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

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Abstract

Iodine containing disinfection byproducts (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.

Keywords: iodinated disinfection byproducts, chlorination, chloramination, drinking water, mass spectrometry, iodo-trihalomethanes, iodo-haloacetic acids, haloacetaldehydes

1. 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 et al. 2007; Krasner 2009; Jones et al. 2011; Shah et al. 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 been reported to be more toxic than their corresponding brominated and chlorinated analogues (Richardson et al. 2007; Plewa et al. 2008; Richardson et al. 2008a; Attene-Ramos et al. 2010; Plewa et al. 2010; Pals et al. 2011; Wei et al. 2013a; Yang et al. 2014; Richardson et al. 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; Ye et al. 2014; Wendel et al. 2016) 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 et al. 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 et al. 2013; Pan et al. 2016), iodo-benzene sulfonic acids (Gong et al. 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 et al. 2006; Krasner et al. 2006; Krasner et al. 2008; Krasner et al. 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 analysed in drinking water using U.S. EPA Method 551 (USEPA 1995). Moreover, the formation of iodoacetaldehyde (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.

2. Experimental

2.1. 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 Table 1).

Table 1 - CAS number and main physical-chemical properties of the target analytes.

Target Compound	**Abbrev.**	**CAS Number**	**Provider**	**Purity %**	**Molecular weight (u)**	**Log Kow***	**Henry's Law constant* [atm-m^3/mol] (25 ºC)**	**Vapour pressure* [mm Hg] (25 ºC)**	**Water solubility* [mg/L] (25 ºC)**	**pKa****	**Boiling point* [ºC]**
IODO-TRIHALOMETHANES	*I-THMs*										
Dichloroiodomethane	DCIM	594-04-7	CanSyn	>95	210.83	2.03	6.82x10^{-4}	9.14	717	32.4	*132*
Chlorobromoiodomethane	CBIM	34970-00-8	CanSyn	>95	255.28	2.11	2.23x10^{-4}	1.25	346	33.1	175
Dibromoiodomethane	DBIM	593-94-2	CanSyn	90-95	299.73	2.20	7.30x10^{-5}	0.58	162	48.9	198
Chlorodiiodomethane	CDIM	638-73-3	CanSyn	90-95	302.28	2.53	1.45 x10^{-4}	0.29	82	33.2	205
Bromodiiodomethane	BDIM	557-95-9	CanSyn	90-95	346.73	2.62	4.73x10^{-5}	0.15	38	49.8	226
Triiodomethane(Iodoform)	TIM	75-47-8	Sigma-A	99	393.73	3.03	3.06x10^{-5}	0.02	*100*	50.8	*218*
IODO-HALO ACIDS	*I-HAAs*										
Iodoacetic acid	IAA	64-69-7	Sigma-A	98	185.95	0.85	4.09x10^{-8}	0.032	24260	3.0	221
Chloroiodoacetic acid	CIAA	53715-09-6	CanSyn	>90	220.39	1.03	1.44x10^{-4}	0.018	11320	2.3	249
Bromoiodoacetic acid	BIAA	71815-43-5	CanSyn	>90	264.85	1.12	4.71x10^{-9}	0.005	5414	1.9	268
Diiodoacetic acid	DIAA	598-89-00	CanSyn	>90	311.85	1.53	3.05x10^{-9}	0.0005	1282	2.3	291
HALOACETALDEHYDES	*HALs*										
Iodoacetaldehyde	IAL	55782-51-9	AldLab	95	169.95	0.59	5.06x10^{-6}	4.40	19190	-7.2	148
Chloroacetaldehyde	CAL	107-20-0	Sigma-A	50	78.50	0.09	2.39x10^{-5}	*64.27*	110700	-7.3	*86*
Bromoacetaldehyde	BAL	17157-48-1	AldLab	95	122.95	0.18	7.82x10^{-6}	19.80	69020	-7.2	115
Dichloroacetaldehyde	DCAL	79-02-7	TCI Am.	86	112.94	0.27	8.42x10^{-6}	*55.40*	62700	-7.7	*89*
Dibromoacetaldehyde	DBAL	3039-13-2	CanSyn	97	201.85	0.45	9.01x10^{-7}	1.32	17760	-7.5	174
Bromochloroacetaldehyde	CBAL	98136-99-3	CanSyn	85	157.39	0.36	1.47x10^{-5}	4.10	34780	-7.6	150

