New *N*-nitrosodimethylamine (NDMA) precursors that react with ozone: Implications for water reuse

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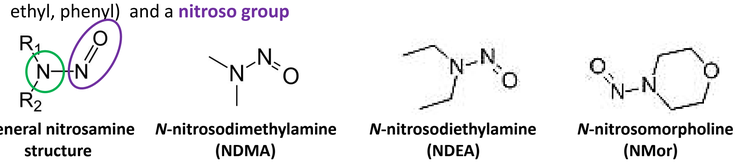
Key Terms

DBP = Disinfection Byproduct

An unintentional product resulting from a disinfection process

Nitrosamines

A class of compounds containing an **amine group** with various substituents (e.g., methyl, ethyl, phenyl) and a **nitroso group**



General nitrosamine structure | *N*-nitrosodimethylamine (NDMA) | *N*-nitrosodiethylamine (NDEA) | *N*-nitrosomorpholine (NMor)

Figure 1: Example nitrosamine compounds

Introduction

Nitrosamines are a toxic class of disinfection byproducts commonly associated with chloramination, but recent studies indicate that direct formation during ozonation is a possible pathway. Six nitrosamines are listed in U.S. EPA's Unregulated Contaminant Monitoring Rule 2, several nitrosamines are included on the most recent U.S. EPA Contaminant Candidate List, and the California Department of Public Health (CDPH) has already established drinking water notification levels of 10 ng/L for N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine, and N-nitrosodi-n-propylamine.

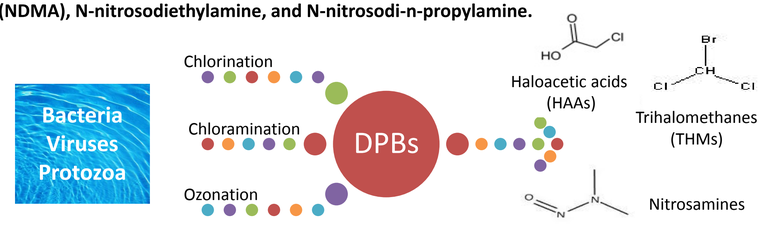


Figure 2: Representation of the disinfection process and formation of disinfection byproducts

Ozonation is a promising treatment step for water reuse. Compared to the "gold standard" with reverse osmosis and advanced oxidation, ozone requires less energy and does not result in a waste brine. This makes ozone more cost-effective. However, the formation of nitrosamines may be a significant barrier to the use of ozonation in water reuse applications, particularly for potable reuse.

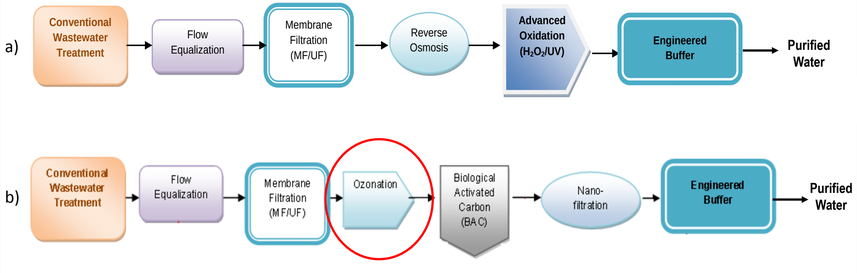


Figure 3: Water reuse treatment processes: a) "gold standard" and b) ozonation

Research Issue

Initial Question:

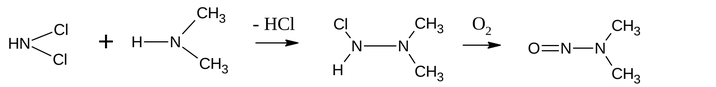
What compounds (precursors) are in wastewater that react with ozone to form NDMA?

? + O_3 → NDMA

Hypothesis:

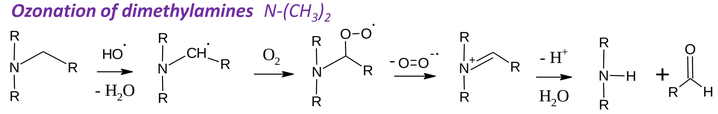
Research suggests that compounds with the **N-N-$(CH_3)_2$** building block will form NDMA.

