WATER RESEARCH 47 (2013) 1308–1316

Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

The contribution of dissolved organic nitrogen and chloramines to nitrogenous disinfection byproduct formation from natural organic matter

Yi-Hsueh Chuang, Angela Yu-Chen Lin, Xiao-huan Wang, Hsin-hsin Tung[*]

Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei City 10673, Taiwan

ARTICLE INFO

Article history:
Received 24 July 2012
Received in revised form
20 November 2012
Accepted 27 November 2012
Available online 17 December 2012

Keywords:
Nitrogenous disinfection byproduct
Haloacetonitrile
N-nitrosodimethylamine
Chloramination

ABSTRACT

The direct incorporation of chloramines and dissolved organic nitrogen (DON) may provide the nitrogen for nitrogenous disinfection byproducts (N-DBPs). This study explores the contributions of natural DON and chloramine incorporation to the formation of N-DBPs during chloramination. This study also evaluates the relationship between N-DBPs and carbonaceous DBPs by investigating four sources of dissolved organic matter with different DON-to-dissolved organic carbon (DOC) ratios. During chloramination, dihaloacetonitrile (DXAN) formation is correlated with the summation of trihalomethanes (THMs) and dichloroacetic acids (DXAAs) yield in molar basis at pH > 6. This study tests the formation kinetics of THMs, DXAAs, and DXANs during chloramination, explores the changes in DBP formation potential before and after a sequence of ozonation and chloramination, and tracks the nitrogen source of dichloroacetonitrile. The results support the hypothesis that THMs, DXAAs, and DXANs mainly derive from similar precursors upon chloramination. In addition, the precursor of HANs was approximately 10% (on a molar basis) of that of THMs and HAAs combined. The N-nitrosodimethylamine (NDMA) formation potential is correlated with DON/DOC in hydrophilic and transphilic fractions. Isotope ^{15}N-labeled monochloramine coupled with LC-electrospray ionization-tandem mass spectrometry was used to explore the nitrogen source of NDMA formed in chloraminated organic fractions. The results indicate that the nitroso group of the formed NDMA originates mainly from chloramines.

1. Introduction

Dissolved organic nitrogen (DON) is an important precursor of nitrogenous disinfection byproducts (N-DBPs) such as haloacetonitriles (HANs) and N-nitrosodimethylamine (NDMA) (Lee et al., 2007). These potential carcinogens can form during the chlorine or chloramine disinfection process. The use of chloramines has recently gained in popularity because it can effectively control trihalomethanes (THMs) and haloacetic acids (HAAs). However, chloramination may increase the formation of toxic N-DBPs (Lee et al., 2007), especially in water with frequent algae blooms, which may lead to higher organic nitrogen concentration.

Some studies have reported that HANs may be derived from organic nitrogen moieties of dissolved organic matter (DOM). Amino acids, heterocyclic nitrogen in nucleic acids (e.g. cytosine), algae cells, and extracellular organic matter have been suggested as the likely precursors of HANs upon reacting with chlorine or chloramines (Bond et al., 2009; Fang et al., 2010; Yang et al., 2010, 2011; 2012; Young and Uden,

---

[*] *Corresponding author*. Tel.: +886 2 3366 4404; fax: +886 2 2392 8830.
E-mail address: htung@ntu.edu.tw (H.-h. Tung).

0043-1354/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2012.11.046

1994). Studies also report that dichloroacetonitrile (DCAN) tends to form at higher concentration with free chlorine in organic fractions with high DON concentration (Dotson et al., 2009). However, this association (DCAN vs. DON) is not clear upon chloramination in natural waters (Lee et al., 2007; Yang et al., 2008). During chloramination, DCAN can form via the hydrolysis of N-chloroimine produced through the direct incorporation of chloramines into diketone moieties of DOM (Yang et al., 2008). Specific ultraviolet absorbance (SUVA) ($R^2 = 0.88$) is positively correlated with DCAN in chloraminated natural waters (Yang et al., 2008), suggesting these diketone moieties for HAN formation may be generated from the aromatic content within DOM upon chloramination. These moieties might also serve the precursor pool for THMs or HAAs, since studies have revealed correlations among dichloroacetic acid (DCAA), chloroform, DCAN, and the intensity of excitation-emission matrix fluorescence spectra at Regions II + IV (i.e., aromatic-like and microbial byproducts) in chloraminated natural waters or surrogate compounds (Bond et al., 2009; Lee et al., 2007; Yang et al., 2008). In addition, transformation of β-diketone moieties into THMs or HAAs is likely fast reactions during oxidation (e.g., chlorination) (Dickenson et al., 2008; Gallard and von Gunten, 2002). HANs derived from these moieties might be kinetically coherent with that of THMs or HAAs, yet the relationship of the formation kinetics among these DBPs has not been reported.

