



The role of aromatic precursors in the formation of haloacetamides by chloramination of dissolved organic matter



Julien Le Roux^{a, b}, Maolida Nihemaiti^{a, c}, Jean-Philippe Croué^{a, c, *}

^a Water Desalination and Reuse Center, 4700 KAUST, Thuwal 23955-6900, Saudi Arabia

^b LEESU (UMR MA 102), Université Paris-Est - AgroParisTech, 61 avenue du Général de Gaulle, 94010 Créteil cedex, France

^c Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form

16 October 2015

Accepted 18 October 2015

Available online 21 October 2015

Keywords:

Chloramination

Disinfection byproducts

Haloacetamides

Dissolved organic matter

Aromatic compounds

ABSTRACT

Water treatment utilities are diversifying their water sources and often rely on waters enriched in nitrogen-containing compounds (e.g., ammonia, organic nitrogen such as amino acids). The disinfection of waters exhibiting high levels of nitrogen has been associated with the formation of nitrogenous disinfection byproducts (N-DBPs) such as haloacetonitriles (HANs) and haloacetamides (HAcAms). While the potential precursors of HANs have been extensively studied, only few investigations are available regarding the nature of HAcAm precursors. Previous research has suggested that HAcAms are hydrolysis products of HANs. Nevertheless, it has been recently suggested that HAcAms can be formed independently, especially during chloramination of humic substances. When used as a disinfectant, monochloramine can also be a source of nitrogen for N-DBPs. This study investigated the role of aromatic organic matter in the formation of N-DBPs (HAcAms and HANs) upon chloramination. Formation kinetics were performed from various fractions of organic matter isolated from surface waters or treated wastewater effluents. Experiments were conducted with ¹⁵N-labeled monochloramine (¹⁵NH₂Cl) to trace the origin of nitrogen. N-DBP formation showed a two-step profile: (1) a rapid formation following second-order reaction kinetics and incorporating nitrogen atom originating from the organic matrix (e.g., amine groups); and (2) a slower and linear increase correlated with exposure to chloramines, incorporating inorganic nitrogen (¹⁵N) from ¹⁵NH₂Cl into aromatic moieties. Organic matter isolates showing high aromatic character (i.e., high SUVA) exhibited high reactivity characterized by a major incorporation of ¹⁵N in N-DBPs. A significantly lower incorporation was observed for low-aromatic-content organic matter. ¹⁵N-DCAcAm and ¹⁵N-DCAN formations exhibited a linear correlation, suggesting a similar behavior of ¹⁵N incorporation as SUVA increases. Chloramination of aromatic model compounds (i.e., phenol and resorcinol) showed higher HAcAm and HAN formation potentials than nitrogenous precursors (i.e., amino acids) usually considered as main precursors of these N-DBPs. These results demonstrate the importance of aromatic organic compounds in the formation of N-DBPs, which is of significant importance for water treatment facilities using chloramines as final disinfectant.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Surface waters are often impacted by human activities (e.g., agriculture, industries, and municipal wastewater effluent discharges) resulting in their enrichment in nitrogen-containing compounds (i.e., ammonia and organic nitrogen such as amino

acids) (Westerhoff and Mash, 2002). The disinfection of waters exhibiting high levels of nitrogen has been associated with the formation of nitrogenous disinfection byproducts (N-DBPs) (Bond et al., 2011). N-DBPs generally form in significantly lower concentrations than regulated DBPs, but have been a growing concern over the past decade because of their higher health risk (Muellner et al., 2007; Plewa et al., 2004). *In vitro* mammalian cell tests have demonstrated that haloacetonitriles (HANs), halonitromethanes (HNMs), and haloacetamides (HAcAms) are more cytotoxic and genotoxic (i.e., up to 2 orders of magnitude) than non-nitrogenous molecules such as trihalomethanes (THMs) and haloacetic acids

* Corresponding author. Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

E-mail addresses: julien.le-roux@u-pec.fr (J. Le Roux), maolida.nihemaiti@postgrad.curtin.edu.au (M. Nihemaiti), jean-philippe.croue@curtin.edu.au (J.-P. Croué).

