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 (AI_{mod}), 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

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of abundant species of I-DBPs in the presence of iodide. Thus, the suitability of adopting chloramination as an alternative disinfection method should be reevaluated, particularly when iodide is present in raw water.

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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; Cemeli 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 (TOCl). 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, bromiodoacetic 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., 1998; Bichsel and von Gunten, 1999, 2000; Hua and Reckhow, 2007; Ding and Zhang, 2009). It was found that chloramination favors the formation of I-DBPs because chloramines can oxidize I^- to HOI but without formation of iodate (IO_3^-), which is an inert and non-toxic form of iodine (Bichsel and von Gunten, 1999, 2000). However, partially due to lack of appropriate analytical method for I-DBPs, most of these studies use iodine containing trihalomethanes (I-THMs) or the group parameter, total organic iodine (TOI) as the representative of the whole pool of I-DBPs. Considering the potential health effect of I-DBPs are directly depending on their molecule structures, it is necessary to extensively characterize and compare the molecular species of I-DBPs formed with different disinfectants.

To date, only a few I-DBPs have been identified by gas chromatography/mass spectrometry (GC/MS) (Richardson et al., 2007; Plewa et al., 2008; Richardson et al., 2008). However, recent studies have shown that a significant portion of unknown halogen containing DBPs would be polar/highly polar (Zhang et al., 2008; Ding and Zhang, 2009; Zhang et al., 2012a; Zhang et al., 2014). Ding and Zhang (2009) have successfully identified 17 polar/highly polar I-DBPs using the precursor ion scan (PIS) method via electrospray ionization-triple quadrupole mass spectrometry (ESI-tqMS). However, the unit mass resolution of tqMS is still too low to allow nominally isobaric ions to be mass-resolved and may bias the compositional interpretation of I-DBPs. Recently, ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been successfully used to characterize the previously unknown Cl-DBPs and Br-DBPs (Zhang et al., 2012a;

Zhang et al., 2012b; Lavonen et al., 2013; Zhang et al., 2014). The ultra-high resolution and mass accuracy of FT-ICR MS combined with electrospray ionization (ESI) allows the determination of unambiguous and exact molecular formulas (Stenson 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 (99%) 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 $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ 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 NaHCO_3 , 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 Cl_2 . For chloramination, 1-L water samples were chloraminated in sealed 1-L amber glass bottles with 5.0 mg/L monochloramine (as Cl_2). 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 $\text{Na}_2\text{S}_2\text{O}_3$.

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 C_{18} 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

Table 1
Simulated drinking water sample composition and treatment applied.

Sample name	Components	Disinfection	SPE
SRFA control	3.0 mg/L SRFA as C, 90.0 mg/L NaHCO ₃ , and 200 µg/L potassium iodide as I [−]	Not applied	Applied
SRFA+NaClO	3.0 mg/L SRFA as C, 90.0 mg/L NaHCO ₃	Chlorination	Applied
SRFA+NH ₂ Cl	3.0 mg/L SRFA as C, 90.0 mg/L NaHCO ₃	Chloramination	Applied
SRFA+I+NaClO	3.0 mg/L SRFA as C, 90.0 mg/L NaHCO ₃ , and 200 µg/L potassium iodide as I [−]	Chlorination	Applied
SRFA+I+NH ₂ Cl	3.0 mg/L SRFA as C, 90.0 mg/L NaHCO ₃ , and 200 µg/L potassium iodide as I [−]	Chloramination	Applied

conditioned with methanol and acidified ultrapure water. For complete removal of inorganic ions, the cartridge was rinsed with 10 mL 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 negative ion mode electrospray ionization (ESI[−]). Sample extract was dissolved in methanol and injected into the electrospray source at 3 µL/min using a syringe pump. The operating conditions for ESI[−] consisted of a 4.0 kV emitter voltage, 4.5 kV capillary column introduce voltage, and −320 V capillary column end voltage. The mass range was set to m/z 150–800. The data size was set to 4 M words, and 256 scans were acquired for each spectrum.

