

THE ROLE OF HYDROXYLAMINE AS A NITRIFICATION INTERMEDIATE IN N-NITROSAMINE FORMATION

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NDMA FORMATION

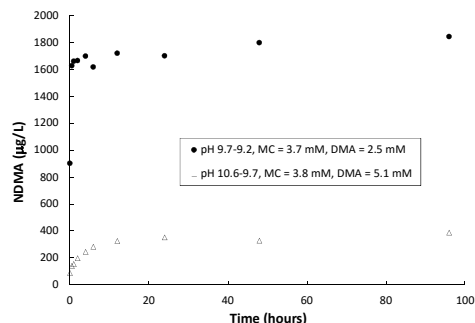


Figure 3. NDMA formation kinetics with the addition of DMA (2.5 or 5.1 mM) to 3.7 mM NH_2Cl in 13 mM bicarbonate buffer.

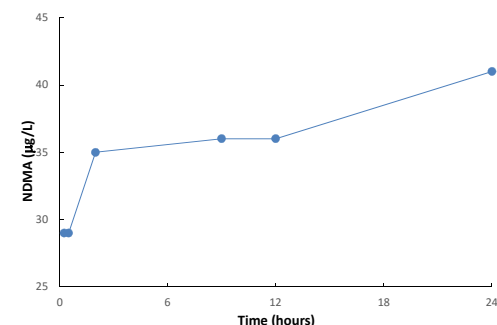


Figure 4. NDMA formation kinetics with 10 μM DMA and 0.48 mM NH_2Cl in 5 mM bicarbonate buffer. The pH of both DMA and NH_2Cl solution were adjusted to 10 ± 0.1 before mixing.

Figure 3 shows approximately one order of magnitude higher NDMA formation occurred when the DMA concentration was decreased by half, an illogical result. This was attributed to pH drift, which was 0.5-1.0 log units throughout the 100-hour experiment and illustrates that pH has a significant role in the NDMA reaction mechanism. In Figure 4, the pH was control at 10 ± 0.1 . Ongoing experiments are being conducted between pH 6-10 with various DMA and NH_2Cl concentrations.

CURRENT AND FUTURE WORK

Upcoming experiments will focus on results from batch kinetic experiments with DMA, chloramines, and hydroxylamine, performed over a range of pH and dissolved oxygen conditions. Liquid/liquid extraction along with gas chromatography – mass spectrometry (GC-MS) and the TONO assay will be used to measure NDMA and total *N*-nitrosamines, respectively. Results from these experiments will be used to postulate a novel reaction mechanism for *N*-nitrosamines, one that likely involves intermediates from the breakdown of monochloramine, the predominant chloramine species present at the pH range of interest in distribution systems (pH 7-9), and one that is especially relevant to systems undergoing nitrification.

REFERENCES AND FUNDING ACKNOWLEDGMENTS

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The formation of *N*-nitrosamines, and *N*-Nitrosodimethylamine (NDMA) in particular, in drinking water systems that use chloramines is a concern because of their potential carcinogenicity and occurrences in finished water at toxicologically relevant levels. According to the IRIS database, a 10^{-6} lifetime cancer risk level for NDMA in drinking water is 0.7 ng/L. The widely accepted mechanism for NDMA formation involves a nucleophilic substitution between dichloramine and unprotonated secondary amines to form an unsymmetrical dimethylhydrazine (UDMH) intermediate, followed by UDMH oxidation to form NDMA. This reaction takes days to occur and involves a spin-forbidden reaction, specifically the incorporation of ground-state molecular oxygen as a triplet to form NDMA, which is thermodynamically unfavorable. As such, it is possible that other *N*-nitrosamine formation pathways exist in chloramination systems, which would have implication for control strategies to curb formation of these compounds. Zeng and Mitch (2016) showed that nitrification in storage facilities and distribution systems can lead to the elevated concentrations of NDMA and total Nitrosamines. However, the underlying reaction mechanisms have not been elucidated.

Preliminary experiments were completed using a chemiluminescence-based total *N*-nitrosamine (TONO) assay and demonstrated that the reaction between hydroxylamine (NH_2OH , a nitrification intermediate formed during nitrification process), monochloramine (NH_2Cl) and dimethylamine (DMA, a model NDMA precursor) produces significantly more TONO within hours compared to the reaction between monochloramine and DMA only. Our hypothesis is that the reaction is initiated by the break down of monochloramine, forced by hydroxylamine and dissolved oxygen, to form peroxyxynitrite. This reaction is not spin-forbidden so it is more energy favorable. Peroxyxynitrite is a known nitrosating agent and likely to react with the precursors such as dimethylamine to form NDMA and other *N*-Nitrosamines.

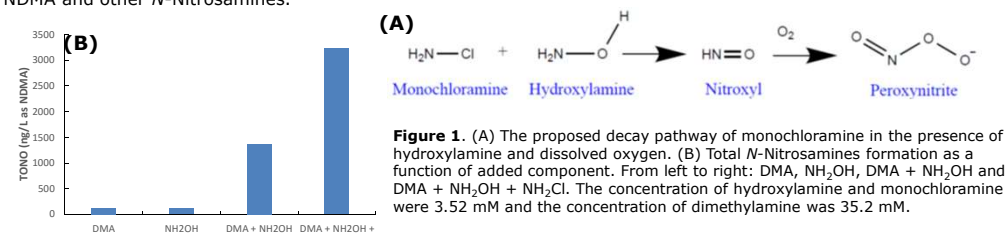


Figure 1. (A) The proposed decay pathway of monochloramine in the presence of hydroxylamine and dissolved oxygen. (B) Total *N*-Nitrosamines formation as a function of added component. From left to right: DMA, NH_2OH , DMA + NH_2OH and DMA + NH_2OH + NH_2Cl . The concentration of hydroxylamine and monochloramine were 3.52 mM and the concentration of dimethylamine was 35.2 mM.

METHODS

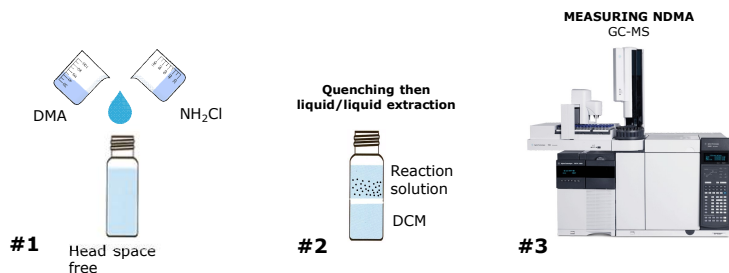


Figure 2. Illustrative graphic of the experimental protocol used for NDMA batch kinetic experiments

A schematic of the experimental protocol is shown in Figure 2.

Monochloramine was prepared by adding hypochlorite (OCl^-) to ammonium chlorite (NH_4Cl) solution at 4.53:1 $\text{Cl}_2\text{:N}$ mass ratio. UV absorbance at $\lambda = 245$ nm was used to quantify monochloramine concentration.

The bicarbonate buffer was used for pH 10, borate buffer for pH 9, phosphate buffer for pH 8 and 7. The pH of both DMA and NH_2Cl solutions were adjusted with buffer solution to the desired value before mixing.

Reaction solution was quenched by 100 mg quenching salts (1.8 g ascorbic acid, 1 g KH_2PO_4 and 39 g Na_2HPO_4)

NDMA was extracted by liquid/liquid extraction using dichloromethane (DCM) and quantified by GC-MS.