(HAAs) (Plewa et al., 2008). Nitrogen in N-DBPs can also be derived from chloramines when used as disinfectants. Water utilities have been increasingly switching to monochloramine as an alternative to chlorine in order to limit the production of regulated THMs and HAAs. Nevertheless, concern has been raised regarding the formation of N-DBPs (e.g., N-nitrosodimethylamine – NDMA) produced from the reaction between monochloramine and secondary or tertiary amines (Mitch and Sedlak, 2004).

Among N-DBPs, dichloroacetonitrile (DCAN) and dichloroacetamide (DCAcAm) are the most frequently detected species in drinking water treatment plants (Krasner et al., 2006). While the potential precursors of HANs have been extensively studied, only few investigations are available regarding the nature of HACams precursors. HACams were first reported to be intermediate products of HANs hydrolysis and ultimately decomposed to HAAs (Glezer et al., 1999; Reckhow et al., 2001). More recently, it was found that HACams can be formed independently from HANs during chlorination and chloramination processes (Huang et al., 2012). Two different pathways have been proposed to describe the formation of HANs and HACams (Fig. S1). First, the Decarboxylation Pathway occurs by rapid chlorination or chloramination of α -amine groups of free amino acids to form a nitrile, followed by hydrolysis to release HANs and carbonic acid (Trehly et al., 1986). HANs are then further hydrolyzed to HACams and HAAs (Reckhow et al., 2001). The second pathway proposed for HANs formation is the Aldehyde Pathway, where nitrogen from monochloramine (NH_2Cl) is incorporated into aldehydes to produce nitriles. The reaction between NH_2Cl and formaldehyde forms cyanogen chloride (CNCl) (Pedersen et al., 1999), and chloroacetonitrile is formed from chloroacetaldehyde (Kimura et al., 2013). Haloacetaldehydes (HACAls) are carbonaceous DBPs frequently detected in disinfected waters, and often represent the third major class of DBPs after THMs and HAAs (Krasner et al., 2006). Chloroacetaldehyde has been demonstrated to be a precursor of N,2-dichloroacetamide upon chloramination (Kimura et al., 2013). The reaction involves the incorporation of the nitrogen atom of monochloramine (NH_2Cl) to form the amide group through the formation of a carbinolamine intermediate.

In addition to the Aldehyde Pathway, most studies about HANs and HACams formation mechanisms focused on the chlorination of nitrogenous precursors (e.g., amino acids, amines, pyrimidines) or matrices enriched in nitrogenous moieties (e.g., algae cells, extracellular organic matter) (Bond et al., 2009; Fang et al., 2010; Oliver, 1983; Reckhow et al., 2001; Yang et al., 2010, 2011, 2012). In the case of aquatic humic substances, a positive correlation was found between their nitrogen content and their tendency to form HAN upon chlorination (Reckhow et al., 1990). Studies performed with labeled ^{15}N -chloramines ($^{15}\text{NH}_2\text{Cl}$) on nitrogenous organic (N-org) precursors and fractions of dissolved organic matter (DOM) found that nitrogen in HANs or CNCl originated from both organic precursors and NH_2Cl (Yang et al., 2010). Recent studies suggested that aromatic moieties of DOM may contribute to a substantial HAN formation upon chloramination (Chuang et al., 2013; Huang et al., 2012; Yang et al., 2008, 2010). During chloramination, the formation of DCAN or CNCl did not correlate with the DON/DOC ratios of DOM fractions. However, good correlations were observed with their SUVA values and thus with their aromatic carbon content (Yang et al., 2008). A mechanism describing the chloramination of a β -diketone moiety was proposed based on the Decarboxylation Pathway, showing the incorporation of nitrogen through the formation of an N-chloroimine and leading to DCAN as a hydrolysis product. Approximately 90% of nitrogen in DCAN and CNCl was reported to originate from NH_2Cl reaction with Suwannee River DOM (Yang et al., 2010). Recent kinetics experiments also suggest similarities between HANs, THMs, and HAAs precursors (Chuang

et al., 2013). Kinetics of DCAN and trichloronitromethane (TCNM) formation upon chloramination using $^{15}\text{NH}_2\text{Cl}$ were proposed to involve two reaction mechanisms: formation from N-org precursors following a second-order reaction; and formation by incorporation of nitrogen from NH_2Cl , linearly correlated with chloramines exposure (Chuang and Tung, 2015).

