Formation of iodo-trihalomethanes, iodo-haloacetic acids, and haloacetaldehydes during chlorination and chloramination of iodine containing waters in laboratory controlled reactions

Cristina Postigo[1,*], Susan D. Richardson[2], Damia Barceló[1,3]

1. Water and Soil Quality Research Group, Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain
2. Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States
3. Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, 17003 Girona, Spain

ARTICLE INFO

ABSTRACT

Iodine containing disinfection by-products (I-DBPs) and haloacetaldehydes (HALs) are emerging disinfection by-product (DBP) classes of concern. The former due to its increased potential toxicity and the latter because it was found to be the third most relevant DBP class in mass in a U.S. nationwide drinking water study. These DBP classes have been scarcely investigated, and this work was performed to further explore their formation in drinking water under chlorination and chloramination scenarios. In order to do this, iodo-trihalomethanes (I-THMs), iodo-haloacetic acids (I-HAAs) and selected HALs (mono-HALs and di-HALs species, including iodoacetaldehyde) were investigated in DBP mixtures generated after chlorination and chloramination of different water matrices containing different levels of bromide and iodide in laboratory controlled reactions. Results confirmed the enhancement of I-DBP formation in the presence of monochloramine. While I-THMs and I-HAAs contributed almost equally to total I-DBP concentrations in chlorinated water, I-THMs contributed the most to total I-DBP levels in the case of chloraminated water. The most abundant and common I-THM species generated were bromochloroiodomethane, dichloroiodomethane, and chlorodiiodomethane. Iodoacetic acid and chloroiodoacetic acid contributed the most to the total I-HAA concentrations measured in the investigated disinfected water. As for the studied HALs, dihalogenated species were the compounds that predominantly formed under both investigated treatments.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

It is well established that the nature and quantity of the disinfection by-products (DBPs) formed during water disinfection processes are related to the disinfecting agent applied and the conditions under which the disinfection process is carried out (e.g., pH, temperature, and disinfectant dose and contact time). Other factors playing a relevant role in DBP formation are the organic (e.g., natural organic matter (NOM) and anthropogenic organic pollutants) and inorganic precursors (e.g., bromide (Br⁻) and iodide (I⁻)) present in the source water to be disinfected (Hua and Reckhow, 2007; Krasner, 2009; Jones et al., 2011; Shah and Mitch, 2012).

Research on the formation of iodine containing disinfection by-products (I-DBPs) in disinfected waters has recently become a new matter of scientific concern, since these compounds have

* Corresponding author. E-mail: cprqam@cid.csic.es (Cristina Postigo).

been reported to be more toxic than their corresponding brominated and chlorinated analogues (Richardson et al., 2007, 2008a; Plewa et al., 2008, 2010; Attene-Ramos et al., 2010; Pals et al., 2011; Wei et al., 2013a; Yang et al., 2014; Richardson and Postigo, 2015; Jeong et al., 2016). This DBP class forms after disinfection of source waters that contain I^- or different iodine sources, such as X-ray contrast media (Duirk et al., 2011; Wang et al., 2014; Wendel et al., 2014, 2016; Ye et al., 2014) and microbially derived organic matter (Wei et al., 2013b). I-DBPs also form during iodine-based disinfection of drinking water and wastewater (Smith et al., 2010; Hladik et al., 2016). According to peer-reviewed studies, the higher I^- content of the source water, the higher the potential of the water to generate I-DBPs (Hua et al., 2006; Richardson et al., 2008a; Zhang et al., 2015), particularly during chloramine-based disinfection treatments (Richardson and Postigo, 2015). While many I-DBP classes have been reported to date in treated drinking water or wastewaters, i.e., iodo-trihalomethanes (I-THMs), iodo-acids (Cancho et al., 2000; Plewa et al., 2004; Krasner et al., 2006; Richardson et al., 2008a; Pan et al., 2016), iodo-amides (Plewa et al., 2008; Chu et al., 2012), iodo-phenols (Richardson et al., 2008b; Vikesland et al., 2013; Yang and Zhang, 2013; Pan et al., 2016), iodo-benzene sulfonic acids (Gong and Zhang, 2015), and iodoacetaldehyde (IAL) (Jeong et al., 2015), most of the research done in this area was mainly focused on I-THMs. This can be explained by the lack of analytical standards, that were commercially available for many compounds only recently, and the lack of analytical methods with sufficient sensitivity for their detection in disinfected water.

Halogenated aldehydes (HALs) were reported as the third largest DBP class by weight in a U.S. Nationwide DBP Occurrence Study (Weinberg et al., 2002; Krasner et al., 2006). This DBP class exerts higher cytotoxicity to mammalian cells than regulated trihalomethanes and haloacetic acids (Jeong et al., 2015). The formation and occurrence of the whole spectrum of mono-HALs, di-HALs, and tri-HALs in disinfected waters, including iodine containing species, has been scarcely investigated (Jeong et al., 2015). Peer-reviewed DBP occurrence studies including HALs considered only a mixture of di-HALs and tri-HALs as target compounds (Koudjonou and LeBel, 2006; Krasner et al., 2006, 2008, 2009; Serrano et al., 2011; Mao et al., 2016), and in most cases, chloral hydrate was the only HAL investigated, as it is the only HAL included in the list of chlorinated DBPs to be analyzed in drinking water using U.S. EPA Method 551 (US EPA, 1995). Moreover, the formation of IAL during chloramination of source water containing iodide was recently reported (Jeong et al., 2015) and it has not been further investigated.