The FT-ICR mass spectrometer was externally calibrated for a 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: ¹²C_{0–100}, ¹³C_{0–2}, ¹H_{0–200}, ¹⁴N_{0–3}, ¹⁶O_{0–30}, ³²S_{0–2}, ³⁵Cl_{0–4}, ³⁷Cl_{0–2} and ¹²⁷I_{0–2} atoms. 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 C₁₈ 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 C₁₈ 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 CH₂ 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.

$$z^* = (\text{modulus}[\text{NM}/14]) - 14 \quad (1)$$

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 (AI_{mod}), which is a suitable parameter for the identification of aromatic and polycyclic structures in NOM from ultrahigh resolution mass spectrometry data, was calculated from the molecular formulas according to Koch and Dittmar (2006) to estimate the fraction of aromatic

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.

($0.5 < AI_{\text{mod}} < 0.67$) and polycyclic aromatic structures ($0.67 \leq AI_{\text{mod}}$). The AI_{mod} 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 chloramine-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.

$$AI_{\text{mod}} = \frac{1 + nC - 0.5 \times nO - 0.5 \times nH - 0.5 \times nCl - 0.5 \times nI}{nC - 0.5 \times nO} \quad (2)$$

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+NH₂Cl sample (438 formulas of one chlorine-containing components, 156 formulas of two chlorine-containing components, and 3 formulas of three-chlorine-containing components) (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. Fig. 4a shows the van Krevelen diagram of I-DBPs and the Cl-DBPs identified in the chloramination samples. Compared to the Cl-DBPs, the I-DBPs cluster in an area with a relatively low H/C value (0.4–1.2). In addition, compared to the I-DBPs, 144 of the Cl-DBPs (29%) have aromatic structures and 65 of the Cl-DBPs (13%) have polycyclic aromatic structures. Fig. 4b compares I-DBPs and Cl-DBPs using the carbon number against AI_{mod} plot. The carbon numbers of I-DBPs range from 7 to 18, while the carbon numbers of Cl-DBPs range from 8 to 23. It is interesting that, compared to Cl-DBPs, I-DBPs cluster in the upper left of the plot with relatively high AI_{mod} (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, but the half-life of HOI during chloramination is much longer than that during chlorination, leading to the formation of more I-DBPs during chloramination (Bichsel and von Gunten, 2000; Krasner et al., 2006; Hua and Reckhow, 2007). In this study the number and peak intensities of I-DBPs in the SRFA+I+NH₂Cl sample were

Fig. 4. van Krevelen diagram (a) and AI_{mod} 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.

significantly greater than those in the SRFA+I+NaClO sample. Compared to 206 I-DBPs detected in the SRFA+I+NH₂Cl sample, only 15 I-DBPs were found in the SRFA+I+NaClO sample. Both chlorine and monochloramine can oxidize I[−] to HOI, which can react with NOM to form I-DBPs. During chlorination, HOCl/OCl[−] can further oxidize HOI to IO₃[−], which is stable and unreactive toward NOM, with a reaction rate constant of $8.2\text{--}52 \text{ M}^{-1} \text{ s}^{-1}$ (Bichsel and von Gunten, 1999). The reaction rate constant of monochloramine and HOI is smaller than $2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (Bichsel and von Gunten, 1999), whereas the reaction rate constant of HOI and NOM is $0.1\text{--}0.4 \text{ M}^{-1} \text{ s}^{-1}$ (Bichsel and von Gunten, 2000). 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; Krasner 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 the 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 sample, lots of Cl-DBPs were found in both chloramination and chlorination samples. Table 2 shows number of DBPs identified in chlorination and chloramination samples. In total, 646 formulas of one-chlorine-containing components, 451 formulas of two-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
Number of DBPs detected in different samples.

Sample	Number of DBPs						
	1Cl	2Cl	3Cl	4Cl	1I	2I	1Cl+1I
SRFA+NaClO	673	488	186	70	0	0	0
SRFA+NH ₂ Cl	438	156	3	0	0	0	0
SRFA+I+NaClO	646	451	167	50	9	0	6
SRFA+I+NH ₂ Cl	380	112	5	0	178	13	15

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>.