* Physical-chemical properties were obtained with EPI Suite™ (Estimation Program Interface for Microsoft® Windows, v 4.0. United States Environmental Protection Agency (U.S. EPA), Washington, DC, USA. Available for download at http://goo.gl/K7LOh2)

** Value estimated with the on-line ACE and JChem acidity and basicity calculator. Available at https://goo.gl/7SiUmh. In the case of the haloacetaldehydes, corresponds to the hydrated form of the aldehyde.

n/a, not available; text in italics indicate experimental value

All reagents and reactants used, unless otherwise specified, were purchased from Sigma-Aldrich. The list of solvents used includes Chromasolv® grade methanol (≥99.9%, MeOH), methyl-*tert*-butyl ether (≥99.8%, MTBE), and hexane (≥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) (≥98%). Anhydrous Na_2SO_4 was used to dry the DBP extracts. Sulfuric acid (95-97%, H_2SO_4), hydrochloric acid (≥37%, HCl), and sodium hydroxide (≥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).

2.2. Disinfection reactions

Chlorination and chloramination reactions were performed in a headspace-free Pyrex® glass reaction vessel at room temperature (22-26ºC) 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 h. All disinfection reactions were carried out at a pH value 7.5 using 10 mM of phosphate buffer, and either H_2SO_4 or NaOH (1M) 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 µg/L 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.

2.3. 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. and Richardson et al. (Richardson et al. 2008a; Duirk et al. 2011). 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 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. (Jeong et al. 2015)).

Further details on the analytical instrumentation used and the analytical protocols followed are provided in the following sub-sections.

2.3.1. Analysis of iodo-trihalomethanes

As recommended by Duirk et al. (Duirk et al. 2011), the residual oxidant present in water was quenched with sodium sulfite (20% in excess of the initial oxidant concentration) and analytes were extracted immediately. Duirk et al.'s procedure for analyte extraction was applied with slight variations as follows: 90 mL of water was first acidified to pH<0.5 with 4.5 mL of concentrated H_2SO_4; then, 25 g of dried Na_2SO_4 was added to the sample, and after complete dissolution, addition of the internal standard (IS) (10 µL x 25 µg/mL of 1,2-dibromopropane in methanol) and 2.5 mL of MTBE (the extracting solvent) were consecutively done. Samples were placed on an orbital action shaker for 30 min. After settling, the MTBE layer at the top was removed and dried with a Na_2SO_4 column. Half of the extract was directly injected into the gas chromatography/mass spectrometry (GC/MS) instrument for analysis of target I-THMs, and half was kept for analysis of I-HAAs (see section 2.3.2).

A total of six I-THMs (see Table 1) were measured in the extract using GC/electron ionization (EI)-MS by means of a 7890A GC system connected to a 7000B GC/MS Triple Quad (Agilent Technologies). One µL of each extract was injected via a 7683B Series injector (Agilent) in splitless mode (split flow=50 mL/min, splitless time=1.5 min) onto a Zebron ZB-5 capillary column (30 m, 0.25 mm ID, 0.25 µm film thickness, Phenomenex, Torrance, CA). The injection port temperature was set at 250ºC and the GC/MS transfer line at 280ºC. The GC program consisted of an initial temperature of 50ºC, which was held for 2 min, followed by an increase at a rate of 9ºC/min to 140ºC, then to 155 ºC (2ºC/min), and then increased again at a rate of 15ºC/min to 285ºC, temperature held for 10 min. The temperature gradient was carried out at a constant He flow of 1.2 mL/min.

Analyses were performed in the selected ion monitoring mode (SIM) by recording up to four ions per analyte. Quantification, based on peak areas, was performed by the internal standard method. Calibration curves were constructed with a minimum of five calibration data points using least squares linear regression analysis. The calibration range expanded from the method reporting limit to 75 µg/L. Ions monitored for each analyte and method performance parameters are summarized in Table 2.

Table 2 – Retention time and ions monitored for each target I-THM.

