Water Research 93 (2016) 65–73

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Organic chloramines in drinking water: An assessment of formation, stability, reactivity and risk

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ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form
11 January 2016
Accepted 4 February 2016
Available online 11 February 2016

Keywords:
Amino acids
Disinfection by-products
Organic chloramines
Chlorination
Health risk assessment
Liquid chromatography–mass spectrometry

ABSTRACT

Although organic chloramines are known to form during the disinfection of drinking water with chlorine, little information is currently available on their occurrence or toxicity. In a recent *in vitro* study, some organic chloramines (e.g. *N*-chloroglycine) were found to be cytotoxic and genotoxic even at micromolar concentrations. In this paper, the formation and stability of 21 different organic chloramines, from chlorination of simple amines and amino acids, were studied, and the competition between 20 amino acids during chlorination was also investigated. For comparison, chlorination of two amides was also conducted. The formation and degradation of selected organic chloramines were measured using either direct UV spectroscopic or colorimetric detection. Although cysteine, methionine and tryptophan were the most reactive amino acids towards chlorination, they did not form organic chloramines at the chlorine to precursor molar ratios that were tested. Only 6 out of the 21 organic chloramines formed had a half-life of more than 3 h, although this group included all organic chloramines formed from amines. A health risk assessment relating stability and reactivity data from this study to toxicity and precursor abundance data from the literature indicated that only *N*-chloroglycine is likely to be of concern due to its stability, toxicity and abundance in water. However, given the stability of organic chloramines formed from amines, more information about the toxicity and precursor abundance for these chloramines is desirable.

1. Introduction

Since the discovery in the early 1970s of disinfection by-products (DBPs) in chlorinated drinking water, extensive studies have been undertaken to understand the formation of DBPs and their management (Richardson, 2003). Although more than 600 DBPs have now been identified, only minimal information on the occurrence or toxicity of many of these DBPs is available. A recent toxicological study identified several classes of nitrogen-containing DBPs, including haloacetamides, halonitriles and organic halamines, to be of highest interest with respect to potential toxicity (Bull et al., 2011). In addition, Bull et al. (2011) also suggested high priority be given to the characterisation of the toxicological properties of organic halamines that have varying chemical properties (e.g. stability and hydrophobicity). Since then, studies have been conducted on the haloacetamides, halonitriles and many other classes of nitrogen-containing DBPs (Bond et al., 2011; Liew et al., 2012), however there remains very little published information regarding the occurrence or toxicity of organic halamines in drinking water.

Although water-related toxicological studies of organic chloramines are limited, several biomedical studies of the potential for adverse health effects from organic chloramines have been published. Organic chloramines have been found to cause protein-DNA cross-links (Kulcharyk and Heinecke, 2001), inhibit DNA repair (Pero et al., 1996), and affect the rates of cellular apoptosis and the kinetics of the cell cycle (Englert and Shacter, 2002; Hosako et al., 2004), which are all common characteristics of carcinogens. A significant *in vitro* cytotoxicity and genotoxicity has also been observed in WIL2-NS cells (human lymphoblastoid) that were treated with *N*-chloroglycine, *N*-chloroethanolamine, *N*-chlorohistamine, and *N*-chlorolysine formed *in situ* at low micromolar concentrations (Laingam et al., 2012).

Organic chloramines may be formed when dissolved organic nitrogen (DON), represented by functional groups such as amino acids, amides and amines within the dissolved organic carbon (DOC), present in water systems reacts with free chlorine (Hunter

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http://dx.doi.org/10.1016/j.watres.2016.02.006
0043-1354/

and Faust, 1967) or inorganic chloramines (Isaac and Morris, 1983; Snyder, 1982). The general equations for the formation of organic (mono/di) chloramines from addition of hypochlorous acid are shown below:

$$R - NH_2 + HOCl \rightleftarrows R - NHCl + HOCl \rightleftarrows R - NCl_2 \quad (1)$$

$$R_2 - NH + HOCl \rightleftarrows R_2 - NCl \quad (2)$$

The reactions between amino acids and free chlorine are believed to be the main contributor to the formation of organic chloramines (Ellis and Soper, 1954; Yoon and Jensen, 1993). After formation, organic chloramines can degrade to different disinfection by-products, such as aldehydes and nitriles, depending on the chlorine to nitrogen ratio (Nweke and Scully, 1989). The stability of different organic chloramines has been reported to be quite variable, ranging from a half-life of 13 min to more than 48 h (Armesto et al., 1996; Hand et al., 1983; Scully and Bempong, 1982). In general, more basic organic chloramines are more stable (Pitman et al., 1969). The presence of an α-hydrogen can reduce organic chloramine stability, as it can promote dehydrohalogenation reactions (Hui and Debiemme-Chouvy, 2013).

To accurately assess the risk associated with the presence of organic chloramines in drinking water, it is important to understand both the formation and stability of this class of compounds, in addition to their toxicity. In this study, the formation and degradation of a range of organic chloramines from 21 amino acids and three amines were investigated at pH 7–8. The chlorination of two amides was also studied. A health risk assessment of organic chloramines in drinking water was conducted based on the relationship between the stability and toxicity of the organic chloramines, and also their reactivity and precursor abundance.