References

- Bichsel, Y., von Gunten, U., 1999. Oxidation of iodide and hypiodous acid in the disinfection of natural waters. *Environ. Sci. Technol.* 33 (22), 4040–4045.
- Bichsel, Y., von Gunten, U., 2000. Formation of iodo-trihalomethanes during disinfection and oxidation of iodide containing waters. *Environ. Sci. Technol.* 34 (13), 2784–2791.
- Cemeli, E., Wagner, E.D., Anderson, D., Richardson, S.D., Plewa, M.J., 2006. Modulation of the cytotoxicity and genotoxicity of the drinking water disinfection byproduct iodoacetic acid by suppressors of oxidative stress. *Environ. Sci. Technol.* 40 (6), 1878–1883.
- Ding, G., Zhang, X., 2009. A picture of polar iodinated disinfection byproducts in drinking water by (UPLC/ESI-tqMS). *Environ. Sci. Technol.* 43 (24), 9287–9293.
- Gong, T., Zhang, X., Li, Y., Xian, Q., 2016. Formation and toxicity of halogenated disinfection byproducts resulting from linear alkylbenzene sulfonates. *Chemosphere* 149, 70–75.
- Hertkorn, N., Frommberger, M., Witt, M., Koch, B.P., Schmitt-Kopplin, Ph., Perdue, E.M., 2008. Natural organic matter and the event horizon of mass spectrometry. *Anal. Chem.* 80 (23), 8908–8919.
- Hsu, C.S., Qian, K., Chen, Y.C., 1992. An innovative approach to data analysis in hydrocarbon characterization by on-line liquid chromatography-mass spectrometry. *Anal. Chim. Acta* 264 (1), 79–89.
- Hua, G., Reckhow, D.A., 2007. Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water Res.* 41 (8), 1667–1678.
- Karpel Vel Leitner, N., Vessella, J., Dore, M., Legube, B., 1998. Chlorination and formation of organoiodinated compounds: the important role of ammonia. *Environ. Sci. Technol.* 32 (11), 1680–1685.
- Kim, S., Rodgers, R.P., Marshall, A.G., 2006a. Truly “exact” mass: elemental composition can be determined uniquely from molecular mass measurement at similar to 0.1 mDa accuracy for molecules up to similar to 500 Da. *Int. J. Mass Spectrom.* 251 (2–3), 260–265.
- Kim, S., Kaplan, L.A., Hatcher, P.G., 2006b. Biodegradable dissolved organic matter in a temperate and a tropical stream determined from ultra-high resolution mass spectrometry. *Limnol. Oceanogr.* 51 (2), 1054–1063.
- Koch, B.P., Dittmar, T., 2006. From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Commun. Mass Spectrom.* 20 (5), 926–932.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scimenti, M.J., Onstad, G.D., Thruston Jr., A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40 (23), 7175–7185.
- Lavonen, E.E., Gonsior, M., Tranvik, L.J., Schmitt-Kopplin, P., Koehler, S.J., 2013. Selective chlorination of natural organic matter: identification of previously unknown disinfection byproducts. *Environ. Sci. Technol.* 47 (5), 2264–2271.
- Liu, J., Zhang, X., 2014. Comparative toxicity of new halophenolic DBPs in chlorinated saline wastewater effluents against a marine alga: halophenolic DBPs are generally more toxic than haloaliphatic ones. *Water Res.* 65, 64–72.
- Ohno, T., He, Z., Sleighter, R., Honeycutt, C.W., Hatcher, P.G., 2010. Ultra high resolution mass spectrometry and indicator species analysis to identify marker components of soil- and plant biomass-derived organic matter fractions. *Environ. Sci. Technol.* 44 (22), 8594–8600.
- Pan, Y., Li, W., An, H., Cui, H., Wang, Y., 2016a. Formation and occurrence of new polar iodinated disinfection byproducts in drinking water. *Chemosphere* 144, 2312–2320.
- Pan, Y., Zhang, X., Li, Y., 2016b. Identification, toxicity and control of iodinated disinfection byproducts in cooking with simulated chlor(am)inated tap water and iodized table salt. *Water Res.* 88, 60–68.