I-THMs	Retention time (min)	SIM ions (m/z)[a]	Linearity (MRL - 75 µg/L)	Absolute recovery[b] (%)	Relative recovery[c] (%) ± RSD	Method reporting limit (MRL) (µg/L)
DCIM	7.2	210,175,127,**83**	0.9999	82	68.5 ±11.7	0.3
CBIM	9.3	256,175,**127**,129	0.9999	88	73.7 ±12.6	0.3
DBIM	11.2	256,**173**,127,221	0.9998	128	107.5 ±7.8	0.3
CDIM	11.7	302,254,**175**,127	0.9997	134	112.3±10.5	0.3
BDIM	13.6	346,**219**,254,127	0.9991	141	117.8 ±9.2	0.3
TIM	15.7	394,**267**,254,127	0.9986	114	95.3 ±10.4	1.5
IS	*8.0*	***121**,123*	-	-	-	-

[a] In bold font, base peak ion used for quantification.

[b] Average value for the absolute recovery of the analyte calculated by comparing the peak areas obtained after analysis of n=3 purified water samples fortified at a concentration of 5 µg/L of the target analytes and a standard solution in MTBE at equivalent concentration: $(\text{Area}_{water}*100)/\text{Area}_{standard}$.

[c] Average value for the relative recovery of the analyte with respect to that obtained for the internal standard: $(\text{AR}_{analyte}*100)/\text{AR}_{IS}$. RSD: relative standard deviation.

2.3.2. Analysis of iodo-haloacetic acids

After water extraction using the protocol explained for the analysis of I-THMs in section II, 0.5 mL of the final extract was derivatized with diazomethane (methylated) for the analysis of iodoacids (I-HAAs). For derivatization, diazomethane was freshly prepared from Diazald (Sigma Aldrich, St. Louis, MO) with a diazomethane generator with a System 45 ™ screw-threat connection (Sigma Aldrich) following the instructions provided by the manufacturer. Briefly, 0.367 g of Diazald were dissolved in 1 mL carbitol (Sigma Aldrich) in the inner part of the diazomethane generator, and 3 mL of MTBE were added in the outer part of the reactor. After closing the reactor, it was immersed in ice, and then the reaction was initiated by adding 1.5 mL KOH (37%) to the inner vessel and allowed to proceed for 1 h. After the reaction is finished, 0.250 mL of diazomethane MTBE-based solution was added to 0.5 mL of the extract and allowed to react for 30 min. Once the reaction time is finished, 50 mg of high purity activated silica (Davisil Grade 636, pore size 60 Å, 35-60 mesh particle size) (Sigma Aldrich) was added to quench the reaction and allowed to react for 30 min.

A total of four I-HAAs (see Table 1) were measured in the derivatized extract using GC/negative chemical ionization (NCI)-MS by means of a 7890A GC system connected to a 5975C Inert XL EI/CI MSD mass spectrometer (Agilent Technologies). One µL of each extract was injected via a 7683B Series injector (Agilent) in splitless mode (split flow=50 mL/min, splitless time=1.5 min) onto a Zebron ZB-5 capillary column (30 m, 0.25 mm ID, 0.25 µm film thickness, Phenomenex, Torrance, CA). The temperature of the injection port was set to 280 ºC. The GC program consisted of an initial temperature of 40ºC, which was held for 1 min, followed by an increase at a rate of 10ºC/min to 180ºC, and increased again at a rate of 20ºC/min to 300ºC. Then, the temperature was held for 15 min. The temperature gradient was carried out at a constant He flow of 1.2 mL/min. Methane at a flow of 2.25 mL/min was used as chemical ionization gas. Transfer line, MS source, and MS quad temperatures were 280 ºC, 200 ºC and 150 ºC, respectively.

Analyses were performed in the SIM mode by recording the m/z corresponding to iodine (m/z 127) for all compounds and the m/z 160 in the case of the internal standard (1,2-dibromopropane). Quantification, based on peak areas, was performed by the internal standard method. Calibration curves were constructed with a minimum of five calibration data points using least squares linear regression analysis. The calibration range expanded from the method reporting limit to 5 µg/L. Method performance parameters are summarized in Table 3.

