INORGANIC CHLORAMINES AS DRINKING WATER DISINFECTANTS: BENEFITS AND CHALLENGES

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WHAT ARE CHLORAMINES?

- Group of disinfectants formed by combining chlorine and ammonia
- Also known as total chlorine and combined chlorine
- Inorganic vs Organic chloramines
- Used as a “secondary” disinfectant
CHLORAMINES: WHAT ARE (SOME OF) THE ISSUES?

- Public Perception
- Effectiveness
- Chemistry
- Health Effects
- Interfering Organic Nitrogen
- Nitrification
- Other
CHLORAMINES IN THE NEWS

Erin Brockovich speaks out against adding chloramine to Nipomo's water supply

Residents Against Chloramine

RWSA, Do Not Use Chloramines in Our Drinking Water

Keep Cool When it Comes to Chloramines (Part 1 of 2)

CHLORAMINE
Fish Can't Live With It,
Harmful Ammonia

WHY SHOULD WE!
MICROORGANISMS OF CONCERN IN WATER
Death Rate for Typhoid Fever
United States, 1900-1960

DBP FORMATION

\[ \text{CL}_2 + \text{NOM} \rightarrow \text{DBPS} \]

- Temperature
- Time
- pH
CONTROL OF CHLORINATED BY-PRODUCTS IN WATER

• Removal of DBP Precursors
  ✓ GAC
  ✓ Enhanced Coagulation
  ✓ Membranes

• Alternative Disinfectants
  ✓ Chloramines
  ✓ Chlorine Dioxide
  ✓ Ozone
  ✓ Ultraviolet radiation
Comparison of THM Formation in Ohio River Water

- 5.5 mg/L Chlorine
- Original THM Standard

Graph showing the comparison of Trihalomethanes (ug/L) over contact time (hours) for Free Chlorine and Chloramines.
CHLORAMINES AS DISINFECTANTS
(Compared to Free Chlorine)

Benefits
• Form fewer Chlorinated DBPs
• More stable in the distribution system
• Fewer distribution system tastes and odors

Challenges
• Removal required for susceptible groups (methemoglobinemia)
• Weaker disinfectant
• Interference by organic nitrogen
• May result in nitrification
HISTORY OF CHLORAMINE USE

1907-----Rashig develop procedure for chloramine production for hydrazine

1917-----Chloramines first used in Ottawa Canada (prereacted chloramines)

1917-----Chloramines first used in US, Denver (prereacted chloramines)

1926-----Preammoniation first used in Greenville, TN

1930’s---Chloramines gained in popularity due to greater stability over chlorine.

1940’s---Chloramine use decreased due to ammonia restrictions in WW2 and breakpoint chlorination discovery

1980’s---Chloramines increase in popularity due to Cl-DBP formation
PERCENTAGE OF POPULATION RECEIVING CHLORAMINATED WATER
## MODE OF CHLORAMINE APPLICATION

<table>
<thead>
<tr>
<th>Mode</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preformed</td>
<td>Cl$_2$ + NH$_3$ premixed</td>
</tr>
<tr>
<td>Preammonication</td>
<td>NH$_3$ Cl$_2$</td>
</tr>
<tr>
<td>Postammoniation</td>
<td>Cl$_2$ NH$_3$</td>
</tr>
<tr>
<td>Concurrent</td>
<td>Cl$_2$ + NH$_3$ added simultaneously</td>
</tr>
</tbody>
</table>
Where Chloramines are formed at Metropolitan’s WTPs (no ozone)

- Raw Water
- Rapid Mix
- Flocculation/Sedimentation (no sed. basins for direct filtration plants)
- Filtration (dual- or tri-media, backwash with chlorinated water)
- To Clearwell

- Acid
- Alum or Ferric, Cationic Polymer, Caustic Soda, Chlorine
- Filter Aid, Chlorine
- Chlorine, Ammonia, Caustic Soda
INORGANIC CHLORAMINE FORMATION

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{Cl}^- \quad \text{(Hypochlorous acid)} \]

\[ \text{HOCl} \leftrightarrow \text{OCl}^- + \text{H}^+ \quad \text{(Hypochlorite ion)} \]

\[ \text{HOCl} + \text{NH}_3 \leftrightarrow \text{H}_2\text{O} + \text{NH}_2\text{Cl} \quad \text{(Monochloramine)} \]

\[ \text{HOCl} + \text{NH}_2\text{Cl} \leftrightarrow \text{H}_2\text{O} + \text{NHCl}_2 \quad \text{(Dichloramine)} \]

\[ \text{HOCl} + \text{NHCl}_2 \leftrightarrow \text{H}_2\text{O} + \text{NCl}_3 \quad \text{(Trichloramine)} \]
Distribution of inorganic chloramine species

