JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com

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www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

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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ARTICLE INFO

Article history:
Received 19 December 2016
Revised 30 March 2017
Accepted 7 April 2017
Available online xxxx

Keywords:
Iodinated disinfection by-products
Chlorination
Chloramination
Drinking water
Mass spectrometry
Iodo-trihalomethanes
Iodo-haloacetic acids
Haloacetaldehydes

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.

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

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http://dx.doi.org/10.1016/j.jes.2017.04.009
1001-0742/

Please cite this article as: Postigo, C., et al., Formation of iodo-trihalomethanes, iodo-haloacetic acids, and haloacetaldehydes during chlorination and chloramination of iodine containing..., J. Environ. Sci. (2017), http://dx.doi.org/10.1016/j.jes.2017.04.009

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 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; 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 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; 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 analyzed in drinking water using U.S. EPA Method 551 (USEPA, 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 Supporting Information (SI), Table S1). 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).

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 mM of phosphate buffer, and either H_2SO_4 or NaOH (1 M) 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

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