Table 3 – Retention time and ions monitored for each target I-HAAs

I-HAAs	Retention time (min)	SIM ions (m/z)	Linearity		Absolute recovery[a] (%)	Relative recovery[b] (%)±RSD	Method reporting limit (MRL) (µg/L)
			Range (µg/L)	R^2			
IAA	5.90	127	MRL-5	0.9937	79.0	88.6±3.6	0.1
CIAA	7.74	127	MRL-5	0.9931	96.8	108.5±4.8	0.1
BIAA	9.01	127	MRL-5	0.9984	107.8	120.9±4.4	0.1
DIAA	10.69	127	MRL-5	0.9943	113.6	127.6±4.1	0.1
IS	*4.89*	*160*	-	-	-	-	-

[a] Average value for the absolute recovery of the analyte calculated by comparing the peak areas obtained after analysis of n=3 purified water samples fortified at a concentration of 1 µg/L of the target analytes and a standard solution in MTBE at equivalent concentration: $(Area_{water}*100)/Area_{standard}$.

[b] Average value for the relative recovery of the analyte with respect to that obtained for the internal standard: $(AR_{analyte}*100)/AR_{IS.}$ RSD: relative standard deviation.

2.3.3. Analysis of monohalo- and dihalo-acetaldehydes

Analysis of monohalo- and dihalo-acetaldehydes was performed following the analytical procedure described by Jeong et al. (2015). The method consists in derivatizing of the compounds with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) (for 2 hours at 35ºC) and liquid-liquid extracting the oximes formed with hexane. The extract obtained was evaporated under nitrogen to 0.3 mL and then analyzed by means of GC-EI-MS analysis in the SIM mode using a 7890A GC system connected to a 7000B GC/MS Triple Quad (Agilent Technologies). One µL of each extract was injected via a 7683B Series injector (Agilent) in splitless mode (split flow=50 mL/min, splitless time=1.5 min) onto a Zebron ZB-5 capillary column (30 m, 0.25 mm ID, 0.25 µm film thickness, Phenomenex, Torrance, CA).

The injection port temperature was set at 250ºC and the GC/MS transfer line at 280ºC. A slightly modified GC program was applied. It consisted of an initial temperature of 50ºC, which was held for 2 min. The temperature was increased at a rate of 9ºC/min to 140ºC, then at a rate of 2ºC/min to 155ºC, and finally at a rate of 15ºC/min to 285ºC. Then, the temperature was held for 10 min. The temperature gradient was carried out at a constant He flow of 1.2 mL/min. The ions (m/z values) selected for mono-HAL and di-HAL analysis and their retention time are shown in Table 4.

Table 4 – Retention time and ions monitored for each target HALs

HALs	Retention time (min)	SIM ions (m/z)[a]	Linearity		Method reporting limit (MRL) (µg/L)
			Range (µg/L)	R^2	
CAL	12.7	**238**, 243, 245, 273, 275	MRL-8	0.9979	0.05
BAL	14.4	**287**, 289, 290, 317, 319	MRL-10	0.9950	0.25
IAL	16.8	*127*, **238**, 335, 365	MRL-8	0.9990	0.5
CBAL	15.8	**272**, 274, 275, 316, 318	MRL-10	0.9971	0.25
DCAL	13.8	91, **272**, 273, 274, 307	MRL-8	0.9933	0.05
DBAL	18.2	135, **316**, 318, 397	MRL-8	0.9935	0.05
IS	*4.9*	*107,* ***121,*** *123*	-		-
SS	*21.3*	***319***	-		-

[a] In bold font, base peak ion used for quantification

2.4. TOC, SUVA, bromide, and iodide measurements

Total organic carbon (TOC) measurements were carried out by means of a Shimadzu TOC-V_{CSH} analyzer (Shimadzu Europa GmbH, Duisburg, Germany). 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)-MS. Average values of TOC, SUVA, bromide and total iodine in the source waters used for the experiments are summarized in Table 5.

Table 5 – 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.

2.5. 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.

3. Results and discussion

3.1. 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 (Table 2 and 3). Concentrations of I-THMs and I-HAAs measured in the disinfected water samples are summarized in Figure 1 and in Table 6.

