Factors that Mitigate the Formation of Emerging Disinfection By-Products in Recycled Water

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ARC Linkage Project LP0989326
‘Treating wastewater for potable reuse: removal of chemicals of concern using advanced oxidation processes’

Supporting the WCWA Groundwater Replenishment Trial with further research into the safety of recycled water for indirect potable reuse

ARC LP0989326 (2009-2012) Funding and Project Partners
What do we find in RO water?

7 halogenated DBPs
1 inorganic DBP
1 N-nitrosamine
8 VOCs
6 metals
2 complexing agents
2 phenols
2 misc organic chemicals


Chloramination in RO treatment

- Biofouling of RO membranes is mitigated through chloramination
- Typically achieved by combining hypochlorite and ammonia
- Chloramination will form disinfection by-products

**Key Project Objectives**

**WP 1.** N-nitrosamines: what factors contribute to formation in RO treatment?

**WP 2.** Iodo-organic compounds: occurrence and formation

**WP 3.** Characterisation of residual DOC in RO permeate

**WP 4.** Energy and cost benefit analysis of different treatment configurations

**APA Project:** Benzotriazoles and benzothiazoles: occurrence and degradation

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**Assessment of N-nitrosamine Precursors**

- Impossible to measure every compound that may form N-nitrosamines
- Formation Potential (FP)
  - Based on Mitch et. al. (2003) “NDMA precursor analysis”
  - High monochloramine dose (140 mg/L), pH 7, 7-day contact time

Monochloramine (140 mg/L)
Phosphate (10 mM)

Quench with excess Ascorbic Acid (20 mM)

pH 7, room temp., 7 days

Analyse for N-nitrosamines
Measuring N-nitrosamine Precursors

- The formation potential test uses very extreme conditions.
- Gives information on the maximum N-nitrosamine formation.
- Usually unrelated to formation at realistic conditions.

NDMA formation using monochloramine = 140 mg/L

NDMA formation using monochloramine = 3 mg/L

N-nitrosamine Precursor Removal

WWTP Precursor Removal
NDMA = 94%

RO Precursor Removal
NDMA = 99.9%

Data from February 2011
Activated sludge treatment reduces N in ocean outfall
Two processes: nitrification and denitrification

OrgN $\rightarrow$ NH$_3$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO$_3^-$ $\rightarrow$ N$_2^-$ $\rightarrow$ N$_2$
WWTP Performance Criteria

Table 4.1
Criteria for discriminating among the biological treatment processes

<table>
<thead>
<tr>
<th>Biological Treatment</th>
<th>$\text{NH}_4^+$ (mg/L as N)</th>
<th>$\text{NO}_2^-$</th>
<th>$\text{NO}_3^-$</th>
<th>Inorganic N $^1$ (mg/L as N)</th>
<th>SRT (days)</th>
<th>CBOD$_5$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No nitrification</td>
<td>&gt;10</td>
<td>&lt;1</td>
<td>&lt;2</td>
<td>&gt;10</td>
<td>&lt;5</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Partial or poor</td>
<td>2 to 10</td>
<td>&gt;1</td>
<td>&gt;2</td>
<td>&gt;10</td>
<td>--</td>
<td>&gt;10</td>
</tr>
<tr>
<td>nitrification</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&gt;10</td>
<td></td>
<td>&gt;10</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Good nitrification</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Partial denitrification</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&gt;7</td>
<td>&gt;10</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Good denitrification</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&gt;7</td>
<td>&gt;10</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

$^1$Strong criteria are in bold, whereas weak criteria are in italics. The project team focused on the strong criteria.


Beenyup WWTP: Nitrification

- Beenyup WWTP typically has good nitrification and ammonia < 2 mg/L

Secondary WW Ammonia

Good nitrification (~96.5% removal)
Beenyup WWTP: Denitrification

- Beenyup WWTP typically has average denitrification, with nitrate > 10 mg/L

Impact of Nitrification on NDMA Precursor Removal

- Graph showing the impact of nitrification on NDMA precursor removal.
Precursor removal is best correlated with ammonia removal.

Nitrification is important for removal of N-nitrosamine precursors.
Key Conclusions: Precursors

1. NDMA (N-nitrosodimethylamine) has the greatest formation potential in both primary and secondary WW, followed by N-nitrosopyrrolidine, and N-nitrosopiperidine.
2. Nitrification is the most important removal mechanism for N-nitrosamine precursors in secondary wastewater treatment.
3. The concentration of NDMA precursors do not directly predict NDMA concentrations.

Chloramine Speciation in RO Treatment

• Monochloramine is the most effective chloramine for disinfection.
• However, speciation depends on Cl₂: N ratio and pH.
• Organic chloramines may also form.

- Monochloramine is the most effective chloramine for disinfection.
- Organic chloramines have poor bactericidal properties.
- Interfere in measurement of inorganic chloramines.
Chloramine speciation will depend on the method of formation, especially formation of dichloramine.

- **Pre-formed monochloramine**: Ammonia and hypochlorite mixed prior to injection to wastewater.
- **In-line formed monochloramine**: Ammonia and hypochlorite injected separately into wastewater.

**Impact of Monochloramine Dose on NDMA Formation**

NDMA formation over 24 hours
Key Conclusions: Optimising Chloramination

1. Method of chloramine formation does impact on chloramine speciation, however....
2. Pre-formed and inline formed monochloramine formed similar NDMA concentrations, except when monochloramine = 10 mg/L.
3. Current chloramine speciation in Beenup Advanced Water Recycling Plant promotes monochloramine formation

Formation of Iodo-DBPs in Water Recycling

- Iodinated organic compounds:
  - known to induce medicinal taste and odours
  - more toxic than their brominated and chlorinated analogues
- New I-THM method developed and published:

Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass-spectrometry

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Formation of I-THM in Beenyup Pilot Plant

- I-THMs form without addition of iodide to wastewater

**Regulated THM4 (ug/L)**

- Secondary WW: 10
- Post-MF: 20
- RO Feed: 30
- RO Permeate: 40
- RO Reject: 50

**I-THM (ng/L)**

- Secondary WW: 1,000
- Post-MF: 2,000
- RO Feed: 3,000
- RO Permeate: 4,000
- RO Reject: 5,000

Key:
1. Secondary WW
2. Post-MF
3. RO Feed
I-THM Speciation

- I-THM concentrations after chloramination increase when iodide is added
- Formation of high molecular weight I-THMs increases with iodide addition

Key Conclusions: I-THMs

1. I-THMs were detected during water recycling treatment
2. There are similar formation trends for both I-THMs and regulated THMs
3. While increasing the iodide concentration did not increase iodine incorporation in THMs, the I-THMs speciation did change (probably related to Br/I ratio)
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