Less information is available about HACams precursors and formation mechanisms, since HACams were first reported as DBPs in a 2000–2002 drinking water survey (Krasner et al., 2006; Weinberg et al., 2002). Although DCAcAm yields from amino acids are considerably lower than those of DCAN, comparable levels (i.e., median concentrations of 1.3 and 1 $\mu\text{g/L}$, respectively) have been observed in US drinking waters (Bond et al., 2012; Krasner et al., 2006). Therefore, unknown precursors appear to be responsible for the majority of HACAm formation (Bond et al., 2012). The formation of HACams from algal exopolymeric substances (EPS), municipal wastewater treatment plant effluents (Huang et al., 2012), natural waters (Chu et al., 2013), bacterial cells (Huang et al., 2013), natural organic matter (NOM) fractions, and free amino acids (Chu et al., 2010a, 2010b) has been previously studied. The hydrophilic acid fraction isolated from an algal-impacted water enriched in nitrogen (i.e., high DON/DOC ratio), exhibited the highest DCAcAm formation potential during both chlorination and chloramination, which was associated with the presence of protein-like organic matter (Chu et al., 2010b). However, DCAcAm was recently found to be preferentially formed by chloramination of humic materials, while chlorination of wastewater effluents and algal EPS tended to form more DCAN (Huang et al., 2012). These results suggested that the mechanism of HACams formation is independent from that of HANs. Overall, HACams formation mechanisms remain unclear, and the precursors of HACams in natural waters still need to be characterized.

This study investigated the role of aromatic organic matter in the formation of N-DBPs (i.e., especially HACams) upon chloramination, with emphasis on the formation kinetics of HACams and HANs. Various fractions of organic matter isolated from different waters (i.e., surface waters, treated wastewater) as well as model compounds were studied to understand the factors controlling N-DBPs formation. Experiments were conducted with $^{15}\text{NH}_2\text{Cl}$ to trace the origin of nitrogen in the formed DBPs.

2. Materials and methods

2.1. Materials

All reagents were of analytical or laboratory grade and were used without further purification. MilliQ water was produced with a Millipore system (18.2 M Ω cm). Sodium hypochlorite (NaOCl, 5.65–6%, Fisher Scientific) and ammonium chloride (Acros Organics, 99.6%) were used to prepare chloramine reagents. ^{15}N -labeled ammonium chloride was purchased from Sigma–Aldrich (98%). Sodium thiosulfate (Fisher Scientific) was used to quench residual chloramines. Methyl tert-butyl ether (MTBE) and ethyl acetate (>99%, Fisher Scientific) were used for DBP extractions without further purification. A THM calibration mix (chloroform – TCM, dichlorobromomethane – CHCl_2Br , chlorodibromomethane – CHClBr_2 , and bromoform – TBM), a mixed standard (EPA 551B Halogenated Volatiles Mix) containing haloacetonitriles (HANs), trichloronitromethane (TCNM, or chloropicrin) and haloketones (HKs), and a mixed standard containing 9 HAAs (EPA 552.2 Methyl Ester Calibration Mix) were supplied from Supelco (Sigma–Aldrich). Chloro-, bromo-, dichloro-, and trichloroacetamide were obtained from Sigma–Aldrich. Other haloacetamides (HACams) were purchased from Cansyn Chem. Corp. Decafluorobiphenyl (99%, Sigma–Aldrich, Supelco) was used as a surrogate standard. 2-

Download English Version:

<https://daneshyari.com/en/article/6365466>

Download Persian Version:

<https://daneshyari.com/article/6365466>

[Daneshyari.com](https://daneshyari.com)