Table 6 – Concentrations of target DBPs in μg/L measured in the generated DBP mixtures

SAMPLE	IODO-TRIHALOMETHANES						IODO-HALOACETIC ACIDS				MONOHALO- AND DIHALO-ACETALDEHYDES					
	DCIM	BCIM	DBIM	CDIM	BDIM	TIM	IAA	CIAA	BIAA	DIAA	CAL	DCAL	BAL	DBAL	BCAL	IAL
NL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NL_Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.2	1.4	n.d.	n.d.	n.d.	n.d.
NL_NH$_2$Cl	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	0.2	n.d.	n.d.	0.2	2.3	n.d.	n.d.	n.d.	0.7
NL_Cl_10	0.8	0.9	0.2	0.9	0.7	n.d.	0.3	0.4	0.3	n.d.	0.1	0.6	0.8	0.2	0.5	n.d.
NL_NH$_2$Cl_10	1.0	2.1	0.6	1.2	0.7	n.d.	0.4	0.9	0.3	0.4	<MRL	0.8	n.d.	0.6	0.6	0.9
NL_Cl_5	1.4	1.1	0.2	1.2	1.0	n.d.	0.6	0.6	n.d.	n.d.	0.1	0.7	0.7	0.2	0.4	n.d.
NL_NH$_2$Cl_5	1.3	2.8	1.0	1.6	0.8	0.7	0.9	1.7	1.3	1.0	n.d.	0.4	n.d.	0.5	0.3	0.9
SR	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MRL	n.d.	n.d.	n.d.	n.d.
SR_Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.3	n.d.	n.d.	0.2	1.6	n.d.	n.d.	n.d.	n.d.
SR_NH$_2$Cl	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	1.2	n.d.	n.d.	0.2	2.2	n.d.	n.d.	n.d.	0.6
SR_Cl_10	1.1	0.8	0.2	1.0	n.d.	n.d.	0.3	0.8	0.2	n.d.	0.1	0.1	0.8	0.2	0.3	n.d.
SR_NH$_2$Cl_10	1.1	2.0	0.4	1.4	0.8	n.d.	0.6	0.5	0.7	0.6	<MRL	0.5	n.d.	0.6	0.6	0.8
SR_Cl_5	1.9	1.1	0.3	1.8	n.d.	n.d.	0.4	1.8	0.3	0.4	0.1	0.9	0.8	0.2	0.3	
SR_NH$_2$Cl_5	1.4	2.6	0.7	2.1	0.6	0.7	0.7	1.7	1.7	0.9	n.d.	0.4	n.d.	0.5	0.3	0.8
LLOB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n/a	n/a	n/a	n/a	n/a	n/a
LLOB_Cl	0.5	1.1	0.7	n.d.	0.5	n.d.	0.4	n.d.	0.1	n.d.	0.6	4.6	0.6	2.6	0.7	0.7
LLOB_NH$_2$Cl	0.6	1.4	0.8	0.7	0.6	n.d.	0.3	0.4	0.2	n.d.	0.2	3.1	0.8	2.1	4.1	0.5

*n.d. not detected, n/a: target compound not analyzed in the sample, <MRL: concentration below the method reporting limit

(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))