In this context, the present study aimed at further exploring the formation of I-DBPs, including I-THMs, iodo-haloacetic acids (I-HAAs), and IAL in chlorinated and chloraminated waters with different NOM type and iodide and bromide content. In order to do this, DBP mixtures generated in lab-scale controlled disinfection reactions carried out at conditions similar to those commonly used at drinking water treatment plants were chemically characterized by gas chromatography–mass spectrometry (GC–MS). Furthermore, mono-HALs and di-HALs were also investigated in the DBP mixtures generated, in order to increase the knowledge on the formation of HALs during disinfection treatments.

1. Experimental

1.1. Chemicals and reagents

DBP standards for target analysis were purchased from Sigma-Aldrich (Barcelona, Spain), Can Syn Chem. Corp (Toronto, ON), Aldlab Chemicals (Woburn, MA), and TCI America (Waltham, MA) (see the list of the target analytes and further details in Appendix A, Table S1). All reagents and reactants used, unless otherwise specified, were purchased from Sigma-Aldrich. The list of solvents used includes Chromasolv® grade methanol ($\geq$99.9%, MeOH), methyl-*tert*-butyl ether ($\geq$99.8%, MTBE), and hexane ($\geq$99.8%, HEX). The pH of the disinfection reactions was buffered with potassium phosphate dibasic trihydrate ($K_2HPO_4 \cdot 3H_2O$) and potassium phosphate monobasic (KH_2PO_4) ($\geq$98%). Anhydrous Na_2SO_4 was used to dry the DBP extracts. Sulfuric acid (95–97%, H_2SO_4), hydrochloric acid ($\geq$37%, HCl), and sodium hydroxide ($\geq$98%, NaOH, pellets) used to modify/adjust the pH of the solutions were ACS grade.

Reverse osmosis-isolated NOM from Nordic Lake (NL) (Skarnes, Norway) and Suwannee River (SR) (Georgia, USA) was purchased from the International Humic Substances Society (IHSS) (St. Paul; MN, USA). Purified water (18 MΩ/cm) from an Aurum ultrapure water system (Sartorius, Madrid, Spain) was used to prepare all reagent solutions and to dissolve the tested NOM.

Free chlorine solutions ($HOCl/OCl^-$) were obtained after proper dilution of a sodium hypochlorite (NaOCl) solution (10%, *w/v* reagent grade) (Panreac, Barcelona, Spain). Free chlorine was combined with ammonium chloride (NH_4Cl) to produce monochloramine (NH_2Cl) solutions. Chlorine and NH_2Cl concentrations of the prepared dosing solutions and disinfected waters were measured by means of the N,N-diethyl-p-phenylene diamine–ferrous ammonium sulfate (DPD–FAS) titration method (Greenberg, 1985). Reagents purchased for this measurement were: barium diphenylamine-4 sulfonate for redox titration, potassium dichromate (>99%, $Cr_2K_2O_7$), ethylenediaminetetraacetic acid disodium salt dihydrate (99–101%, EDTA), DPD salt (>98%), ammonium iron (II) sulfate hexahydrate (99%), ortho-phosphoric acid (85%, H_3PO_4), and sodium phosphate dibasic (99%, Na_2HPO_4).

1.2. Disinfection reactions

Chlorination and chloramination reactions were performed in a headspace-free Pyrex® glass reaction vessel at room temperature (22–26°C) in the dark, under continuous stirring using a magnetic stir plate and a polytetrafluoroethylene (PTFE)-coated stir bar. The reaction time was set to 72 ± 1 hr. All disinfection reactions were carried out at a pH value 7.5 using 10 mmol/L of phosphate buffer, and either H_2SO_4 or NaOH (1 mol/L) to adjust the solution pH.

DBP mixtures were generated from NL and SR solutions prepared at a concentration of 5 mg/L of NOM isolate, that were also fortified with 500 μg/L of bromide (as KBr) and two different levels of iodide (as KI), i.e., 50 and 100 μg/L, in order to promote the formation of iodinated and brominated DBPs. These bromide and iodide levels were reported to occur in source water used for drinking water production (Cancho et al., 2000; Weinberg et al., 2002; Krasner et al., 2006; Richardson et al., 2008a; Duirk et al., 2011).

Disinfection reactions were also performed with surface water from the Llobregat River (Barcelona, Spain). This river is heavily impacted along its course by the effluents of industrial and municipal wastewater treatment plants and contains high concentrations of bromide (Br⁻) and iodide (I⁻) that originate from salt mine discharges in its upper stretch. Median concentrations of 932 μg/L of Br⁻ and 2.67 μg/L of I⁻ were measured in the river's lower stretch (Fernandez-Turiel et al., 2003). The Llobregat River water used in the experiments was collected near the intake of a drinking water treatment plant that serves part of Barcelona and its metropolitan area. All water was collected at once in amber glass bottles from the midpoint of the river, and stored in the dark in a cold room (4°C) until use.

Characteristics of the source waters used in the reactions are shown in Table 1.

The chlorine/monochloramine dose, i.e., 4 mg/L for NL NOM solutions, 5 mg/L for SR NOM solutions and 7.5 mg/L for Llobregat river water, was selected according to the specific chlorine demand of each source water that resulted in ca. 0.5 mg/L of residual chlorine at the end of the disinfection reaction. Monochloramine reactions were carried out with the addition of preformed NH_2Cl freshly prepared at a 0.7 Cl/N molar ratio.

1.3. DBP measurements

I-THMs and I-HAAs were extracted from the water by means of liquid–liquid extraction (LLE) with MTBE and analyzed using GC–MS, following the analytical protocols used by Duirk et al. (2011) and Richardson et al. (2008a). One-half of the LLE extract was used to determine I-THMs by means of GC–electron ionization (EI)–MS; and one-half was further derivatized with diazomethane (see details in Appendix A) to enable detection of I-HAAs (through their corresponding methyl esters) by GC-negative chemical ionization (NCI)–MS.