Chloramination of dimethylamines *N-$(CH_3)_2$*



can form nitrosamines

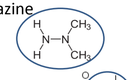
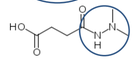
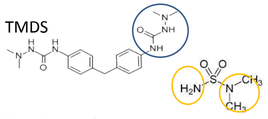
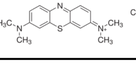
Ozonation of dimethylamines *N-$(CH_3)_2$*

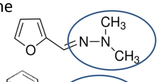
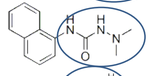
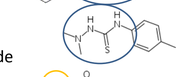
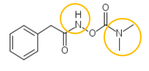


forms an aldehyde as the major product

Methodology

Choosing Precursors to Test:

Name	Structure	Yield	Ref.
1,1-Dimethylhydrazine (UDMH)		80%	1
Daminozide		55%	1
TMDS		27%	2
Dimethylsulfamide (DMS)		52%	1
Methylene blue (and other dyes)		8.3 x 10^{-3} %	3

Group	Ex. Structure	Similarity
Dimethylhydrazone		UDMH
Dimethyl-semicarbazide		TMDS
Dimethyl-thiosemicarbazide		
Dimethyl-carbamate		DMS

1. Schmidt and Brauch, 2008
2. Kosaka et al., 2009
3. Oya et al., 2008

Figure 4: Strategy for determining potential NDMA precursors

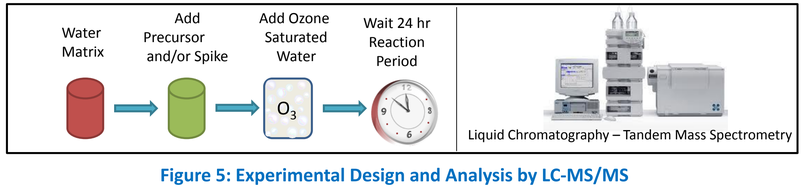
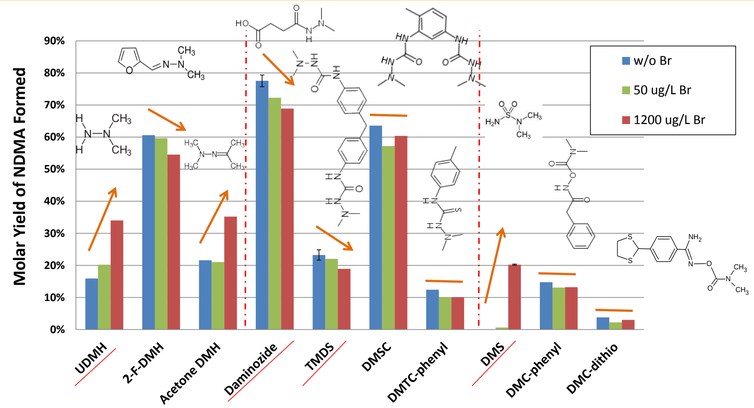


Figure 5: Experimental Design and Analysis by LC-MS/MS

Results



*Target compounds at 100 uM, ozone spiked at 1 mM (~10 fold excess), pH 7

Figure 6: Molar Yield for Precursors in Deionized Water

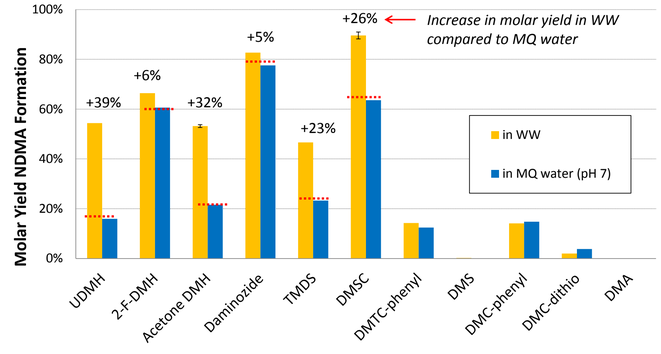


Figure 7: Molar Yield for Precursors in Wastewater

Conclusions & Implications

- Molar Yields vary
  - » Structural differences play a role
- Low NDMA formation with chloramination
  - » Different group of precursors for ozone
- Increased formation in wastewater
  - » Constituents that cause this?
- Ozone for water reuse is a concern
  - » Mitigation and/or prevention

Future Work

- Investigate wastewater constituents to isolate the cause of increased formation
- Identification of precursors in wastewater influent
- Investigate reaction kinetics and transformation products

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