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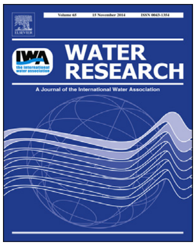

N-nitrosodimethylamine (NDMA) formation from the ozonation of model compounds

Erica J. Marti [a,b], *Aleksey N. Pisarenko* [c], *Julie R. Peller* [d], *Eric R.V. Dickenson* [a,*]

[a] *Southern Nevada Water Authority, Applied Research & Development Center, PO Box 99954, Las Vegas, NV 89193, USA*
[b] *University of Nevada, Las Vegas, Civil & Environmental Engineering and Construction, Las Vegas, NV, USA*
[c] *Trussell Technologies, San Diego, CA, USA*
[d] *Indiana University Northwest, Chemistry Department, Gary, IN, USA*

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ABSTRACT

Nitrosamines are a class of toxic disinfection byproducts commonly associated with chloramination, of which several were included on the most recent U.S. EPA Contaminant Candidate List. Nitrosamine formation may be a significant barrier to ozonation in water reuse applications, particularly for direct or indirect potable reuse, since recent studies show direct formation during ozonation of natural water and treated wastewaters. Only a few studies have identified precursors which react with ozone to form *N*-nitrosodimethylamine (NDMA). In this study, several precursor compound solutions, prepared in ultrapure water and treated wastewater, were subjected to a 10 M excess of ozone. In parallel experiments, the precursor solutions in ultrapure water were exposed to gamma radiation to determine NDMA formation as a byproduct of reactions of precursor compounds with hydroxyl radicals. The results show six new NDMA precursor compounds that have not been previously reported in the literature, including compounds with hydrazone and carbamate moieties. Molar yields in deionized water were 61–78% for 3 precursors, 12–23% for 5 precursors and <4% for 2 precursors. Bromide concentration was important for three compounds (1,1-dimethylhydrazine, acetone dimethylhydrazone and dimethylsulfamide), but did not enhance NDMA formation for the other precursors. NDMA formation due to chloramination was minimal compared to formation due to ozonation, suggesting distinct groups of precursor compounds for these two oxidants. Hydroxyl radical reactions with the precursors will produce NDMA, but formation is much greater in the presence of molecular ozone. Also, hydroxyl radical scavenging during ozonation leads to increased NDMA formation. Molar conversion yields were higher for several precursors in wastewater as compared to deionized water, which could be due to catalyzed reactions with constituents found in wastewater or hydroxyl radical scavenging.

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* *Corresponding author*. Tel.: +1 702 856 3668.
E-mail addresses: erica.marti@snwa.com, echemie@gmail.com (E.J. Marti), aleksp@trusselltech.com (A.N. Pisarenko), jpeller@iun.edu (J.R. Peller), eric.dickenson@snwa.com (E.R.V. Dickenson).

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1. Introduction

Nitrosamines, particularly *N*-Nitrosodimethylamine (NDMA), have received a great deal of attention as harmful nitrogenous disinfection byproducts. NDMA is classified as a B2 carcinogen by the U.S. Environmental Protection Agency, it is listed on the third Contaminant Candidate List (US EPA, 2012a, b), and it was part of the Unregulated Contaminant Monitoring Rule 2 (US EPA, 2013). Although no federal regulations have been established for NDMA, the California Department of Public Health has set a drinking water notification level of 10 ng/L (CPDH, 2013). The E−6 (1 in 1,000,000) cancer risk level for drinking water is 0.7 ng/L (US EPA IRIS, 2012). In addition to many direct anthropogenic sources (e.g., rubber manufacturing, circuit board manufacturing and rocket fuel production), NDMA is formed as a disinfection byproduct (DBP) in drinking water and wastewater treatment.

As potable water demands and shortages rise, more communities are considering reuse of wastewater as an option for increasing the overall water supply. Ozone is effective for treating pathogens and trace organic contaminants and, therefore, is a promising treatment technology for potable water reuse applications. Its treatment versatility for pre- and post-disinfection, decolorizing, taste and odor removal, coagulation assistance, and zero residual are some of the other advantages. However, the formation of ozone byproducts, such as NDMA, could be a barrier to the use of ozone in potable water reuse.