Mono-HALs and di-HALs measurements were carried out by means of O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) derivatization, and subsequent LLE with HEX as described in Jeong et al. (2015)).

Further details on the analytical instrumentation used and the analytical protocols followed are provided in Appendix A (Sections II, III and IV).

1.4. Total organic carbon (TOC), SUVA (specific UV absorbance), bromide, and iodide measurements

TOC measurements were carried out by means of a Shimadzu TOC-V$_{CSH}$ analyzer (Shimadzu Europa GmbH, Duisburg, Germany). Ultraviolet (UV) absorbance at 254 nm to calculate SUVA was measured with an Agilent 8453 UV–visible spectrophotometer. Bromide measurements were carried out by means of ion chromatography. Iodide, approximated by total iodine content, was measured with inductively coupled plasma (ICP)–mass spectrometry (MS). Average values of TOC, SUVA, bromide and total iodine in the source waters used for the experiments are summarized in Table 1.

1.5. Quality assurance (QA)/quality control (QC)

The blanks performed and analyzed were (a) purified water that followed the same sample extraction protocols used for iodo-THMs, iodo-acids, and HALs, (b) the source water, i.e., NL NOM solution, SR NOM solution and Llobregat River water, with no disinfectant, (c) purified water treated with chlorine and monochloramine, and (d) purified water fortified with 500 μg/L of Br⁻ and 100 μg/L of I⁻ treated with chlorine and monochloramine. These blanks were performed to discard potential origin of DBPs from artifacts or source water contaminants.

2. Results and discussion

2.1. Formation of I-DBPs in disinfected iodine containing waters

Trace concentrations (below the method reporting limits, MRLs) of the I-THMs, dibromoiodomethane (DBIM) and chlorodiiodomethane (CDIM), and the I-HAAs, iodoacetic acid (IAA) and chloroiodoacetic acid (CIAA), were only found in the blank that consisted of purified water with 500 μg/L of Br⁻ and 100 μg/L of I⁻ treated with monochloramine (Appendix A Tables S2 and S3). Concentrations of I-THMs and I-HAAs measured in the disinfected water samples are summarized in Fig. 1 and in Appendix A Table S5.

Overall, and as expected, the formation of the target iodine containing DBPs was enhanced after monochloramine disinfection and at increasing I⁻ concentrations of the source waters. Chloramination was previously shown to preferentially form I-DBPs compared to chlorine because, unlike monochloramine, chlorine rapidly oxidizes hypoiodous acid to iodate, which serves as a sink for iodide. In the presence of chloramine, hypoiodoius acid reacts with NOM to form I-DBPs, which act as a sink for iodide (Bichsel and Von Gunten, 2000).

In this regard, total concentrations of I-THMs found in chloraminated water (up to 8.2 μg/L) were between 1.5–18 times higher than those measured in chlorinated water. This wide range is explained by the different iodide concentrations

Table 1 – Characteristics of the source water matrices tested.					
Source water	Abbrev.	TOC (mg/L)	SUVA$_{254}$ (L/mg-M)	Bromide (μg/L)	Total iodine[*] (μg/L)
Suwannee River (n = 3)	SR	5.4 ± 0.5	1.8 ± 0.1	<10	2.2 ± 0.2
Nordic Lake (n = 3)	NL	4.9 ± 0.9	1.5 ± 0.2	<10	1.8 ± 0.9[*]
Llobregat River (n = 3)	LLOB	6.8 ± 0.7	4.3 ± 0.2[*]	788 ± 83	17.7 ± 0.7

Method limits of quantification (LOQs): total organic carbon (TOC) – 0.05 mg/L, bromide – 10 μg/L, total iodine– 1 μg/L.
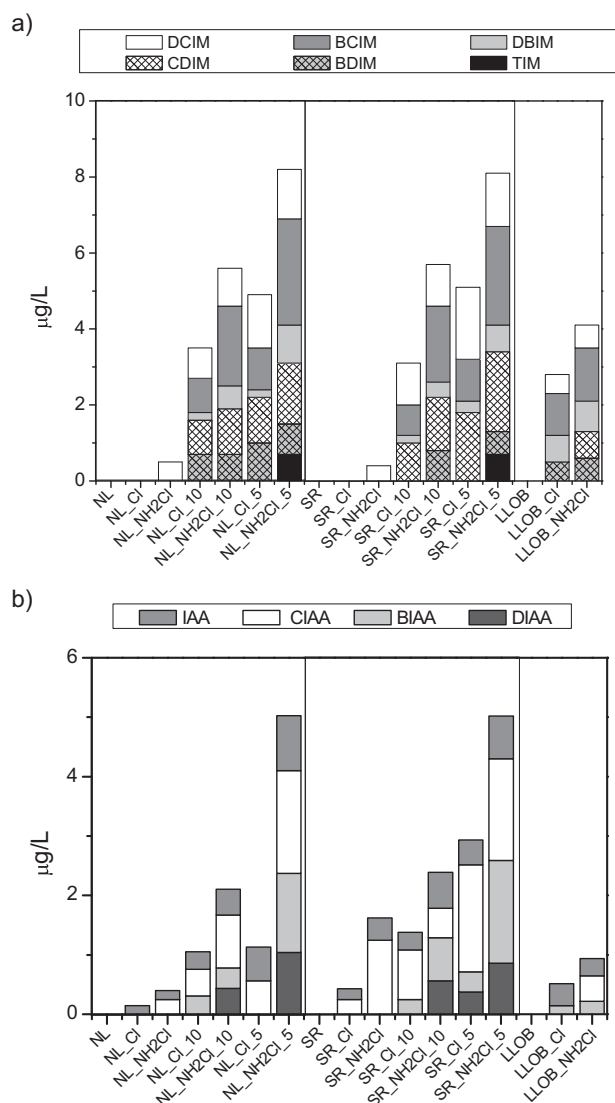[*] n = 2.

