Novel Treatment to Reduce Bromide and Iodide in Drinking Water Sources

ARC Linkage Project LP100100285

WaterRA Science Talks to Industry

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Some Challenges in WA Drinking Water Supply

- High concentrations of bromide and iodide in many source waters
- WA groundwaters and surface waters
  \[\text{[bromide]}: \text{<0.05 mg/L (LOD) to ~3 mg/L}\]
- Perth Seawater Desal Plant RO-treated water
  \[\text{[bromide]} < 0.2 \text{ mg/L}\]
- WA groundwaters and surface waters
  \[\text{[iodide]} < 0.01 \text{ mg/L (LOD) to ~0.1 mg/L}\]
- Some iodide concentrations as high as ~0.5-0.6 mg/L
Significance of Bromide and Iodide - Australian Drinking Water Guidelines

- Bromide not subject to guideline value

- Iodide

  ✓ 2011 [iodide] ≤ 0.5 mg/L

  ✓ 2004 [iodide] ≤ 0.1 mg/L
Other Significance of Bromide and Iodide

- Potential to form brominated and iodinated disinfection by-products (DBPs) upon disinfection

- Br-DBPs and I-DBPs are usually of greater health concern than corresponding Cl-DBPs

E.g. Iodoacetic acid is the most genotoxic DBP known

- Some Br-DBPs and I-DBPs known to induce tastes and odours

E.g. CHI$_3$ organoleptic threshold concentration: 0.03 - 1 µg/L
For Improved Water Quality

Need to develop effective and economical methods of removal of bromide and/or iodide during drinking water treatment

Very few practical methods currently available

- Membrane techniques: expensive, energy intensive, not suitable for waters with high concentrations of DOC
- Ion exchange processes inefficient due to competing anions (e.g. sulfate, chloride)
ARC LP Project Objectives

- To better understand the impact of high concentrations of bromide and iodide in source waters

- To develop innovative new water treatment processes to selectively remove both bromide and iodide from potable water sources
Project Objective 1

To better understand the impact of high concentrations of bromide and iodide in source waters
Transformation Pathways of Bromide and Iodide During Water Treatment

- Chlorination
- Ozonation
- Chloramination

Br\(_{\text{aq}}\), I\(_{\text{aq}}\) → HOI, HOBr

Chloramination: X

NOM → Br-Org DBPs, I-Org DBPs

Ozonation: \(\text{BrO}_3^-\)

IO\(_3^-\) → 😊
Impact of High Bromide/Iodide Study

Two source waters chosen with:

- High bromide and iodide concentrations
- Minimal water treatment (only chlorination) before distribution

GW: chlorination 4 mg/L
SW: chlorination 2 mg/L
Water Quality Characteristics

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>DOC (mg/L)</th>
<th>Bromide, Br⁻ (µg/L)</th>
<th>Iodide, I⁻ (µg/L)</th>
<th>Iodate, IO₃⁻ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW Raw Water</td>
<td></td>
<td>1.2</td>
<td>677</td>
<td>72</td>
<td>9</td>
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<tr>
<td>Distribution System</td>
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<td>1.2</td>
<td>662</td>
<td>&lt;10</td>
<td>125</td>
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<tr>
<td>SW Raw Water</td>
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<td>3.5</td>
<td>399</td>
<td>87</td>
<td>5</td>
</tr>
<tr>
<td>Distribution System</td>
<td></td>
<td>3.5</td>
<td>60</td>
<td>&lt;10</td>
<td>141</td>
</tr>
</tbody>
</table>

- Initial bromide concentration decreased after chlorination
  - More significantly where DOC conc higher → Br-Org DBPs

- Majority of initial iodide converted to iodate upon chlorination (we have found bromide catalyses this conversion)
Organic DBP Formation in Distribution System Samples
Formation of Br-, I- and Cl-Org DBPs: Molar Proportions of Trihalomethanes

- Molar Ratio $\text{Cl}_2 : \text{Br}^{-}$ was approx. 6 : 1

- Despite much higher relative amount of chlorine to formed bromine in the system, bromine incorporation into THMs dominated over chlorine incorporation

- Much higher reactivity of bromine for reactions with NOM leading to THM formation than chlorine
AOX: Adsorbable Organic Halogen

- Measurement of major fraction of all Cl-, Br- and I- organic DBPs

\[ \text{AOX} \rightarrow \text{Known DBPs} + \text{Unknown organic halogens} \]
Br-Org DBPs (AOBr) predominate, even though ratio of Cl\textsubscript{2}:Br is high

- Much higher reactivity of bromine for reactions with NOM leading to bromine incorporation than chlorine
Br-Org DBPs (AOBr) and Cl-Org DBPs formed in similar abundance, even though ratio of Cl₂:Br is high.