2. Methods and materials

2.1. Chemicals

Amino acids (alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glycine, glutamic acid, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tyrosine and valine) (purity ≥ 97%); amines (dimethylamine, diethylamine and ethanolamine) (purity ≥ 97%); amides (acetamide and acrylamide) (purity ≥ 97%); and aqueous sodium hypochlorite (10–15% chlorine) were purchased from Sigma Aldrich (New South Wales, Australia). The amino acid taurine (purity 99%); was purchased from AK Scientific (California, USA); potassium iodide and formic acid (purity 99%) were purchased from Ajax FineChem (New South Wales, Australia); and glacial acetic acid was purchased from Chem Supply (South Australia, Australia). Monochlor F reagent was purchased from Hach Pacific (Victoria, Australia). The internal standards [^{2}H3] alanine (alanine-d_3), [^{2}H3] leucine (leucine-d_3) and [^{2}H3] glutamic acid (glutamic acid-d_3) were purchased from CDN Isotopes (Quebec, Canada; distributed by SciVac, Hornsby, Australia); [^{2}H2] glycine (glycine-d_2), [^{2}H5] phenyl [^{2}H3] alanine (phenyl-d_5-alanine-d_3) and *N*-acetylglycine were purchased from Sigma Aldrich. Methanol (ChromHR grade) was purchased from Mallinckrodt Baker (New Jersey, USA). Highly purified water (≥18.2 Ω cm) was produced using an ion exchange system (IBIS Technology, Western Australia, Australia), followed by an Elga Purelab Ultra system with a 0.2 μm filter (Elga, High Wycombe, UK).

The concentration of sodium hypochlorite in the standard chlorination solution was confirmed by measuring the UV absorbance at 292 nm using a Cary 60 UV–Vis spectrometer from Agilent Technologies (California, USA) with a deuterium arc lamp. A molar absorptivity of sodium hypochlorite of 350 M^{-1} cm^{-1} (Morris, 1966) was assumed.

2.2. Formation of organic chloramines

Organic chloramines were prepared by adding sodium hypochlorite to specific precursor aqueous solutions at a molar ratio of sodium hypochlorite to precursors (amino acids and amines) of 0.2. The same ratio was used for the chlorination of the amides. This molar ratio has been shown to minimise side reactions and to promote monochloramine formation (Li et al., 2011). The formation of organic chloramines (and chloramides) was assessed and confirmed by scanning the UV absorbance between λ = 195 and 400 nm, using the Cary 60 UV–Vis spectrophotometer. A peak between λ = 250–280 nm is expected if an organic chloramine (or chloramide) is formed. Some precursors (tyrosine, phenylalanine, tryptophan, dimethylamine, diethylamine, ethanolamine, acetamide and acrylamide) also have UV absorption in the region of λ = 250–280 nm. For these precursors, the formation of organic chloramines (or chloramides) was confirmed by obtaining a UV spectrum (λ = 195–400 nm) of the chlorine solution before and after addition of the N-containing precursor. It was assumed that disappearance of the free chlorine peak at 292 nm indicated that all chlorine had reacted, and that only organic chloramines (or chloramides) were formed. All UV measurements of chlorinated precursors were background subtracted using the UV absorbance from the solvent (highly purified water), cuvette and precursors used in the experiment.

2.3. Measurement of degradation of organic chloramines

The rates of degradation of organic chloramines were measured over 60 min at time intervals as indicated in Table 1. The rate was measured four times for each individual organic chloramine. Two different measurement methods described in our previous work (How et al., 2015) were used to determine the rate of formation and degradation of organic chloramines. Briefly, a direct UV method measuring λ = 255 nm was used to measure the degradation of organic chloramines where there was no interference from its precursor or its by-products in the spectral region λ = 250–280 nm. A triiodide colorimetric method was used for the measurement for organic chloramines with interferences from their precursor or their by-products in the spectral region λ = 250–280 nm. For the triiodide colorimetric method, glacial acetic acid (125 μL) and potassium iodide (125 μL of a 15 g L^{-1} solution) were added to 2.5 mL of sample. Organic chloramines will oxidise the iodide into triiodide, producing a pale yellow solution in an acidic environment. The absorbance of the sample was measured at λ = 353 nm and the concentration of organic chloramine was determined using an external calibration. The triiodide colorimetric method will measure the sum of all oxidants including inorganic monochloramine (MCA), inorganic di/tri-chloramines or organic di/tri-chloramines. Monochlor F was used to measure the concentration of inorganic monochloramine and it was assumed that inorganic di/tri-chloramines were not formed under the reaction conditions used.

Table 1
Time interval and duration used for the determination of the stability of selected organic chloramines.

Direct UV method	Time interval	1 min	5 min	10 min
	Duration	1–10 min	10–30 min	30–60 min
Triiodide method	Time interval	5 min		10 min
	Duration	1–30 min		30–60 min