a)

b)

Fig. 1 – Concentrations of (a) iodo-trihalomethanes (I-THMs) and (b) iodo-haloacetic acids (I-HAAs) in the tested waters after chlorination (CL) and chloramination (NH₂Cl) reactions (NL: Nordic Lake NOM solutions, SR: Suwannee River NOM solutions, LLOB: Llobregat River water; NL, SR, NL_Cl, SR_Cl, NL_NH₂Cl, SR_NH₂Cl, LLOB_Cl, and LLOB_NH₂Cl: ambient source water conditions (no addition of Br⁻ or I⁻); NL_Cl_10, SR_Cl_10, NL_NH₂Cl_10, SR_NH₂Cl_10: addition of 500 μg/L of Br⁻ and 50 μg/L of I⁻ (ratio of 10:1), and NL_Cl_5, SR_Cl_5, NL_NH₂Cl_5, SR_NH₂Cl_5: addition of 500 μg/L of Br⁻ and 100 μg/L of I⁻ (ratio of 5:1)).

of the water matrices tested. In the case of I-HAAs, total concentrations measured in chloraminated water reached up to 5.0 μg/L and were between 1.7 and 4.4 times higher than in chlorinated water. IAL was formed in all tested waters treated with chloramine at concentrations ranging between 0.5 and 0.9 μg/L. Furthermore, IAL was also generated after chlorination of LLOB water at a concentration of 0.7 μg/L.

The formation pattern of I-DBPs, i.e., total amount and species formed during the investigated disinfection treatments, was very similar in NL NOM and SR NOM solutions. However, a completely different I-DBP formation pattern was

found during disinfection of LLOB water. This could be attributed to the characteristics of the NOM, and the Br⁻ and I⁻ content of each source water matrix evaluated (shown in Table 1). NOM of the tested aqueous matrices was evaluated by means of SUVA₂₅₄ measurements. According to these measurements, NOMs present in NL and SR solutions were very similar (1.5 and 1.8 L/mg-M, respectively); and less aromatic than NOM present in LLOB water. In the light of the results, I-THMs and I-HAAs were preferentially generated by less aromatic NOM fractions, as it was reported elsewhere for I-THMs (Jones et al., 2012; Liu et al., 2017).

The incorporation of bromine and iodine into the different NOMs tested and consequently, the formation of Br- and I-DBPs during water disinfection, is also impacted by the Br⁻ and I⁻ levels present in the source water, as previously reported by several authors (Richardson et al., 2008a; Jones et al., 2012; Allard et al., 2015). In addition to I⁻ concentration in water, other factors like I⁻/DOC and Br⁻/I⁻ concentration ratios are also relevant to I-DBP formation and speciation (Jones et al., 2012). In the present study, the Br⁻/I⁻ concentration ratio in the LLOB river sample (44) was at least 3.5 times higher than that of iodine-spiked SR and NL NOM solutions (2.7–12.6), and the I⁻/DOC ratio in the LLOB water (2.6) was lower than that of iodine-spiked SR and NL NOM solutions (9.2–20.4). According to the amount and type of DBPs detected after disinfection of the tested matrices, the formation of I-THM and I-HAA was enhanced in water with low Br⁻/I⁻ and high I⁻/DOC concentration ratios, as shown in Fig. 2.

Despite the similarity of I-DBP levels formed in SR NOM and NL NOM solutions, some differences were observed. These can be summarized in the formation of bromodiiodomethane (BDIM) (0.7–1 μg/L) during chlorination of Br⁻ and I⁻ fortified NL NOM solutions, and the overall formation of lower levels of I-HAAs in NL NOM solutions (1.6 μg/L on average) than in SR NOM solutions (2.3 μg/L on average). These differences could be attributed to differences in these NOMs chemical structure, despite their similar SUVA values.

Fig. 3 shows the contribution of each iodinated DBP to total I-DBP concentrations in the disinfected waters. Considering the investigated I-DBPs, I-THMs and I-HAAs contributed on average almost equally to the total concentration of I-DBPs formed during chlorination, being responsible for 52% and 46%, respectively, of the total I-DBP concentrations measured. The exclusive detection of I-HAAs in NL_Cl and SR_Cl (see Fig. 3) is explained by the different sensitivities of the analytical methodologies used for the analysis of these DBP classes, lower for I-HAAs than for I-THMs (Appendix A Tables S2 and S3). I-THMs were found on average to be the most relevant I-DBP class in terms of abundance (55% of total I-DBP concentrations) in chloraminated DBP mixtures, followed by I-HAAs (34%) and IAL (15%).