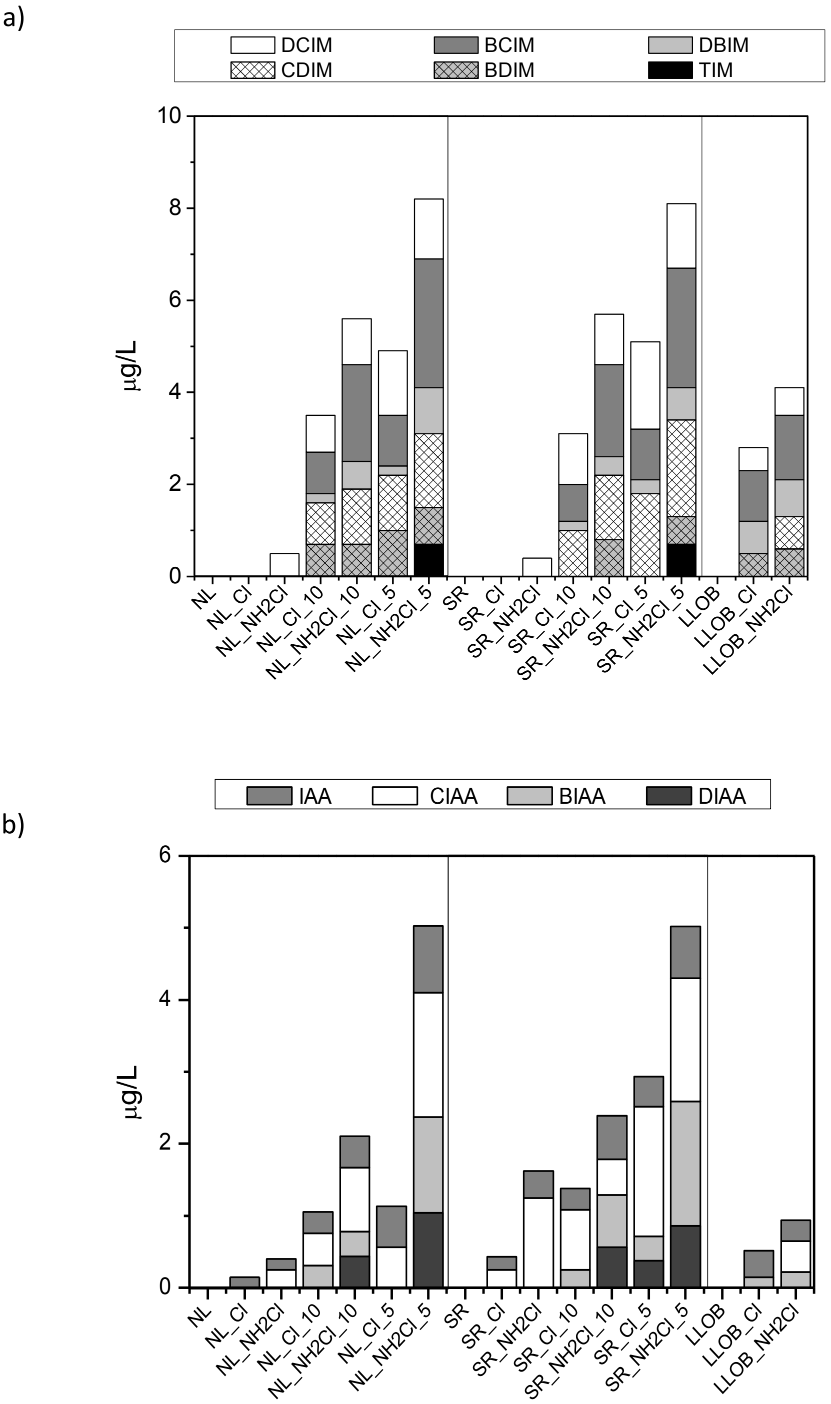


Figure 1. Concentrations of a) I-THMs and b) I-HAAs in the tested waters after chlorination (CL) and chloramination (NH$_2$Cl) reactions (NL: Nordic Lake NOM solutions, SR: Suwannee River NOM solutions, LLOB: Llobregat River water; NL, SR, NL_Cl, SR_Cl, NL_NH$_2$Cl, SR_NH$_2$Cl, LLOB_Cl, and LLOB_NH$_2$Cl: 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)).

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, hypoiodous acid reacts with NOM to form I-DBPs, which act as a sink for iodide (Bichsel et al. 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 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 5). NOM of the tested aqueous matrices was evaluated by means of $SUVA_{254}$ 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 Figure 2.

