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The roles of tertiary amine structure, background organic matter and chloramine species on NDMA formation

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ARTICLE INFO

Article history:

Received 24 July 2012

Received in revised form

12 October 2012

Accepted 7 November 2012

Available online 23 November 2012

Keywords:

Nitrosamines

NDMA

Chloramination

Formation potential

Disinfection by-products

Tertiary amines

ABSTRACT

N-nitrosodimethylamine (NDMA), a probable human carcinogen, is a disinfection by-product that has been detected in chloraminated and chlorinated drinking waters and wastewaters. Formation mechanisms and precursors of NDMA are still not well understood. The main objectives of this study were to systematically investigate (i) the effect of tertiary amine structure, (ii) the effect of background natural organic matter (NOM), and (iii) the roles of mono vs. dichloramine species on the NDMA formation. Dimethylamine (DMA) and 20 different tertiary aliphatic and aromatic amines were carefully examined based on their functional groups attached to the basic DMA structure. The wide range (0.02–83.9%) of observed NDMA yields indicated the importance of the structure of tertiary amines, and both stability and electron distribution of the leaving group of tertiary amines on NDMA formation. DMA associated with branched alkyl groups or benzyl like structures having only one carbon between the ring and DMA structure consistently gave higher NDMA yields. Compounds with electron withdrawing groups (EWG) reacted preferentially with monochloramine, whereas compounds with electron donating group (EDG) showed tendency to react with dichloramine to form NDMA. When the selected amines were present in NOM solutions, NDMA formation increased for compounds with EWG while decreased for compounds with EDG. This impact was attributed to the competitions between NOM and amines for chloramine species. The results provided additional information to the commonly accepted mechanism for NDMA formation including chloramine species reacting with tertiary amines and the role of the leaving group on overall NDMA conversion.

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1. Introduction

Nitrosamines are a group of compounds classified as probable human carcinogens in water at concentrations as low as 0.2 ng/L associated with a 10^{-6} lifetime cancer risk (US EPA, 2002). They form as disinfection by-products (DBPs) in chloraminated and chlorinated drinking waters and wastewaters (Choi and Valentine, 2002a,b; Choi et al., 2002; Mitch and

Sedlak, 2002, 2004). N-nitrosodimethylamine (NDMA) is the most commonly detected and reported nitrosamine in drinking water. Although there are currently no federal regulations for nitrosamines in drinking water in the United States, the Environmental Protection Agency (USEPA) has recently identified nitrosamines as one of three potential groups of contaminants highlighted for possible regulatory action in the near future (Roberson, 2011).

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<http://dx.doi.org/10.1016/j.watres.2012.11.014>

Although an organic nitrogen precursor is required for NDMA formation, there is no strong correlation between dissolved organic nitrogen concentrations and NDMA formation potentials in natural waters (Pehlivanoglu-Mantas and Sedlak, 2008; Dotson et al., 2009; Aydin et al., 2012). Research evaluating the NDMA formation potential of several compounds has encompassed dimethylamine (DMA) (Mitch et al., 2003a, b), tertiary and quaternary amines with DMA functional groups (Lee et al., 2007; Kemper et al., 2010; Shen and Andrews, 2011a, b), natural organic matter (NOM) and fractions of NOM (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008), polyelectrolytes and ion-exchange resins (Gough et al., 1977; Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011), fungicides, pesticides, and herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008), pharmaceuticals, cosmetics (Sacher et al., 2008; Shen and Andrews, 2011a, b), and wastewater effluent/impacted waters (Krasner et al., 2004; Sedlak et al., 2005; Krasner et al., 2009; Krauss et al., 2009; Shah et al., 2012).