2.2. I-THM and I-HAA speciation

The most abundant I-THMs were bromochloroiodomethane (BCIM), dichloroiodomethane (DCIM) and CDIM, with average concentrations above 1 μg/L in the investigated disinfected water. These were also the I-THMs usually found in drinking water plant effluents and distribution networks (Richardson et al., 2008a; Ioannou et al., 2016). Trace levels of DCIM were
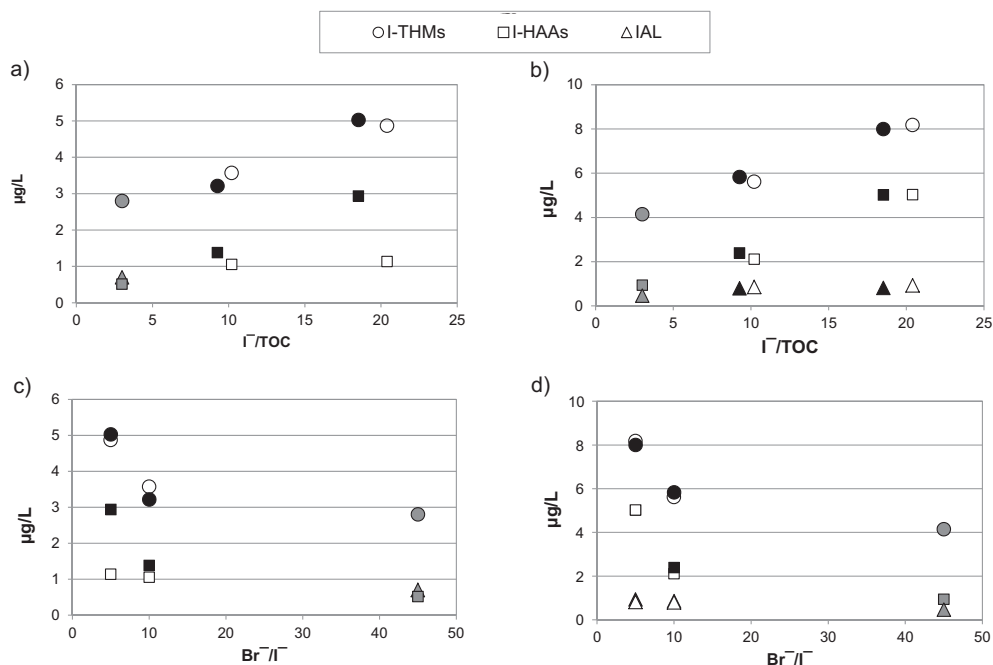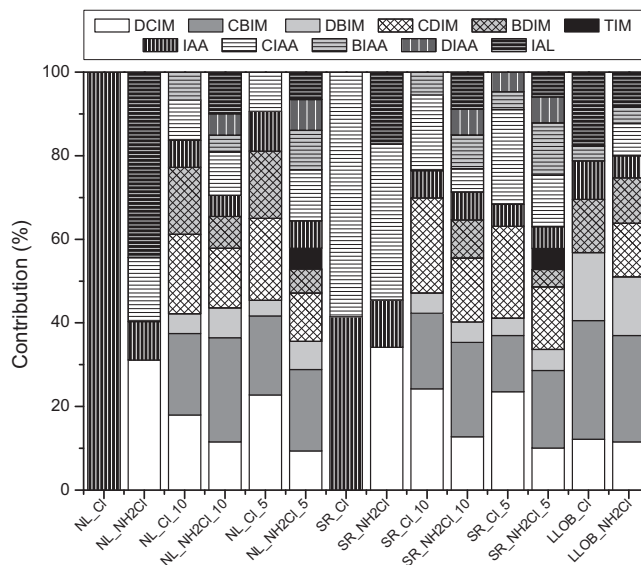
Fig. 2 – Total concentration of I-THMs, I-HAAs and iodoacetaldehyde (IAL) as a function of Br^-/I^- and I^-/total organic carbon (TOC) ratios in chlorinated (a) and (c) and chloraminated water samples (b) and (d). (Gray: LLOB waters, black: SR NOM solutions and white: NL NOM solutions).

	DCIM	BCIM	DBIM	CDIM	BDIM	TIM	IAA	CIAA	BIAA	DIAA	IAL
HOCl/OCl$^-$	14.4	14.1	4.8	11.9	6.4	0.0	25.5	16.9	2.8	0.7	2.5
NH$_2$Cl	17.2	15.9	5.4	9.8	5.4	1.4	7.0	14.4	5.4	3.6	14.5

Fig. 3 – Contribution (in %) of each iodine containing disinfection by-products (I-DBP) to the total I-DBP concentration measured in the investigated chlorinated (Cl) and chloraminated (NH$_2$Cl) samples, and average contribution observed in each treatment (0 was used in the calculation of average values shown in the table when a specific DBP was not present) NL: Nordic Lake NOM solutions, SR: Suwannee River NOM solutions, LLOB: Llobregat River water; NL, SR, NL_Cl, SR_Cl, NL_NH$_2$Cl, SR_NH$_2$Cl, LLOB_Cl, and LLOB_NH$_2$Cl: ambient source water conditions (no addition of Br^- or I^-); NL_Cl_10, SR_Cl_10, NL_NH$_2$Cl_10, SR_NH$_2$Cl_10: addition of 500 μg/L of Br^- and 50 μg/L of I^- (ratio of 10:1), and NL_Cl_5, SR_Cl_5, NL_NH$_2$Cl_5, SR_NH$_2$Cl_5: addition of 500 μg/L of Br^- and 100 μg/L of I^- (ratio of 5:1)).

found in the original NL (0.5 μg/L) and SR solutions (1.1 μg/L), i.e., with no Br^- or I^- added, after chloramination treatment, which can be attributed to the low total iodine levels originally present in these NOM matrices. This may indicate that this is the I-THM most easily formed in waters with low Br^- and I^- content.

Low concentrations of iodoform (TIM) (0.7 μg/L) were only detected in chloraminated NL and SR NOM solutions containing high I^- levels (100 μg/L). TIM was reported to be the main I-THM species formed during chloramination of water fortified with I^- at levels much higher (200 μg/L and 12.7 mg/L) than those used in the present study and higher than those usually present in surface waters (Liu et al., 2017). However, in a US nationwide DBP occurrence study, TIM was only occasionally detected (0.3–2 μg/L) in the drinking water distribution systems of three water treatment plants after both chlorination and chloramination disinfection (Weinberg et al., 2002).