Much higher reactivity of bromine for reactions with NOM leading to bromine incorporation than chlorine.
Chlorinous Odours in Distribution System Samples
All panellists agreed that a chlorinous odour was present for all distributed waters.
Chlorinous odour was still present in GW Distribution System & SW Treatment Plant Outlet samples

i.e. Chlorinous odour still experienced even when there was not enough chlorine to cause a chlorinous odour

This chlorinous odour may possibly be due to presence of bromine above its OTC
Impact of High Bromide and Iodide: Relevance to Water Industry

When bromide is high, Br-Org DBPs will predominate over Cl-Org DBPs. This is important because Br-Org DBPs are a greater health issue than Cl-Org DBPs.

If chlorine is used, most of the iodide will be converted to harmless iodate.

High bromide may play a role in chlorinous odours present when free chlorine concentration is below its OTC.
Project Objective 2

- To develop innovative new water treatment processes to selectively remove both bromide and iodide from potable water sources
Innovative New Water Treatment Processes

- Chlorination
- Ozonation
- Chloramination

Br⁻, I⁻ → HOI, HOBr

- Quenching with reactive materials → IO₃⁻
- Removal by silver-doped materials

Work Package 1
Work Package 2
Work Package 3
High iodide is an issue in chloramination since I-Org DBPs are favoured because iodate can't be formed.

Bromide is an issue in ozonation because bromate can be formed.
Key Project Objectives of Work Package 3

Develop **treatment options** to:

- mitigate the formation of potentially harmful **I-Orga**nic **DBPs** during disinfection by chloramination by **maximising** conversion of iodide into non-harmful inorganic iodate,

- while also **minimizing** formation of bromate
Mitigation of I-Organic DBP Formation

- Pre-chlorination/post-chloramination
- Pre-ozonation: selective oxidation of I- to IO$_3^-$

Strategy 1

Strategy 2
Strategy 1: Pre-chlorination / Post-chloramination

- Chlorine
- Ammonia addition

Formation of iodate
Minimisation of I-DBPs

Time
Chlorination (different contact times) followed by ammonia addition, with analysis of I-THMs after 24 h

- Low prechlorination times increase I-THM formation
- Longer prechlorination times limit the formation of I-THMs, especially more iodinated THMs like CHI₃
Having a longer pre-chlorination contact time can reduce formation of I-THMs

Chlorine followed by ammonia addition for chloramination can be useful for reduction of problems arising from high iodide in source waters
Strategy 2:
Pre-ozonation:
Selective Oxidation of Iodide to Iodate

with simultaneous bromate and I-THM minimization
Reaction Rates of Oxidation of Iodide and Bromide by Ozone

Oxidation of iodide by ozone really fast compared to the oxidation of bromide
Formation of Iodate and Bromate during Ozonation of Raw Waters

- 100% conversion of iodide into IO$_3^-$ without BrO$_3^-$ formation is possible

Experimental conditions:

- [DOC] = 1.3 mgC/L
- [I$^-$] = 50 µg/L
- [Br$^-$] = 100 µg/L
- pH = 8

100% conversion of iodide into IO$_3^-$ without BrO$_3^-$ formation is possible.
I-Org DBP (I-THM) Formation during Ozonation

- Formation of two I-DBPs, CHCl₂I and CHBrClI, reduced by increasing ozone dose

- Ozonation treatment reduces the formation of I-THMs
Pre-ozonation before Chloramination to reduce I-THM Formation: Relevance to Water Industry

Ozone can quickly oxidise iodide to iodate (so I-DBPs aren’t formed), without formation of bromate, if correct ozone dose used.
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