- Plewa, M.J., Wagner, E.D., Richardson, S.D., Thruston Jr., A.D., Woo, Y.T., Mckague, A.B., 2004. Chemical and biological characterization of newly discovered iodoacid drinking water disinfection byproducts. *Environ. Sci. Technol.* 38 (18), 4713–4722.
- Plewa, M.J., Muellner, M.G., Richardson, S.D., Fasano, F., Buettner, K.M., Woo, Y.T., Mckague, A.B., Wagner, E.D., 2008. Occurrence, synthesis, and mammalian cell cytotoxicity and genotoxicity of haloacetamides: an emerging class of nitrogenous drinking water disinfection byproducts. *Environ. Sci. Technol.* 42 (3), 955–961.
- Reemtsma, T., These, A., 2005. Comparative investigation of low-molecular-weight fulvic acids of different origin by SEC-Q-TOF-MS: new insights into structure and formation. *Environ. Sci. Technol.* 39 (10), 3507–3512.
- Richardson, S.D., Ellington, J.J., Crumley, F.G., Evans, J.J., Plewa, M.J., Wagner, E.D., 2006. Occurrence of iodo-acid DBPs in US chloraminated drinking waters. *Abstr. Pap. Am. Chem. Soc.* 231 (33-ENVR).
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection byproducts in drinking water: a review and roadmap for research. *Mutat. Res.* 636 (1–3), 178–242.
- Richardson, S.D., Fasano, F., Ellington, J.J., Crumley, F.G., Buettner, K.M., Evans, J.J., Blount, B.C., Silva, L.K., Waite, T.J., Luther, G.W., Mckague, A.B., Miltner, R.J., Wagner, E.D., Plewa, M.J., 2008. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ. Sci. Technol.* 42 (22), 8330–8338.
- Schmidt, F., Elvert, M., Koch, B.P., Witt, M., Hinrichs, K., 2009. Molecular characterization of dissolved organic matter in pore water of continental shelf sediments. *Geochim. Cosmochim. Acta* 73 (11), 3337–3358.
- Stenson, A.C., Marshall, A.G., Cooper, W.T., 2003. Exact masses and chemical formulas of individual Suwannee river fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra. *Anal. Chem.* 75 (6), 1275–1284.
- van Krevelen, D.W., 1950. Graphical statistical method for the study of structure and reaction processes of coal. *Fuel* 19, 269–284.
- Yang, M., Zhang, X., 2013. Comparative developmental toxicity of new aromatic halogenated DBPs in a chlorinated saline sewage effluent to the marine polychaete *Platynereis dumerilii*. *Environ. Sci. Technol.* 47 (19), 10868–10876.
- Yang, Y., Komaki, Y., Kimura, S.Y., Hu, H., Wagner, E.D., Marinas, B.J., Plewa, M.J., 2014. Toxic impact of bromide and iodide on drinking water disinfected with chlorine or chloramines. *Environ. Sci. Technol.* 48 (20), 12362–12369.
- Zhang, X.R., Talley, J.W., Boggess, B., Ding, G.Y., Birdsell, D., 2008. Fast selective detection of polar brominated disinfection byproducts in drinking water using precursor ion scans. *Environ. Sci. Technol.* 42 (17), 6598–6603.
- Zhang, H., Zhang, Y., Shi, Q., Hu, J., Chu, M., Yu, J., Yang, M., 2012a. Study on transformation of natural organic matter in source water during chlorination and its chlorinated products using ultrahigh resolution mass spectrometry. *Environ. Sci. Technol.* 46 (8), 4396–4402.
- Zhang, H., Zhang, Y., Shi, Q., Ren, S., Yu, J., Ji, F., Luo, W., Yang, M., 2012b. Characterization of low molecular weight dissolved natural organic matter along the treatment trait of a waterworks using Fourier transform ion cyclotron resonance mass spectrometry. *Water Res.* 46 (16), 5197–5204.
- Zhang, H., Zhang, Y., Shi, Q., Zheng, H., Yang, M., 2014. Characterization of unknown brominated disinfection byproducts during chlorination using ultrahigh resolution mass spectrometry. *Environ. Sci. Technol.* 48 (6), 4396–4402.