I-HAAs were formed at lower concentrations compared to I-THMs. The most abundant I-HAA was CIAA, detected in 86% of the disinfected water samples, with an average concentration of 0.9 μg/L. Lower levels of IAA were formed (0.4 μg/L on average) in all disinfected waters under both chlorination and chloramination treatments. Diiodoacetic acid (DIAA) was generated during chloramination of all NL and SR NOM solutions fortified with Br^- and I^- (0.4–1 μg/L) and during chlorination of SR NOM containing 100 μg/L of I^- (0.4 μg/L). Similar to DIAA, the brominated species bromoiodoacetic acid (BIAA) was below the method limit of detection in the chlorinated NL NOM solution containing 100 μg/L of I^-, whereas 0.3 μg/L of BIAA was found in SR NOM solution containing equivalent I^- levels. From the limited dataset in the present study, this can be attributed to a different composition of the NOM in NL solutions compared to SR solutions that affects the incorporation of Br^- and I^- into the NOM. In any case, higher concentrations of DIAA and BIAA were observed in water samples with higher I^- content. IAA, BIAA and DIAA were found to form at levels usually below 0.1 μg/L in drinking water plants using monochloramine as disinfectant, even when I^- was present at low concentrations in the source water (Richardson et al., 2008a). The occurrence of CIAA in drinking water distribution systems has been scarcely investigated to date.

2.3. Formation of chlorine- and bromine-containing mono-HALs and di-HALs in the DBP mixtures generated

A residual concentration (<MRL, Appendix A Table S4) of dichloroacetaldehyde (DCAL) was found in the blank consisting of SR NOM solution with no disinfectant added. Concentrations of mono-HALs and di-HALs measured in the DBP mixtures generated are shown in Fig. 4 and in Table S5 as SI. Overall, di-HALs, i.e., DCAL, dibromoacetaldehyde (DBAL), and bromochloroacetaldehyde (BCAL), contributed the most to the total concentrations of mono-HALs and di-HALs measured. Contrary to what was observed with I-DBPs, disinfected LLOB water presented higher total concentrations of mono-HALs and di-HALs compared to NL NOM and SR NOM solutions, which suggests that they were preferentially generated by aromatic NOM fractions (as indicated by SUVA values, see Table 1). Furthermore, the formation of bromine containing di-HAL species (DBAL and BCAL) was enhanced in LLOB water, which is likely driven by the high natural
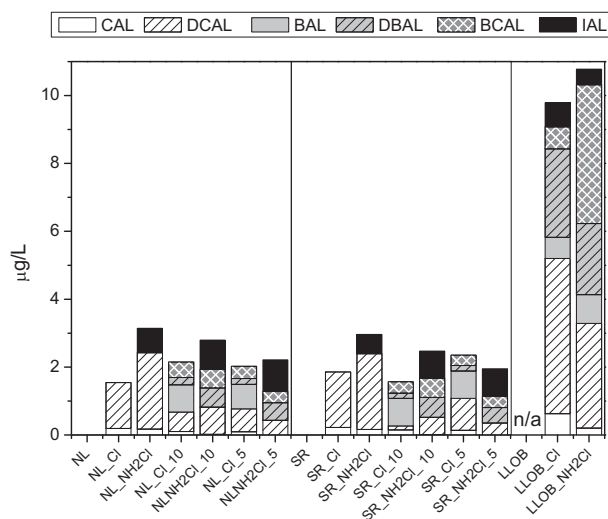

Fig. 4 – Concentrations of mono-haloacetaldehydes (HALs) and di-HALs in the tested waters after chlorination (Cl) and chloramination (NH_2Cl) reactions (NL: Nordic Lake NOM solutions, SR: Suwannee River NOM solutions, LLOB: Llobregat River water; NL, SR, NL_Cl, SR_Cl, NL_NH_2Cl, SR_NH_2Cl, LLOB_Cl, and LLOB_NH_2Cl: ambient source water conditions (no addition of Br^- or I^-); NL_Cl_10, SR_Cl_10, NL_NH_2Cl_10, SR_NH_2Cl_10: addition of 500 μg/L of Br^- and 50 μg/L of I^- (ratio of 10:1), and NL_Cl_5, SR_Cl_5, NL_NH_2Cl_5, SR_NH_2Cl_5: addition of 500 μg/L of Br^- and 100 μg/L of I^- (ratio of 5:1); n/a: sample not available for HAL analysis).

concentrations of Br^- present in this source water. In fact, bromine containing species were formed in NL and SR NOM solutions that were fortified with Br^-. The main difference observed between chlorination and chloramination treatment was the enhancement of IAL formation and the inhibition of chloroacetaldehyde (CAL) formation when monochloramine was used as the disinfectant (and when I^- is present in the waters). Moreover, the results showed an increased formation of BCAL and BAL in waters with a high Br^-/I^- concentration ratio in the presence of monochloramine and chlorine, respectively. At the bromide and iodide concentrations tested, the Br^-/I^- and the I^-/DOC concentration ratios did not significantly affect the formation of IAL (see Fig. 2).

3. Conclusions

Once again, this work proved that chloramination is a disinfection treatment that enhances the formation of iodine containing DBPs in drinking waters. NOM characteristics were also a determinant parameter that affected the formation of the investigated emerging DBP classes. The limited dataset suggests that I-THMs and I-HAAs were preferentially generated in waters with a lower aromatic NOM content, whereas mono-HALs and di-HALs were more likely produced by aromatic NOM fractions. As expected, the presence of Br^- and I^- in the water enhanced the formation of bromine and iodine containing species. Since DBP formation was directly linked to the organic and inorganic DBP precursors that were present in the source water, an in-depth characterization of

the treated source water is required to draw further conclusions. Despite the fact that these experiments were performed at environmental Br$^-$ and I$^-$ levels, further research at full-scale drinking water treatment plants using different disinfection treatments should be performed to fully assess the formation of these emerging DBP classes of concern.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.04.009.

