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Formation of several classes of emerging disinfection by-products in disinfected waters

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Abstract

The present work presents the potential of different source waters to form several classes of emerging disinfection byproducts (DBPs), i.e., haloacetaldehydes and iodine-containing DBPs, which have been scarcely investigated to date. To study this, laboratory controlled chlorination and chloramination reactions were performed with different source waters (in terms of natural organic matter and bromide and iodide content). As expected, the formation of iodo-DBPs (iodo-trihalomethanes, iodo-haloacetic acids, and iodoacetaldehyde) was enhanced in the presence of monochloramine. Overall, iodo-trihalomethanes were the iodo-DBPs that contributed most to total iodo-DBP concentrations. Dihaloacetaldehydes were the main haloacetaldehydes formed under both chlorination and chloramination treatments.

Keywords: iodinated disinfection byproducts, chlorination, chloramination, drinking water, mass spectrometry

1. Introduction

Several classes of halogenated disinfection by-products (DBPs) other than the regulated trihalomethanes (THMs) and haloacetic acids (HAAs) may form during water disinfection treatments. In terms of abundance, halogenated acetaldehydes (HALs) have been reported as the third most abundant halogenated DBP class (in mass) in several studies, after THMs and HAAs. In terms of toxicity, iodine containing DBPs (iodo-DBPs) and nitrogen containing halogenated DBPs, have been reported to be more toxic than regulated DBPs, despite the fact that they are usually formed at comparatively lower concentrations (Richardson *et al.* 2008). However, both aspects (occurrence and toxicity) have been scarcely investigated for many of these emerging DBPs. In this context, the main objective of the present work was to further investigate the formation of several classes of emerging DBPs during chlorination and chloramination of different source waters at lab-scale under controlled conditions.

2. Materials and methods

DBP mixtures were generated after chlorine and chloramine-based disinfection of different source waters (in terms of natural organic matter (NOM) and bromide and iodide content) under controlled conditions. All disinfection reactions were performed at laboratory scale, at a pH value, temperature, and disinfectant doses typically used at water treatment plants. Two different synthetic water matrices were prepared using NOM of the Suwannee River and the Nordic Lake and different bromide and iodide contents. Water from the Llobregat River was also used in the reactions. Different emerging DBPs, i.e., iodo-DBPs and haloacetaldehydes (mono-halogenated and di-halogenated species), were investigated in the DBP mixtures generated by means of gas chromatography-tandem mass spectrometry (GC-MS) using a 7890A GC system connected to a 7000B GC/MS Triple Quad, and a 7683B Series injector (Agilent Technologies). A methyl-tert-butyl ether (MTBE) –based liquid-liquid extraction (LLE) method was used to extract iodo-THMs (iodoform, chloro-diiodomethane, bromo-diiodomethane, chloro-bromo-iodomethane, dichloro-iodomethane, dibromo-iodomethane) and iodo-HAAs (diiodoacetic acid, iodoacetic acid, chloro-iodoacetic acid, bromo-iodoacetic acid) from the generated DBP mixtures (following Duirk *et al.* recommendations (Duirk *et al.* 2011)). The analysis of iodo-HAAs required the derivatization (methylation with diazomethane) of the MTBE extract. The extraction of selected HALs (chloroacetaldehyde, dichloroacetaldehyde, bromochloroacetaldehyde, dibromoacetaldehyde, bromoacetaldehyde, iodoacetaldehyde) was performed following a developed and validated analytical method published elsewhere (Jeong *et al.* 2015), after derivatization of the analytes with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and subsequent liquid-liquid extraction of the oximes formed with hexane. Chromatographic separation was performed with a Zebron ZB-5 capillary column (30 m, 0.25 mm ID, 0.25 µm film thickness, Phenomenex, Torrance, CA) and a temperature gradient. MS determination was performed in the selected ion monitoring mode (SIM). Quantification was performed by the internal standard method.