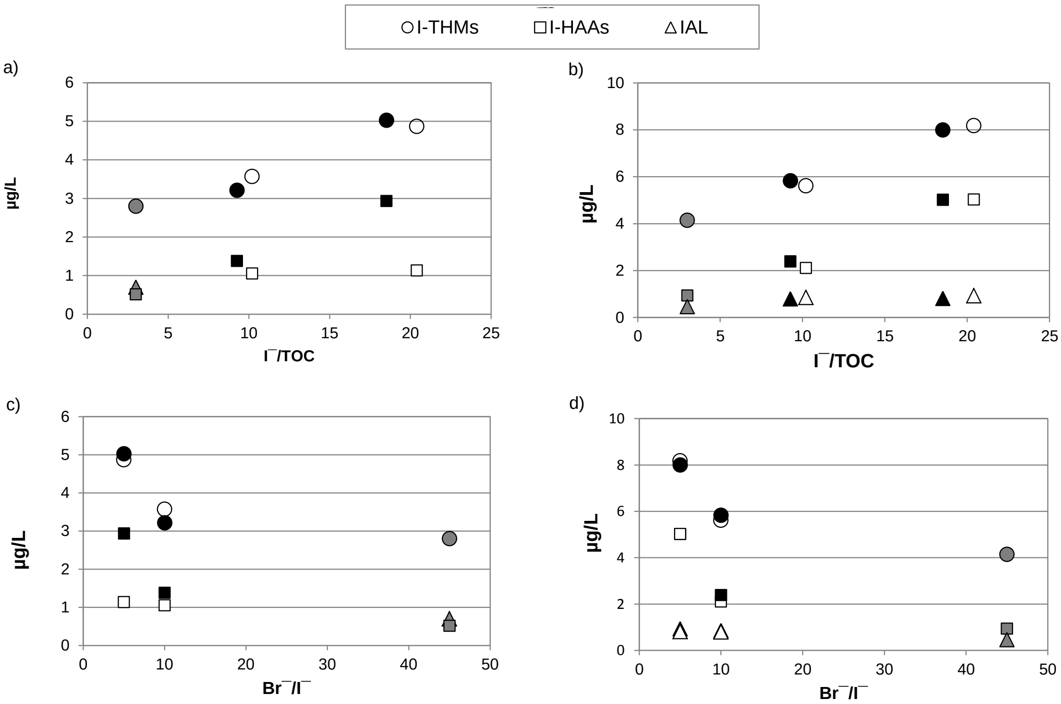
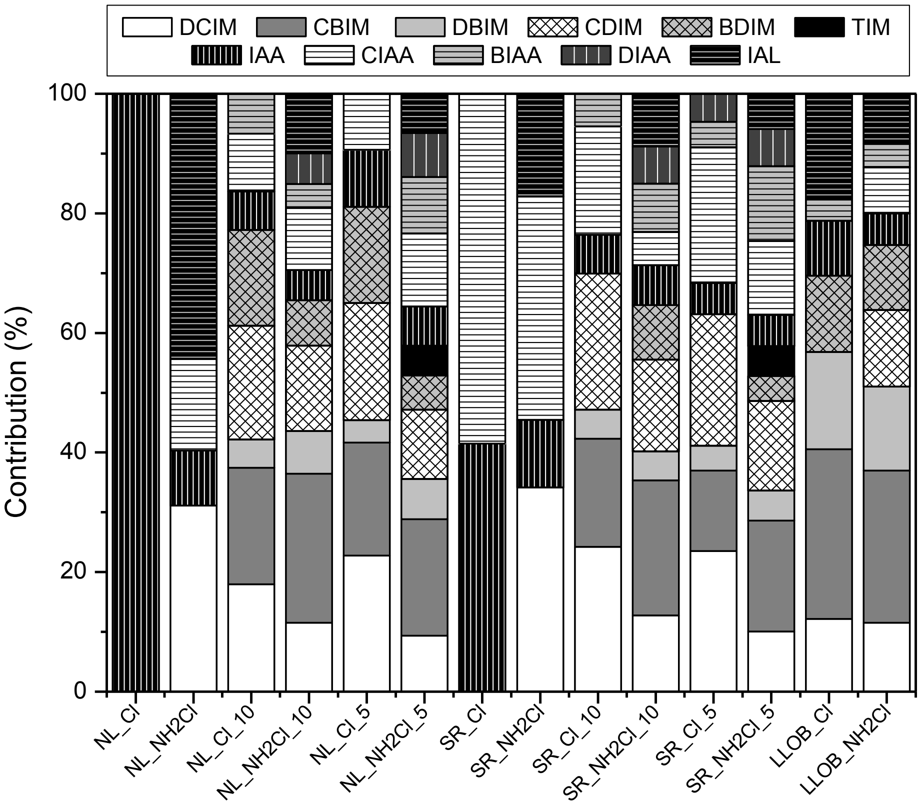


Figure 2. Total concentration of I-THMs, I-HAAs and IAL as a function of Br^-/I^- and I^-/TOC ratios in chlorinated (a) and (c) and chloraminated water samples (b) and (d). (Gray: LLOB waters, black: SR NOM solutions and white: NL NOM solutions).