REFERENCES

Allard, S., Tan, J., Joll, C.A., Von Gunten, U., 2015. Mechanistic study on the formation of Cl-/Br-/I-trihalomethanes during chlorination/chloramination combined with a theoretical cytotoxicity evaluation. Environ. Sci. Technol. 49, 11105–11114.

Attene-Ramos, M.S., Wagner, E.D., Plewa, M.J., 2010. Comparative human cell toxicogenomic analysis of monohaloacetic acid drinking water disinfection byproducts. Environ. Sci. Technol. 44, 7206–7212.

Bichsel, Y., Von Gunten, U., 2000. Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters. Environ. Sci. Technol. 34, 2784–2791.

Cancho, B., Ventura, F., Galceran, M., Diaz, A., Ricart, S., 2000. Determination, synthesis and survey of iodated trihalomethanes in water treatment processes. Water Res. 34, 3380–3390.

Chu, W., Gao, N., Yin, D., Krasner, S.W., Templeton, M.R., 2012. Trace determination of 13 haloacetamides in drinking water using liquid chromatography triple quadrupole mass spectrometry with atmospheric pressure chemical ionization. J. Chromatogr. A 1235, 178–181.

Duirk, S.E., Lindell, C., Cornelison, C.C., Kormos, J., Ternes, T.A., Attene-Ramos, M., Osiol, J., Wagner, E.D., Plewa, M.J., Richardson, S.D., 2011. Formation of toxic iodinated disinfection by-products from compounds used in medical imaging. Environ. Sci. Technol. 45, 6845–6854.

Fernandez-Turiel, J.L., Gimeno, D., Rodriguez, J.J., Carnicero, M., F., V., 2003. Spatial and seasonal variations of water quality in a Mediterranean catchment: the Llobregat River (NE Spain). Environ. Geochem. Health 25, 453–474.

Gong, T., Zhang, X., 2015. Detection, identification and formation of new iodinated disinfection byproducts in chlorinated saline wastewater effluents. Water Res. 68, 77–86.

4500-Cl F. DPD ferrous titrimetric method. In: Greenberg, A. (Ed.), Standard Methods for the Examination of Water and Wastewater, 16th ed. American Public Health Association, Washington, DC, pp. 306–309.

Hladik, M.L., Hubbard, L.E., Kolpin, D.W., Focazio, M.J., 2016. Dairy-impacted wastewater is a source of iodinated disinfection byproducts in the environment. Environ. Sci. Technol. Lett. 3, 190–193.

Hua, G., Reckhow, D.A., 2007. Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. Water Res. 41, 1667–1678.

Hua, G., Reckhow, D.A., Kim, J., 2006. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. Environ. Sci. Technol. 40, 3050–3056.

Ioannou, P., Charisiadis, P., Andra, S.S., Makris, K.C., 2016. Occurrence and variability of iodinated trihalomethanes concentrations within two drinking-water distribution networks. Sci. Total Environ. 543, 505–513.

Jeong, C., Postigo, S., Richardson, J., Simmons, S., Kimura, B., Mariñas, D., Barcelo, P., Liang, E., Wagner, M., Plewa, 2015. Occurrence and comparative toxicity of haloacetaldehyde disinfection byproducts in drinking water. Environ. Sci. Technol. 49, 13749–13759.

Jeong, C.H., Gao, L., Dettro, T., Wagner, E.D., Ricke, W.A., Plewa, M.J., Flaws, J.A., 2016. Monohaloacetic acid drinking water disinfection by-products inhibit follicle growth and steroidogenesis in mouse ovarian antral follicles in vitro. Reprod. Toxicol. 62, 71–76.

Jones, D.B., Saglam, A., Triger, A., Song, H., Karanfil, T., 2011. I-THM formation and speciation: Preformed monochloramine versus prechlorination followed by ammonia addition. Environ. Sci. Technol. 45, 10429–10437.

Jones, D.B., Saglam, A., Song, H., Karanfil, T., 2012. The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation. Water Res. 46, 11–20.

Koudjonou, B.K., LeBel, G.L., 2006. Halogenated acetaldehydes: Analysis, stability and fate in drinking water. Chemosphere 64, 795–802.

Krasner, S.W., 2009. The formation and control of emerging disinfection by-products of health concern. Phil. Trans. R. Soc. A 367, 4077–4095.

Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Sclimenti, M.J., Onstad, G.D., Thruston Jr., A.D., 2006. The occurrence of a new generation of disinfection by-products. Environ. Sci. Technol. 40, 7175–7185.

Krasner, S.W., Lee, C.F.T., Chinn, R., Hartono, S., Weinberg, H., Richardson, S.D., Pressman, J.G., Speth, T.F., Miltner, R.J., Simmon, J.E., 2008. Bromine incorporation in regulated and emerging DBPs and the relative predominance of mono-, di-, and trihalogenated DBPs. Proceedings of Water Quality Technology Conference and Exposition 2008, Cincinnati, OH, pp. 1692–1708.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E., Amy, G., 2009. Occurrence of disinfection byproducts in United States wastewater treatment plant effluents. Environ. Sci. Technol. 43, 8320–8325.

Liu, S., Li, Z., Dong, H., Goodman, B.A., Qiang, Z., 2017. Formation of iodo-trihalomethanes, iodo-acetic acids, and iodo-acetamides during chloramination of iodide-containing waters: Factors influencing formation and reaction pathways. J. Hazard. Mater. 321, 28–36.

Mao, Y.Q., Wang, X.M., Guo, X.F., Yang, H.W., Xie, Y.F., 2016. Characterization of haloacetaldehyde and trihalomethane formation potentials during drinking water treatment. Chemosphere 159, 378–384.

