Sources, Fate and Control of N-Nitrosodimethylamine (NDMA) Precursors

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Acknowledgements

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- SNWA Team: Brett Vanderford, Eric Wert, Beck Trenholm, Oscar Quiñones, Dr. Yue Wang, Janie Zeigler-Holady
## UCMR2 Nitrosamine Occurrence

### TABLE 1  
Nitrosamine occurrence in the UCMR2 survey

<table>
<thead>
<tr>
<th>Nitrosamine</th>
<th>MRL ng/L</th>
<th>Detects %*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBA</td>
<td>4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>NDEA</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>NDMA</td>
<td>2</td>
<td>16.7</td>
</tr>
<tr>
<td>NDPA</td>
<td>7</td>
<td>0.0</td>
</tr>
<tr>
<td>NMEA</td>
<td>3</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>NPYR</td>
<td>2</td>
<td>0.4</td>
</tr>
</tbody>
</table>


*Approximately 6,600 samples were collected for each nitrosamine species.

FIGURE 2  Percentage of samples with detectable levels of NDMA broken into disinfection practices

- Chlorine
  - $n = 3,816$
  - med* = 3.3
  - 90th* = 13.4

- Chloramine
  - $n = 1,295$
  - med* = 3.9
  - 90th* = 15.0

- Other
  - $n = 47$
  - med* = 7.5
  - 90th* = 8.7

- No disinfectant
  - $n = 96$
  - (no detects)

- Not reported
  - $n = 1,351$
  - med* = 6.3
  - 90th* = 18.8

UCMR2 NDMA: Impact of Source Water


CA—chlorine, CL—chloramine, GU—groundwater under the direct influence of surface water, GW—groundwater, MX—mix of ground and surface waters, n—sample size, SW—surface water

*Values are calculated from detectable levels (≥ 2 ng/L).
# UCMR2 NDMA: Impact of Utility Size

## Table 2: Details of NDMA occurrence per size of utilities and chlorine versus chloramine use

<table>
<thead>
<tr>
<th>Utility Size</th>
<th>Population</th>
<th>Utilities in Dataset</th>
<th>Samples in Dataset</th>
<th>Median $\text{ng/L}^*$</th>
<th>90th Percentile $\text{ng/L}^*$</th>
<th>Maximum $\text{ng/L}$</th>
<th>Frequency $%$</th>
<th>SW:GW</th>
<th>Samples ≥ 10 ng/L $%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very small</td>
<td>&lt; 500</td>
<td>9.8/0.4</td>
<td>5.5/0.2</td>
<td>4.2</td>
<td>6.2</td>
<td>7.3</td>
<td>85</td>
<td>2.6:8.0</td>
<td>0</td>
</tr>
<tr>
<td>Small</td>
<td>501—3,300</td>
<td>11/1.3</td>
<td>6.0/0.8</td>
<td>11</td>
<td>46</td>
<td>630</td>
<td>76</td>
<td>1.7:15</td>
<td>5.3</td>
</tr>
<tr>
<td>Medium</td>
<td>3,301—10,000</td>
<td>6.8/1.5</td>
<td>6.5/1.3</td>
<td>8.5</td>
<td>42</td>
<td>110</td>
<td>67</td>
<td>1.1:6.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Large</td>
<td>10,001—50,000</td>
<td>11/2.2</td>
<td>4.0/0.8</td>
<td>5.1</td>
<td>13</td>
<td>20</td>
<td>37</td>
<td>0.9:2.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Very large</td>
<td>50,001—100,000</td>
<td>73/3.0</td>
<td>5.3/2.1</td>
<td>4.1</td>
<td>16</td>
<td>37</td>
<td>52</td>
<td>0.9:3.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Extra large</td>
<td>&gt; 100,000</td>
<td>17/13</td>
<td>31/14</td>
<td>3.5</td>
<td>9.4</td>
<td>94</td>
<td>44</td>
<td>0.7:5.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

MRL—minimum reporting level, NDMA—$N$-nitrosodimethylamine, SW:GW—ratio of number of utilities describing source water as surface water to number of utilities describing source water as groundwater.

*Value indicates NDMA occurrence ≥ MRL (2 ng/L) over total samples collected.

Tertiary amines have the potential for significant NDMA yields. (Mitch and Schreiber, 2008)
Tertiary amines containing β-aromatic substituents are particularly high-yielding NDMA precursors. (Selbes et al. 2013, Le Roux et al. 2011, Shen and Andrews 2011).
Tertiary amines are common in many pharmaceutical and personal care products and other anthropogenic sources, but are not common functional groups in biomolecules and thus not likely to be prevalent in natural sources in the environment.

Quaternary amines form NDMA, but yields are notably lower. (Kemper et al. 2010, Park et al. 2009)
However, quaternary amine-based compounds are highly prevalent in consumer products but concentrations in wastewater have yet to be estimated owing to the inherent difficulty of measuring quaternary amine-containing polymers.
NDMA formation is associated with municipal wastewater, with precursor loads found into the 1,000’s ng/L. (Mitch and Sedlak 2004)
Potable Reuse

- Potable reuse: recycled water used to supplement drinking water supplies
- Indirect potable reuse (IPR): involves an *environmental buffer* and possibly additional drinking water treatment
- Direct potable reuse (DPR): involves an *engineered storage* buffer rather than an environmental buffer

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**Potable Reuse**

Conventional Wastewater Treatment ➔ Advanced Water Treatment ➔ Environmental or Engineered Buffer ➔ Drinking Water Treatment ➔ Water Consumer

*de facto*  
Lake, river, spreading basin, aquifer injection
Greywater and Blackwaters

Teng and Mitch, *Environmental Science and Technology*, In review
Greywater and Blackwaters

- Laundry water was the most significant source of precursors, followed by shower water and urine.