Different mechanisms have been proposed for NDMA formation with different oxidants (e.g., chlorine, chloramines and ozone), as reviewed in detail elsewhere (Bond et al., 2011; Shah and Mitch, 2012). For chloramination, NDMA formation was initially attributed to nucleophilic substitution reaction between monochloramine and unprotonated secondary amines (e.g., DMA) to form unsymmetrical dimethylhydrazine (UDMH) intermediates (Mitch and Sedlak, 2002; Choi and Valentine, 2002a, b). However, further studies have shown that chloramination of UDMH yielded much less NDMA than DMA (Mitch et al., 2009). Moreover, dichloramine has been shown to enhance NDMA formation from DMA through the formation of a chlorinated UDMH (Mitch et al., 2009). In the same study, Mitch and colleagues proposed that NDMA formation from quaternary or tertiary amines includes liberation of DMA moiety via reaction of chlorine or monochloramine and released DMA group further reacts with dichloramine resulting in NDMA formation. After testing of several compounds in recent years as listed above, there are some limitations to explain the formation of NDMA from different precursors using this pathway alone during chloramination. For example, (i) reported NDMA conversion rates from DMA were at most 3.0% and usually 1–2% (Choi and Valentine, 2002a, b; Choi et al., 2002; Mitch and Sedlak, 2002; Schreiber and Mitch, 2005, 2006; Lee et al., 2007; Le Roux et al., 2012a). However, some model compounds (e.g., ranitidine, dimethylbenzylamine, sumatripan) have resulted in significantly higher NDMA yields (>>5%) than DMA (Mitch et al., 2009; Le Roux et al., 2011a; Shen and Andrews, 2011a), (ii) Although the proposed pathway emphasizes the significance of dichloramine in NDMA formation, higher NDMA concentrations was observed at pH 8.8 than both pH 6.9 and 5.1 during chloramination of DMA (Schreiber and Mitch, 2005) and a similar trend was observed for natural waters (Krasner et al., 2012). Monochloramine becomes more stable with increasing pH, and significantly less amount of dichloramine is produced. Le Roux et al. (2011a) reported a decrease in NDMA formation from ranitidine when switched from

monochloramine to dichloramine (i.e., yield decreased from 80.2 to 46.8%). Therefore, the major NDMA formation pathway may not always be limited to dichloramine as the only chloramine species, (iii) the formation of NDMA may also be influenced from the components in the background water matrices (e.g., natural organic matter (NOM), bromide, other ions) (Le Roux et al., 2011b; Shen and Andrews, 2011a,b; Le Roux et al., 2012a; Luh and Marinas, 2012; Shah et al., 2012), and (iv) DMA concentrations detected in surface waters (Gerecke and Sedlak, 2003; Lee et al., 2007) or secondary municipal wastewaters (Mitch and Sedlak, 2004) did not explain the observed levels of NDMA formation.

It is evident that there is still much more to learn about the formation of NDMA in natural waters. For example, the structural characteristics of quaternary or tertiary amines with a DMA group are of importance (Shah and Mitch, 2012). The main objectives of this study were to systematically investigate (i) the effect of tertiary amine structure, (ii) the effect of background NOM, and (iii) the roles of mono vs. dichloramine species on the NDMA formation. In order to explore the effect of tertiary amine structure, DMA and 20 different tertiary aliphatic and aromatic amines were carefully selected based on their functional groups attached to the basic DMA structure. The NOM effect was initially investigated by spiking the selected amines in solution prepared with two NOM fractions alone to eliminate the confounding effects that may come from the other constituents in the background matrices of natural waters. Experiments were also conducted with Myrtle Beach raw and treated (i.e., after conventional clarification processes) waters with negligible bromide concentrations. Finally, the selectivity and sensitivity of amine precursors to monochloramine and dichloramine species were examined for selected compounds.

2. Materials and methods

2.1. Amines

DMA and twenty tertiary amines were tested for nitrosamine formation. Chemical structures and abbreviations of selected amines are given in Fig. 1. All compounds were purchased from certified vendors (Sigma–Aldrich, TCI, Matrix Scientific, and Santa Cruz Biotechnology) and used without further purification. Tertiary aliphatic amines were chosen based on their chain length and functional groups attached to basic DMA structure. Tertiary aromatic amines were also selected with variable functional groups and different heteroatoms present in the ring structures.

2.2. Experimental procedure

Formation potential (FP) tests were conducted in distilled and deionized water (DDW) with or without NOM. The NOM solutions were prepared using (i) two NOM fractions, Myrtle Beach transphilic (MB TPH) or Myrtle Beach hydrophobic (MB HPO), that were available in our laboratory from a previous study (Hong et al., 2007; Karanfil et al., 2008), and (ii) water samples, source water (MB Raw) and after conventional clarification processes before filtration (MB Treated), were also

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