Determinants of disinfectant pretreatment efficacy for nitrosamine control in chloraminated drinking water

Daniel L. McCurry [a], Stuart W. Krasner [b], Urs von Gunten [c, d], William A. Mitch [a, *]

[a] Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA
[b] Metropolitan Water District of Southern California, La Verne, CA 91750, USA
[c] EAWAG, Swiss Federal Institute of Aquatic Science and Technology, CH-8600, Dübendorf, Switzerland
[d] School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

ARTICLE INFO

ABSTRACT

Utilities using chloramines need strategies to mitigate nitrosamine formation to meet potential future nitrosamine regulations. The ability to reduce NDMA formation under typical post-chloramination conditions of pretreatment with ultraviolet light from a low pressure mercury lamp (LPUV), free chlorine (HOCl), ozone (O_3), and UV light from a medium pressure mercury lamp (MPUV) were compared at exposures relevant to drinking water treatment. The order of efficacy after application to waters impacted by upstream wastewater discharges was $O_3 > HOCl \approx MPUV > LPUV$. NDMA precursor abatement generally did not correlate well between oxidants, and waters exhibited different behaviors with respect to pH and temperature, suggesting a variety of source-dependent NDMA precursors. For wastewater-impacted waters, the observed pH dependence for precursor abatement suggested the important role of secondary or tertiary amine precursors. Although hydroxyl radicals did not appear to be important for NDMA precursor abatement during O_3 or MPUV pretreatment, the efficacy of MPUV correlated strongly with dissolved organic carbon concentration (p = 0.01), suggesting alternative indirect photochemical pathways. The temperature dependences during pre- and post-disinfection indicated that NDMA formation is likely to increase during warm seasons for O_3 pretreatment, decrease for HOCl pretreatment, and remain unchanged for MPUV treatment, although seasonal changes in source water quality may counteract the temperature effects. For two waters impacted by relatively high polyDADMAC coagulant doses, pretreatment with HOCl, O_3, and MPUV increased NDMA formation during post-chloramination. For O_3 pretreatment, hydroxyl radicals likely led to precursor formation from the polymer in the latter tests. MPUV treatment of polymer-impacted water increased subsequent NDMA formation through an indirect photochemical process. Many factors may mitigate the importance of this increased NDMA formation, including the low polyDADMAC doses typically applied, and simultaneous degradation of watershed-associated precursors.

1. Introduction

After the recognition in the 1970s that chlorination of drinking water produces potentially carcinogenic halogenated disinfection byproducts (DBPs) (Rook, 1974; Bellar et al., 1974) and subsequent regulatory limitations on certain DBPs (e.g., trihalomethanes (THMs)), drinking water utilities have sought to reduce DBP concentrations in finished waters while maintaining adequate pathogen inactivation (Sedlak and von Gunten, 2011). In the United States, utilities are increasingly considering combinations of strong primary disinfectants (e.g., free chlorine, ozone, UV light) with chloramination to maintain a disinfectant residual in the distribution system. Chloramination generally reduces the concentration of regulated halogenated DBPs, but has been associated with formation of the potent carcinogen, N-nitrosodimethylamine (NDMA) (Mitch et al., 2003; Schreiber and Mitch, 2006a; Shah and Mitch, 2012; Krasner et al., 2013a). A 0.7 ng/L concentration of NDMA in drinking water is associated with a 10^{-6} lifetime excess cancer risk (US EPA, 2012a). NDMA is being considered by the U.S. Environmental Protection Agency for federal regulation in drinking water (US EPA, 2012b).

Among the 7 specific nitrosamines measured by US EPA Method 521, NDMA has been the most frequently detected in chloraminated drinking waters (Russell et al., 2012; Krasner et al., 2013a), although it may be a minor constituent of the total N-nitrosamine pool (Dai and Mitch, 2013). NDMA formation has been associated with wastewater-impacted source waters (Schreiber and Mitch, 2006b) and with the use of certain quaternary amine-based coagulation polymers (i.e., polyDADMAC and polyamines) (Najm and Trussell, 2001; Park et al., 2009; Padhye et al., 2011) or anion exchange resins (Kimoto et al., 1980; Najm and Trussell, 2001; Kemper et al., 2009) during drinking water treatment. The precursors in wastewater-impacted drinking waters have been poorly characterized, but may include tertiary amines, which can be nitrosated to secondary nitrosamines (Geuther, 1865), and quaternary amines. Although NDMA yields from chloramination of most tertiary amines are comparable to the ~2% yield observed from dimethylamine (Mitch and Sedlak, 2004; Mitch and Schreiber, 2008), a subset of tertiary amines (α-aryl-N,N-dimethylamines) can produce NDMA during chloramination at yields of up to 90% (Shen and Andrews, 2011). These functional groups are found in certain pharmaceuticals (e.g., ranitidine) that may occur as microconstituents in wastewaters. Alternatively, quaternary amines produce nitrosamines at lower yields than tertiary amines (Kemper et al., 2010), but are macroconstituents of certain consumer products (e.g., shampoos) that enter sewage. Unfortunately, specific watershed-associated precursors responsible for significant NDMA formation have not yet been identified (Shah and Mitch, 2012; Krasner et al., 2013a).