Previous studies reveal the importance of DON on NDMA formation and their positive correlation in natural waters (Dotson et al., 2009; Lee et al., 2007). Proposed reaction pathways for NDMA formation from DMA and chloramines involve the formation of unsymmetrical dimethylhydrazine (UDMH) or chlorinated-UDMH as intermediates (monochloramine-UDMH and Cl-UDMH process) (Choi and Valentine, 2002; Schreiber and Mitch, 2006). Degradation of tertiary-, quaternary- or poly-amines into DMA during chloramination is also a beginning step for NDMA formation (Kemper et al., 2010; Mitch and Schreiber, 2008; Park et al., 2009). Monochloramine-UDMH or Cl-UDMH pathways indicate that one of the nitrogen atoms (dimethyl group) originates from DMA. These studies suggest that alkylamines provide half of the nitrogen atoms of NDMA. In addition, a number of studies indicate that amine groups on model compounds (e.g., pharmaceuticals and personal care products) can serve the NDMA precursor pool (Le Roux et al., 2011; Shen and Andrews, 2011a, 2011b). Their high NDMA yields suggest an alternative mechanism involving nucleophilic substitution by chloramines, instead of electrophilic substitution (Le Roux et al., 2011; Shah and Mitch, 2012). However, the formation mechanism of NDMA from DOM might be different from these amine-based precursors. Studies report that SUVA cannot act as an indicator for NDMA formation in different water sources (Chen and Valentine, 2007, 2008; Dotson et al., 2009). Nevertheless, the linear relationship between the changes in $SUVA_{272}$ ($-\Delta SUVA_{272}$) and NDMA formation concentration during DOM chloramination suggests that the majority of NDMA precursors are produced through the oxidation of natural organic matter (NOM) (Chen and Valentine, 2007); while the generation of amine-based precursors does not involve the breakage of double bonds (Kemper et al., 2010; Mitch and Schreiber, 2008; Park et al., 2009), which might only reflect minor changes in SUVA value. Information regarding the nitrogen source of NDMA during DOM chloramination was limited. Therefore, exploring nitrogen sources is needed and can help clarify the formation pathways of NDMA in natural waters.

This study explores the nitrogenous DBP formation upon chloramination in natural waters, with an emphasis on the contribution of chloramine incorporation and natural DON. This study also investigates the relationships among DBP species, especially from kinetic and structural aspects. The results of this study provide a better understanding of N-DBP formation in real water.

2. Material and methods

2.1. Water sources and fractionation

Four different DOM sources were investigated in this study: Surface water GP and ST were collected from two eco-ponds. TH was collected from a water reservoir and a model DOM – SRN (Suwannee River NOM, RO isolation, Cat. #1R101N) was purchased from the International Humic Substance Society (IHSS). Raw water from GP and TH were algae-rich with high chlorophyll-A concentrations (64 μg L^{-1} and 70 μg L^{-1}, respectively). Raw waters were filtered with 0.5 μm glass fiber filters. The DOM in the filtrate was concentrated by reverse osmosis (Ouellet et al., 2008). The NOM fractionation technique was applied following a previous study with slight modifications (Yang et al., 2008). XAD-7HP and XAD4 resins were used to separate DOM into six fractions based on hydrophobicity and functional group, the hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), transphilic acid (TPIA), transphilic neutral (TPIN), and hydrophilic (HPI).

2.2. DBP formation potential test

Monochloramine was freshly prepared before each experiment. Ammonium chloride solution (at pH 8.5) was refrigerated (4 °C) for 1 h. Sodium hypochlorite (6–14%, Sigma–Aldrich, USA) was added at a molar ratio of 1 NaOCl:1.2 ammonium chloride to generate a monochloramine concentration of approximately 7000 mg L^{-1} as Cl_2. A phosphate buffer maintained the desired pH of each DBP FP reaction (10 mM). The required dosage of monochloramine in DBP FP tests were adopted from Dotson et al. (2009). The DBP formation potential (DBP FP) tests were conducted (headspace-free) with chloramines: NH_2Cl dosage (as mg-Cl_2 L^{-1}) = 3*[DOC] (mg L^{-1}). The method of NDMA FP testing was adopted from Mitch et al. (2003), with modifications. Samples of 3.5 mg L^{-1} DOC (10 mM phosphate buffered at pH 7.2) were dosed with a high dosage of chloramines (i.e., 45 mg of Cl_2 per mg DOC). The reaction was conducted at 25 °C in the dark for seven days. At the end of the tests, residual chlorines were analyzed by N,N-diethyl-p-phenylenediamine colorimetric method (at 515 nm) (Method 8167, Hach Company, USA), and quenched by ascorbic acid. The THM, HAN, and NDMA concentrations were analyzed immediately. For HAA analysis, the samples were acidified with a 1.5 mL sulfuric acid (98%, Sigma–Aldrich, USA) and preserved at 4 °C (<14 d)