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.

Figure 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 Figure 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 (see Tables 2 and 3). 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%).



	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_2Cl	17.2	15.9	5.4	9.8	5.4	1.4	7.0	14.4	5.4	3.6	14.5

Figure 3. Contribution (in %) of each I-DBP to the total I-DBP concentration measured in the investigated chlorinated (Cl) and chloraminated (NH_2Cl) 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_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)).

3.2. 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 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.

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

A residual concentration (< MRL, see Table 4) 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 Figure 4 and in Table 6. 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 5). 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 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 Figure 2).

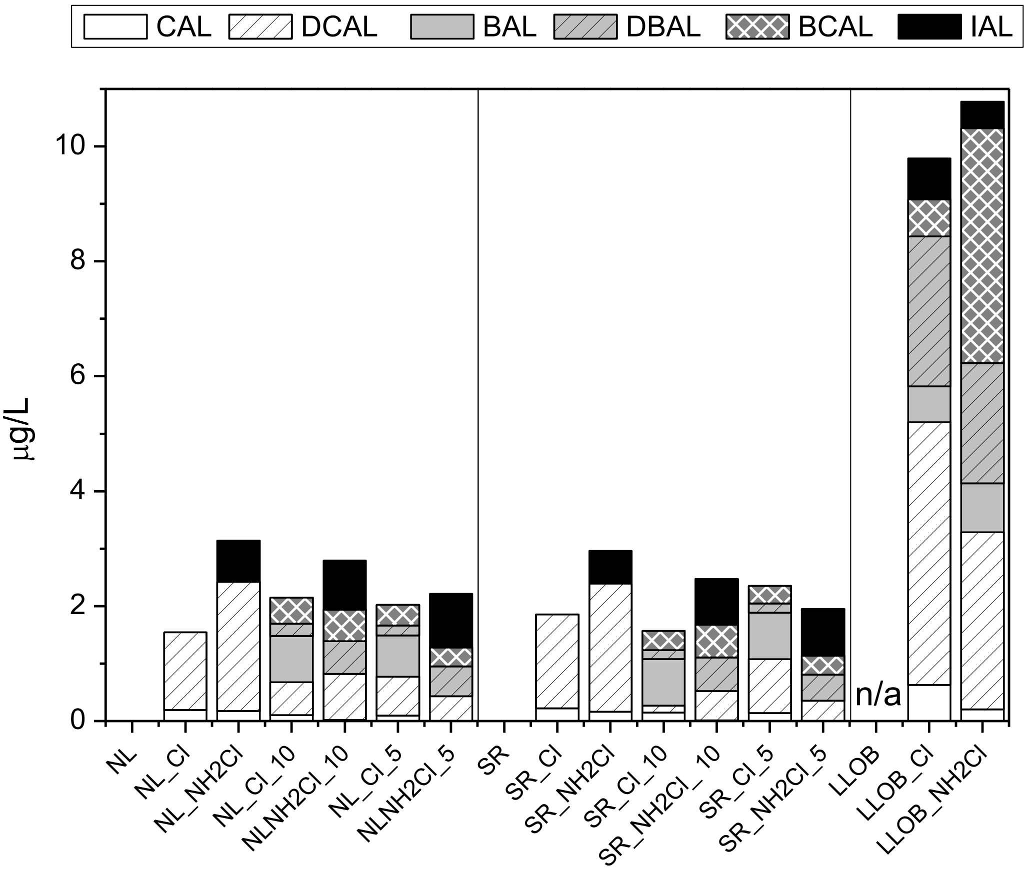


Figure 4. Concentrations of mono-HALs and di-HALs in the tested waters after chlorination (Cl) and chloramination (NH_2Cl) reactions (NL: Nordic Lake NOM solutions, SR: Suwannee River NOM solutions, LLOB: Llobregat River water; NL, SR, NL_Cl, SR_Cl, NL_NH_2Cl, SR_NH_2Cl, LLOB_Cl, and LLOB_NH_2Cl: ambient 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).

4. 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.

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