NDMA formation is commonly associated with chloramination (Mitch et al., 2003; Choi and Valentine, 2002), but recent studies indicate that direct formation during ozonation also occurs (Andrzejewski et al., 2008; von Gunten et al., 2010; Oya et al., 2008; Kosaka et al., 2009; Schmidt and Brauch, 2008; Nawrocki and Andrzejewski, 2011; Pisarenko et al., 2012; Padhye et al., 2013; Hollender et al., 2009). Initially, the chloramination pathway was thought to involve nucleophilic substitution between monochloramine and a secondary amine (Choi and Valentine, 2002; Mitch and Sedlak, 2002). This reaction resulted in unsymmetrical dimethylhydrazine (UDMH), which was subsequently oxidized by chloramines to form NDMA. The modified pathway involves the reaction of dichloramine and a model secondary amine, dimethylamine (DMA), which forms chlorinated unsymmetrical dimethylhydrazine (Cl-UDMH) as an intermediate. Dissolved oxygen oxidizes Cl-UDMH to NDMA (Schreiber and Mitch, 2006). On the other hand, very little is known about the NDMA formation pathway and any intermediates that are formed with ozonation. von Gunten et al. (2010) proposed a mechanism for NDMA formation from dimethylsulfamide (DMS), which is a degradation product of the fungicide tolylfluanid. The mechanism is bromide-catalyzed and results in the loss of $-SO_2$ as a leaving group and N–N bond formation. While UDMH conversion to NDMA is an oxidation reaction, additional pathways for other precursors' reactions with ozone have not been identified.

In order for NDMA to form as a disinfection byproduct from ozonation, certain compounds must be present in the water. Beside DMS and other metabolites of tolylfluanid, a few other precursors have been identified, including daminozide, 1,1-dimethylhydrazine (UDMH), dimethyldithiocarbamate, methylene blue, *N*,*N*-Dimethyl-*p*-phenilenediamine (DMPD), 1,1,1′,1′-Tetramethyl-4,4′-(methylenedi-p-phenylene)disemicarbazide (TMDS), 4,4′-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS) and poly(diallyldimethylammoniumchloride) (polyDADMAC). The chemical structures of these compounds include hydrazines, semicarbazides, sulfamides, and tertiary amines with a dimethylamine functional group (abbreviated as dimethylamine). In particular, compounds with dimethylamine bonded directly to a nitrogen atom or separated with a good leaving group (e.g., $-SO_2$) form NDMA with significant molar conversion yields (i.e., 10–80%) (von Gunten et al., 2010; Kosaka et al., 2009; Schmidt and Brauch, 2008). Precursors with the dimethylamine and no additional nitrogen may also form NDMA upon ozonation, but the yields are <0.01% (Oya et al., 2008; Padhye et al., 2013, 2011).

In more complex water matrices, certain factors have been shown to impact NDMA formation with ozone, including dissolved ions and pH. For example, bromide ions catalyze the reaction of DMS with ozone (von Gunten et al., 2010). Oya et al. (2008) found that NDMA formation by ozonation of dimethylamine dyes increased in river water compared to deionized water. They also noticed increased NDMA formation with increased pH; however, this was attributed to changes in the reaction mechanism at different pH. Dissolved molecular ozone and hydroxyl radicals can be involved in both formation (Andrzejewski et al., 2008; Schmidt and Brauch, 2008) and destruction of NDMA (Mezyk et al., 2004; Lee et al., 2007a), but the extent of each oxidant's role is not well understood.

The goal of this study was to identify specific organic structures that may contribute to the direct formation of NDMA by ozonation. Only a few precursors have been identified in literature and there is much to gain in understanding which compounds lead to NDMA formation. If model precursors can be identified, then specific strategies could be utilized to identify them and remove the precursors prior to ozonation and limit the production of DBPs.

2. Materials and methods

2.1. *Tested waters and equipment*

The tested waters included ultrapure water and pilot-scale membrane bioreactor treated wastewater (0.032 MGD). Ultrapure water was buffered at neutral pH with phosphate buffer (1 mM or 5 mM final concentration). The neutral pH (6.7–7.1) wastewater came from a municipal source with treatment consisting of primary sedimentation with ferric chloride addition, biological secondary treatment with partial nitrification, and tertiary membrane microfiltration (0.40 μm nominal pore size). Table S3 contains water quality information and key treatment parameters. No additional filtration was performed and wastewater was stored at 4 °C for preservation prior to bench-scale work.

Ozonated water was generated using an oxygen-fed generator (model CFS-1A, Ozonia North America, Inc., Elmwood Park, NJ, USA) to diffuse ozone into ultrapure water as described previously (Wert et al., 2009). The ozone stock solution was typically between 65 and 85 mg/L. Aliquots of the

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