Pals, J., Ang, J., Wagner, E.D., Plewa, M.J., 2011. Biological mechanism for the toxicity of haloacetic acid drinking water disinfection byproducts. Environ. Sci. Technol. 45, 5791–5797.

Pan, Y., Li, W., An, H., Cui, H., Wang, Y., 2016. Formation and occurrence of new polar iodinated disinfection byproducts in drinking water. Chemosphere 144, 2312–2320.

Plewa, M.J., Wagner, E.D., Richardson, S.D., Thruston, 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, 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 by-products. Environ. Sci. Technol. 42, 955–961.

Plewa, M.J., Simmons, J.E., Richardson, S.D., Wagner, E.D., 2010. Mammalian cell cytotoxicity and genotoxicity of the haloacetic acids, a major class of drinking water disinfection by-products. Environ. Mol. Mutagen. 51, 871–878.

Richardson, S.D., Postigo, C., 2015. Formation of DBPs: State of the science. In: Karanfil, T., Bill, M., Paul, W., Yuefeng, X. (Eds.), Recent Advances in Disinfection By-products, pp. 189–214.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutat. Res. 636, 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., 2008a. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. Environ. Sci. Technol. 42, 8330–8338.

Richardson, S.D., Thruston Jr., A.D., Krasner, S.W., Weinberg, H.S., Miltner, R.J., Schenck, K.M., Narotsky, M.G., McKague, A.B., Simmons, J.E., 2008b. Integrated disinfection by-products mixtures research: Comprehensive characterization of water concentrates prepared from chlorinated and ozonated/postchlorinated drinking water. J. Toxicol. Environ. Health 71, 1165–1186.

Serrano, M., Silva, M., Gallego, M., 2011. Micro liquid–liquid extraction combined with large-volume injection gas chromatography–mass spectrometry for the determination of haloacetaldehydes in treated water. J. Chromatogr. A 1218, 8295–8302.

Shah, A.D., Mitch, W.A., 2012. Halonitroalkanes, halonitriles, haloamides, and N-nitrosamines: A critical review of nitrogenous disinfection byproduct formation pathways. Environ. Sci. Technol. 46, 119–131.

Smith, E.M., Plewa, M.J., Lindell, C.L., Richardson, S.D., Mitch, W.A., 2010. Comparison of byproduct formation in waters treated with chlorine and iodine: Relevance to point-of-use treatment. Environ. Sci. Technol. 44, 8446–8452.

U.S. EPA, 1995. "Method 551.1: Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection," Revision 1.0 (Available at: goo.gl/erUPQj. Accessed September 2016).

Vikesland, P.J., Fiss, E.M., Wigginton, K.R., McNeill, K., Arnold, W.A., 2013. Halogenation of bisphenol-A, triclosan, and phenols in chlorinated waters containing iodide. Environ. Sci. Technol. 47, 6764–6772.

Wang, Z., Xu, B., Lin, Y.L., Hu, C.Y., Tian, F.X., Zhang, T.Y., Gao, N.Y., 2014. A comparison of iodinated trihalomethane formation from iodide and iopamidol in the presence of organic precursors during monochloramination. Chem. Eng. J. 257, 292–298.

Wei, X., Wang, S., Zheng, W., Wang, X., Liu, X., Jiang, S., Pi, J., Zheng, Y., He, G., Qu, W., 2013a. Drinking water disinfection byproduct iodoacetic acid induces tumorigenic transformation of NIH3T3 cells. Environ. Sci. Technol. 47, 5913–5920.

Wei, Y., Liu, Y., Ma, L., Wang, H., Fan, J., Liu, X., Dai, R.H., 2013b. Speciation and formation of iodinated trihalomethane from microbially derived organic matter during the biological treatment of micro-polluted source water. Chemosphere 92, 1529–1535.

Weinberg, H.S., Krasner, S.W., Richardson, S.D., Thruston Jr., A.D., 2002. The Occurrence of Disinfection By-products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study; EPA/600/R02/068. U.S. Environmental Protection Agency National Exposure Research Laboratory, Athens, GA, pp. 1–460.

Wendel, F.M., Lütke Eversloh, C., Machek, E.J., Duirk, S.E., Plewa, M.J., Richardson, S.D., Ternes, T.A., 2014. Transformation of iopamidol during chlorination. Environ. Sci. Technol. 48, 12689–12697.

Wendel, F.M., Ternes, T.A., Richardson, S.D., Duirk, S.E., Pals, J.A., Wagner, E.D., Plewa, M.J., 2016. Comparative toxicity of high-molecular weight iopamidol disinfection byproducts. Environ. Sci. Technol. 3, 81–84.

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, 10868–10876.

Yang, Y., Komaki, Y., Kimura, S.Y., Hu, H.Y., Wagner, E.D., Mariñas, B.J., Plewa, M.J., 2014. Toxic impact of bromide and iodide on drinking water disinfected with chlorine or chloramines. Environ. Sci. Technol. 48, 12362–12369.

Ye, T., Xu, B., Wang, Z., Zhang, T.Y., Hu, C.Y., Lin, L., Xia, S.J., Gao, N.Y., 2014. Comparison of iodinated trihalomethanes formation during aqueous chlor(am)ination of different iodinated X-ray contrast media compounds in the presence of natural organic matter. Water Res. 66, 390–398.

Zhang, T.Y., Xu, B., Hu, C.Y., Lin, Y.L., Lin, L., Ye, T., Tian, F.X., 2015. A comparison of iodinated trihalomethane formation from chlorine, chlorine dioxide and potassium permanganate oxidation processes. Water Res. 68, 394–403.