Teng and Mitch, *Environmental Science and Technology*, In review
• Loadings of precursors in laundry water were associated more with colored laundry than white laundry.

Teng and Mitch, *Environmental Science and Technology*, In review
Potable Reuse

- Potable reuse: recycled water used to supplement drinking water supplies
- Indirect potable reuse (IPR): involves an *environmental buffer* and possibly additional drinking water treatment
- Direct potable reuse (DPR): involves an *engineered storage* buffer rather than an environmental buffer

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**Potable Reuse Flowchart**

- **Conventional Wastewater Treatment** → **Advanced Water Treatment** → **Environmental or Engineered Buffer** → **Drinking Water Treatment** → **Water Consumer**

  *De facto* Lake, river, spreading basin, aquifer injection
Conventional Wastewater Treatment
- Flow Equalization
- Membrane Filtration (MF/UF)
- Reverse Osmosis
- Advanced Oxidation (H₂O₂/UV)
- Engineered Buffer
- Purified Water

Potable Reuse

Conventional Wastewater Treatment
- Flow Equalization
- Membrane Filtration (MF/UF)
- Ozonation
- Biofiltration
- GAC
- Engineered Buffer
- Purified Water
Full- and Pilot-Scale NDMA Results

NDMA (ng/L)

- Ozone influent
- Ozone effluent
- Reporting Limit

Pilot-Scale NDMA Results

Impact of $\text{O}_3$:TOC on NDMA: Bench-Scale

### Ozone Reactive Precursors

#### Already Established

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-Dimethylhydrazine (UDMH)</td>
<td><img src="structure_1,1-Dimethylhydrazine.png" alt="Structure" /></td>
<td>80%</td>
<td>1</td>
</tr>
<tr>
<td>Daminozide</td>
<td><img src="structure_Daminozide.png" alt="Structure" /></td>
<td>55%</td>
<td>1</td>
</tr>
<tr>
<td>TMDS</td>
<td><img src="structure_TMDS.png" alt="Structure" /></td>
<td>27%</td>
<td>2</td>
</tr>
<tr>
<td>Dimethylsulfamide (DMS)</td>
<td><img src="structure_Dimethylsulfamide.png" alt="Structure" /></td>
<td>52%</td>
<td>1</td>
</tr>
<tr>
<td>Methylene blue (and other dyes)</td>
<td><img src="structure_Methylene_blue.png" alt="Structure" /></td>
<td>$8.3 \times 10^{-3}%$</td>
<td>3</td>
</tr>
</tbody>
</table>

#### Potential NDMA Precursors

<table>
<thead>
<tr>
<th>Group</th>
<th>Ex. Structure</th>
<th>Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylhydrazone</td>
<td><img src="structure_Dimethylhydrazone.png" alt="Structure" /></td>
<td>UDMH</td>
</tr>
<tr>
<td>Dimethyl-Semicarbazide</td>
<td><img src="structure_Dimethyl-Semicarbazide.png" alt="Structure" /></td>
<td>TMDS</td>
</tr>
<tr>
<td>Dimethyl-thiosemicarbazide</td>
<td><img src="structure_Dimethyl-thiosemicarbazide.png" alt="Structure" /></td>
<td>DMS</td>
</tr>
<tr>
<td>Dimethyl-carbamate</td>
<td><img src="structure_Dimethyl-carbamate.png" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>

Ref.:

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

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Entry Routes of Nitrosamine Precursors into a Watershed
Natural Attenuation of NDMA Precursors in an Urban, Wastewater-Dominated Wash
NDMA FP Levels Along the Wash: Field Data

Woods, G. and Dickenson, E. Water Research, In Review
Photolysis Experiment
Photolysis Experiment

Woods, G. and Dickenson, E. Water Research, In Review
Bench-Scale Microcosm Experiment  WQTC Presentation!

NDMA-FP (ng/L) vs. Time (days)

- Sorp (wat + sed)
- Microb (wat)
- Microb (wat + sed)
- Sorp (wat)
- Sorp (DI + sed)
- Microb (DI)
- Microb (DI + sed)

Woods, G. and Dickenson, E. Water Research, In Review
Entry Routes of Nitrosamine Precursors into a Watershed
Nitrification in Distribution Systems

Teng and Mitch, *Environmental Science and Technology*, In review
Nitrification in Distribution Systems

- NDMA increases likely due to release of precursors by nitrifying biofilms.

Teng and Mitch, *Environmental Science and Technology*, In review
Nitrification in Distribution Systems

- Breakpoint chlorination suppressed nitrification and reduced precursor levels

Teng and Mitch, *Environmental Science and Technology*, In review
Summary

• Precursor sources in raw water: wastewater effluent
  – Colored laundry wastewater
• Both chloramine and ozone can react with precursors to form NDMA
  – NDMA can be mitigated by biological filtration treatment
• NDMA precursors can be potentially attenuated in receiving waters, i.e., the environmental buffer
• Nitrifying biofilms can potentially release NDMA precursors within a distribution system
  – mitigated by breakpoint chlorination
Water Research Foundation #4591: Major Sources of Nitrosamine Precursors from Raw Waters and Distribution Systems

Principal Investigators:
Eric Dickenson
Southern Nevada Water Authority
Tanju Karanfil,
Clemson University
William Mitch,
Stanford University
Wednesday Session 11B – Recycled Water
RM: COHIBA 1

4:30
Removing Trace Organic Contaminants Using Biofiltration in Potable Reuse
**Marco Velarde**, University of Nevada, Las Vegas

5:00
A Hazardous Ozone Disinfection Byproduct: NDMA Formation and Implications for Water Reuse
**Erica Marti**, University of Nevada, Las Vegas
Questions or Thoughts?

Contact: eric.dickenson@snwa.com