To meet potential future regulations on nitrosamine levels in drinking waters while retaining chloramines for secondary disinfection, utilities are in urgent need of practical strategies to mitigate nitrosamine formation. Two strategies are being considered: physical removal of precursors prior to chloramination, and precursor abatement by the pretreatments generally applied as primary disinfectants upstream of chloramination. Although NDMA precursors are poorly removed by coagulation, sedimentation, and conventional granular media filtration, wastewater-associated precursors (but not polyDADMAC-derived) are effectively removed by activated carbon (Hanigan et al., 2012). Previous work demonstrated that pretreatment of model precursors or natural waters with free chlorine (HOCl; used here to represent the sum of free chlorine species) (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Selbes et al., 2014), ozone (O_3) (Lee et al., 2007; Selbes et al., 2014), chlorine dioxide (ClO_2) (Lee et al., 2007), permanganate (Chen and Valentine, 2008) or ferrate (Lee et al., 2008) generally reduced NDMA formation during subsequent chloramination. However, pretreatment of polyDADMAC in deionized water either did not affect (HOCl and ClO_2) or increased (O_3) NDMA formation during post-chloramination (Selbes et al., 2014; Park et al., 2015).

Most previous research on pretreatment either used model precursors or treated natural waters with higher pretreatment exposures than are likely to be used in practice. These previous studies do not indicate the ability of pretreatment at exposures relevant to current disinfection practice to mitigate nitrosamine formation from the poorly characterized precursors in authentic drinking waters. However, a recent study (Shah et al., 2012) evaluated the effectiveness for NDMA control of HOCl, O_3, ClO_2, and MPUV pretreatment applied to natural drinking waters at disinfectant exposures relevant to Giardia control, when followed by typical chloramination conditions. The order of efficacy generally was O_3 > HOCl > MPUV >> ClO_2. Increasing pretreatment exposures were associated with increasing formation of other DBPs specific to each pretreatment, suggesting the need to balance NDMA control against the production of other DBPs. However, this initial study did not distinguish types of precursor impacts (e.g., cationic polymer or watershed-associated precursors) or attempt to systematically vary reaction conditions (e.g., pH, temperature) within each water to understand the effect of reaction conditions.

Using pretreatment and chloramination exposures typical for disinfection practice, the overall goal of this research is to characterize the efficacy of pretreatments for control of nitrosamines in authentic drinking waters, and the effect of water quality conditions on nitrosamine mitigation. The first objective of this research was to compare the efficacy for NDMA control of pretreatments by LPUV, which is commonly used during water treatment, but has not been evaluated under realistic treatment conditions, to HOCl, O_3, and MPUV, which were previously shown to be effective (Shah et al., 2012). LPUV lamps emit predominantly at 254 nm while MPUV lamps emit polychromatic light, enabling an evaluation of the effect of UV wavelength between the two most commonly used lamps. A second objective was to characterize the effect on NDMA control of three pretreatment conditions that both shed light on the pathways associated with NDMA precursor transformation and that have practical importance to drinking water treatment. First, this study evaluated the importance of hydroxyl radicals for NDMA control by O_3 and MPUV pretreatment, with implications for plants practicing advanced oxidation processes (AOPs). Second, this work evaluated the effect of pretreatment pH on NDMA control. In the previous work (Shah et al., 2012), although chloramination pH was controlled at pH 8, pretreatments were applied at the ambient pH of the source or treated waters, obscuring the effect of pH on pretreatment. This is important, as where the pretreatment is placed in the process train (e.g., plant influent, settled water, softened water) will result in significantly different pH levels for the pretreatment. Third, this research isolated the importance of temperature for both pretreatment and post-chloramination. The results have important implications for seasonal variations in the efficacy of NDMA control by pretreatment. Lastly, the research evaluated whether differences in pretreatment efficacy varied depending on the type of precursors (i.e., wastewater-impacted source water or cationic polymer usage). Recognizing the poor characterization of nitrosamine precursors in authentic waters, particularly watershed-associated precursors, this work evaluated trends across multiple source waters to determine the extent to which any trends observed were common.

2. Materials and methods

2.1. Source water sampling

Fourteen samples were collected at ten drinking water utilities (i.e., four utilities were sampled twice) upstream of any disinfectant application from a reservoir, the plant influent or the effluents of the sedimentation, filtration or softening units (Table 1). Source waters for utilities 1–8 were impacted by upstream wastewater discharges or were treated with quaternary amine-based polymers (polyDADMAC or polyamine). Table 1 provides basic water quality parameters.

Waters 2B, 6, 7A and 7B were impacted by the use of polyDADMAC and also had measureable sucralose concentrations, suggesting wastewater discharges upstream (Table 1). Although previous work evaluated the effect of HOCl and O_3 pretreatment of polyDADMAC in deionized water, the impact of natural organic matter was unclear, including the potential fractionation of polyDADMAC-associated precursors during coagulation and settling. To isolate the effect of polyDADMAC within natural waters, two additional water samples were collected from pristine drinking water sources (waters 9 and 10 in Table 1; no NDMA was detectable after chloramination as described below) and coagulated with a very high (6 mg/L, water 9) and moderate (1 mg/L, water 10) dose of