFA+I+NH2Cl sample.

Fig. 2. Kendrick mass defect analysis with \( z^* \) of one iodine-containing formulas in SRFA+I+NH2Cl sample.

Fig. 3. van Krevelen diagram of iodine-containing formulas identified in SRFA+I+NH2Cl sample.
(0.5 < AImod < 0.67) and polycyclic aromatic structures (0.67 ≤ AImod). The AImod was calculated according to Eq. (2), in which nC, nO, nH, nCl and nI are the numbers of carbon, oxygen, hydrogen, chlorine, and iodine atoms in the molecular formula. Among the 206 I-DBPs detected in the C18 extracts, 96 of them (~47%) have aromatic structures and 44 of them (~21%) have polycyclic aromatic structures. Recent studies have demonstrated that aromatic I-DBPs are an important category of I-DBPs in chloramination-disinfected water (Pan et al., 2016a; Pan et al., 2016b; Gong et al., 2016). More importantly, recent evidence has shown that aromatic I-DBPs generally are substantially more developmentally toxic than aliphatic I-DBPs (Pan et al., 2016a). Thus more attention should be paid to the aromatic I-DBPs, which might form during chloramination of iodide containing source water.

\[ A_{\text{mod}} = \frac{1 + nC - 0.5 \times nO - 0.5 \times nH - 0.5 \times nCl - 0.5 \times nI}{nC - 0.5 \times nO} \]  

(2)

### 3.3. Comparison of patterns of I-DBPs with those of Cl-DBPs

Previous study has shown that most polar Br-DBPs formed during chlorination have corresponding chlorine-containing analogues, which have identical CHO compositions (Zhang et al., 2014). In this study, all 206 I-DBPs identified in the SRFA+I+NH2Cl sample were compared to the chlorinated components identified in the same sample and the SRFA+NH2Cl sample. In total, 380 formulas of one chlorine-containing components, 112 formulas of two chlorine-containing components, and 5 formulas of three chlorine-containing components were identified in the SRFA+I+NH2Cl sample, while a little more chlorine-containing components were identified in the SRFA+I+NaClO sample, where 451 formulas of one-chlorine-containing components, 167 formulas of two-chlorine-containing components, and 50 formulas of three-chlorine-containing components were identified (Table 2). Among the 178 one-iodine-containing DBPs, 158 of them have corresponding one-chlorine-containing analogues. Three of the 13 two-iodine-containing DBPs have corresponding two-chlorine-containing analogues. 

Among the 138 carbon numbers of Cl-DBPs range from 8 to 23. It is interesting to note that, compared to CI-DBPs, I-DBPs have a cluster in an area with a relatively low H/C value (0.4–1.2). In addition, the carbon numbers of I-DBPs range from 7 to 18, while the carbon numbers of CI-DBPs range from 8 to 23. It is interesting to note that, compared to CI-DBPs, I-DBPs have a cluster in the upper left of the plot with relatively high AImod (0.35–0.8). This finding suggested that precursor molecules with high aromaticity might prefer to form I-DBPs.

### 3.4. Comparison of DBPs patterns in chlorination/chloramination

Previous studies have shown that both chlorine and chloramine can oxidize I⁻ rapidly to HOI, which can react with NOM to form I-DBPs. During chlorination, HOCl/OCI⁻ can further oxidize HOI to IO₃⁻, which is stable and unreactive toward NOM, with a reaction rate constant of 8.2–52 M⁻¹ s⁻¹ (Bichsel and von Gunten, 1999). The reaction rate constant of monochloramine and HOI is smaller than that of HOCl, which can react with NOM to form iodine containing DBPs. During chloramination, HOCl/OCI⁻ can further oxidize HOI to IO₃⁻, which is stable and unreactive toward NOM, with a reaction rate constant of 8.2–52 M⁻¹ s⁻¹ (Bichsel and von Gunten, 1999). The reaction rate constant of IO₃⁻ with NOM is much smaller than that of HOI. This means that the half-life of HOI during chloramination is much longer than that during chlorination, resulting in the formation of more I-DBPs during chloramination than during chlorination (Bichsel and von Gunten, 2000; Kraser et al., 2006; Hua and Reckhow, 2007; Ding and Zhang, 2009). Chloramination has been frequently used as alternative to chlorination to reduce the formation of regulated THMs and HAAs. The above results demonstrated that chloramination may not be a good choice for treating iodide containing source water.

Although I-DBPs were mainly observed in chloramination samples, lots of CI-DBPs were found in both chloramination and chlorination samples. Table 2 shows number of DBPs identified in chlorination and chloramination samples. In total, 451 formulas of one-chlorine-containing components, 167 formulas of three-chlorine-containing components and 50 formulas of four-chlorine-containing components were identified in the SRFA+I+NaClO sample. 673 formulas of one-chlorine-containing components, 488 formulas of two-chlorine-containing components, 186

### Table 2

| Sample                  | Number of DBPs | 1Cl | 2Cl | 3Cl | 4Cl | 11 | 21 | 1Cl+11 |
|------------------------|----------------|-----|-----|-----|-----|----|----|--------|
| SRFA+NaClO             | 673            | 488 | 186 | 70  | 0   | 0  | 0   |
| SRFA+NH₂Cl             | 438            | 156 | 3   | 0   | 0   | 0  | 0   |
| SRFA+I+NaClO           | 646            | 451 | 167 | 50  | 0   | 9  | 0   |
| SRFA+I+NH₂Cl           | 380            | 112 | 5   | 178 | 13  | 15 |

Fig. 4. van Krevelen diagram (a) and AImod against carbon number plot (b) of iodine-containing formulas identified in the SRFA+I+NH₂Cl sample and chlorine-containing formulas identified in the SRFA+NH₂Cl sample.
formulas of three chlorine-containing components and 70 formulas of four chlorine-containing components were identified in the SRFA+NaClO sample. When comparing the formulas of Cl-DBPs found in the SRFA+NH2Cl sample and the SRFA+NaClO sample, it was found that 99% of the formulas with one chlorine and 100% of the formulas with two or three chlorine found in the SRFA+NH2Cl sample were also detected in the SRFA+NaClO sample. A similar overlap in formulas of Cl-DBPs was also observed between the SRFA+I+NH2Cl sample and the SRFA+I+NaClO sample (99% for one chlorine containing formulas and 100% for two or three chlorine containing formulas found in SRFA+I+NH2Cl sample).

4. Conclusions

In this study, 206 formulas of previously unknown polar I-DBPs were identified in chlorinated/chloraminated simulated drinking water. Species of I-DBP formed during chloramination (206 formulas) were much more than that formed during chlorination (15 formulas). More than 68% of the 206 formulas of I-DBPs detected in the C18 extracts have aromatic structures or polycyclic aromatic structures, indicating precursor molecules with high aromaticity might be more reactive and preferential to form I-DBPs during chloramination of iodide-containing water. The results reported here provide valuable information on occurrence of I-DBPs and may help us in minimizing and controlling I-DBPs during drinking water disinfection.

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Appendix A. Supplementary data

All assigned formulas for I-DBPs and Cl-DBPs are available in a spreadsheet file in the supplementary data. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2016.02.157.

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