3. Results and discussion

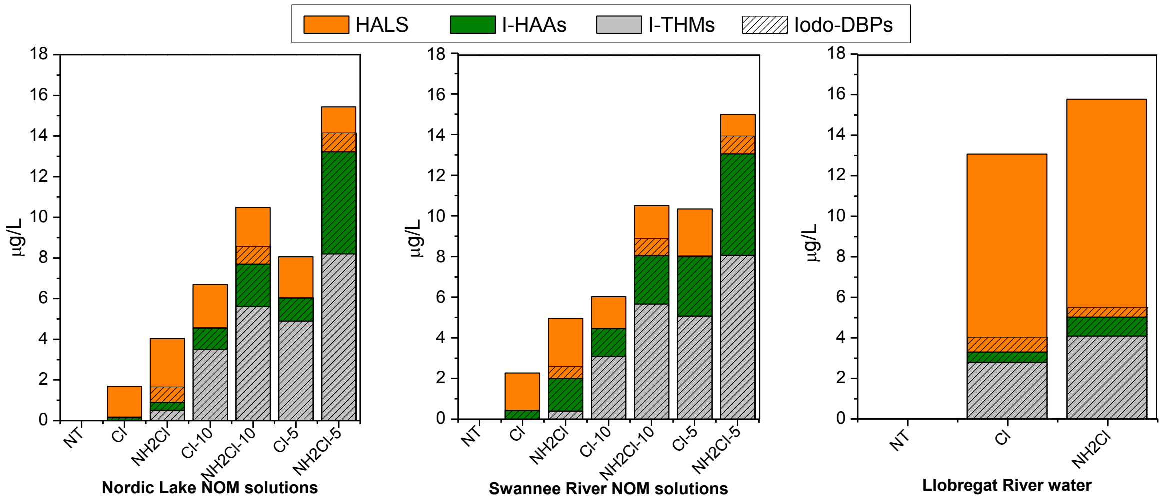

Figure 1. Potential of the different tested solutions to form the selected emerging DBP classes after chlorination (Cl) and chloramination (NH2Cl) treatments (NT: not treated, 10: water containing 500 μg/L of Br^- and 50 μg/L of I^-, and 5: water containing 500 μg/L of Br^- and 100 μg/L of I^-)

Concentrations of the selected DBPs formed in the investigated DBP mixtures are shown in Figure 1. As it can be observed, and as it could be expected as well, the formation of iodo-DBPs was enhanced during monochloramine-based disinfection and at increasing concentrations of iodine in the water. Total iodo-DBP levels were between 1.4 (Llobregat River water) and 11 (Nordic Lake NOM solutions with no iodide or bromide added) times higher in chloraminated than in chlorinated DBP mixtures. Whereas I-THMs and I-HAAs were also formed during water chlorination, IAL was only formed after water chloramination. The formation pattern of the selected DBPs was very similar in Nordic Lake and Suwannee River NOM solutions and differed from that observed in Llobregat river waters. This could be explained by the different characteristics of the water matrices tested. On the one hand, NOM of the Nordic Lake and Suwannee River solutions seems to be less aromatic than that present in Llobregat River water (SUVA254 values were 1.5, 1.8 and 4.3 L/mg-M in Nordic Lake NOM solutions, Suwannee River NOM solutions and Llobregat River water, respectively). Thus, in the light of the results, and previous reports (Jones *et al* 2012, Liu *et al* 2017), I-HAAs and I-THMs are preferentially formed after disinfectant reaction with less aromatic NOM fractions. On the other hand, the Br^-/I^- concentration ratio is higher and the I^-/DOC ratio is lower in the Llobregat river water than in bromine and iodine-spiked Suwannee River and Nordic Lake NOM solutions (44 vs 2.7-12.6 for Br^-/I^-, and 2.6 vs. 9.2-20.4 for I^-/DOC), and these factors may rule bromine and iodine incorporation in the NOM and therefore, the formation of bromine and iodine containing DBPs [4]. The obtained data indicate that iodo-DBP formation is enhanced in waters with low Br^-/I^- and high I^-/DOC concentration ratios. However, iodoacetaldehyde formation seemed not to be affected by these parameters. Iodo-THMs and iodo-HAAs contributed almost equally to total iodo-DBP concentrations in the chlorinated DBP mixtures, whereas iodo-THMs were the main iodo-DBP class in terms of abundance in chloraminated DBP mixtures.

4. Conclusions

As expected, the iodo-DBP formation was enhanced during monochloramine-based disinfection of water (Richardson *et al*. 2008). In agreement with previous publications, the formation of iodo-THMs and iodo-HAAs was also enhanced during disinfection of waters with low aromatic NOM fractions. As for monohalo- and dihaloacetaldehydes, their formation was increased after disinfection of waters with high aromatic NOM fractions. Research at full-scale drinking water treatment plants is required to validate the lab-scale observations on the formation of these emerging DBPs. **Acknowledgements**

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