Total Combined chlorine (%)

pH

- NH₂Cl
- NHCl₂
- NCl₃
# CLORINE TO NITROGEN RATIOS

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 5:1</td>
<td>Free ammonia, monochloramine present</td>
</tr>
<tr>
<td>5:1</td>
<td>No free ammonia present</td>
</tr>
<tr>
<td>&gt;5:1 to 7:1</td>
<td>Ammonia oxidized and chloramine residual breaks down, dichloramine</td>
</tr>
<tr>
<td>7:1</td>
<td>Breakpoint, no chloramine residual</td>
</tr>
<tr>
<td>&gt;7:1</td>
<td>Free chlorine present, no ammonia</td>
</tr>
</tbody>
</table>
BREAKPOINT CHLORINATION CURVE

Monochloramine dominates, free ammonia is present,

Dichloramine (and others) form and decay, free ammonia is not present

Free chlorine increases with dose, free ammonia is not present

Cl:N mass ratio

5:1

7:1
ORGANIC CHLORAMINE FORMATION

\[
\text{HOCl} + \text{RNH}_x \leftrightarrow \text{H}_2\text{O} + \text{RNHCl} \quad \text{(Direct reaction)}
\]

\[
\text{NH}_2\text{Cl} + \text{RNH}_x \leftrightarrow \text{H}_2\text{O} + \text{RNHCl} \quad \text{(Chlorine transfer)}
\]

Organic chloramines are largely nonbiocidal but are react the same inorganic chloramines in detection tests.
Inorganic vs Organic Chloramines on Disinfection

E. coli Survival vs Contact Time (min)

- Inorganic Chloramines
- Chlorinated Glycine

(Organic Chloramine)
Impact of Glycine on Chloramine Disinfection

(Preferential Binding)

E. coli Survival

Contact Time (min)

Ammonia + Gly + Chlorine
COMPARATIVE DISINFECTION EFFECTIVENESS

Contact Time Required for 99% inactivation

Chlorine or chloramine conc. (mg/L)

HOCl, bacteria
HOCl, viruses
NH2Cl, protozoa
NH2Cl, viruses
METHEMOGLOBINEMIA FROM CHLORAMINE EXPOSURE
What is Nitrification?

- Nitrification is the conversion of ammonia to nitrite and nitrite to nitrate.
- Nitrification is caused by bacteria that are chemolithotrophs which means they use inorganic substrate for their energy source.

Ammonia-Oxidizing Bacteria (AOB)

AMMONIA (NH₃) → NITRITE (NO₂) → NITRATE (NO₃)

Nitrite-Oxidizing Bacteria (NOB)
Nitrification in chloraminated water

- In chloraminated water, nitrification is incomplete
- NOB are more sensitive to chloramines than AOB therefore nitrite oxidation does not occur
- Increase in nitrite
- Nitrite has high chlorine demand (5:1, Cl₂:N, by wt)

MWD training
Where Does Nitrification Occur?
Distribution System Reservoirs: Common Inlet/Outlet

Stagnant Zones with:
- Warm temperature
- Long detention time
- Dark environments
- Free ammonia

E.G. Means
Biofilm in Distribution System

Biofilm can protect nitrifiers from disinfectants and unfavorable conditions.
INCOMPLETE NITRIFICATION

$\text{NH}_2\text{Cl}$ plus excess $\text{NH}_3$ when ratio < 5:1

$\text{Nitrosomonas}$

$\text{NO}_2$ + $\text{HOCI}$ $\text{NH}_2\text{Cl}$ → Loss of disinfectant residual

$\text{Organics}$ → Bacterial growth
AMMONIA-OXIDIZING BACTERIA

- Rod-shaped, gram negative bacteria
- Chemoautotrophic, aerobic
- Found in soil, freshwater, marine water, wastewater, *Nitrosomonas* spp. common
- pH 6-9, temperature 20⁰-30⁰C, slow-growth
- Photophobic
- Multiple intracytoplasmic membranes
- “New gang in town”—Ammonia-oxidizing archaea
CROSS-SECTION OF AOB SHOWING INTRACELLULAR MEMBRANES
Enumeration of AOB

- Soriano & Walker medium
- 25\(^\circ\) - 28\(^\circ\) C
- 23 day incubation period
Relationship between Temperature and AOB levels

Ammonia-oxidizing bacteria (mpn/ml)

Temperature
**REGROWTH OF AOB FOLLOWING EXPOSURE TO CHLORAMINES FOR 8 DAYS**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1.7 mg/L Chloramine</th>
<th>2.0 mg/L Chloramine</th>
<th>2.5 mg/L Chloramine</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>15°C</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>25°C</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

Chlorine to nitrogen ratio of 4:1
EARLY INDICATORS OF NITRIFICATION

- Increase in nitrite
- Increase in HPC counts
- Reduction in ammonia
- Reduction in chloramine residual
- Drop in pH
METHODS OF CONTROLLING NITRIFICATION

• Increasing the Chlorine to Nitrogen ratio (to reduce free NH3)
• Increase chloramine dose
• Reduce detention time
• Periodic switch to free chlorine
• Increase pH
• Addition of chlorite ion
• UV/lamps in reservoirs/tanks
SUMMARY

- Nitrification can adversely impact chloramine effectiveness but is controllable
- New bacteria also responsible? Ammonia-oxidizing archaea?
- Unknown mechanism for accelerated breakdown of chloramines?
- Chloramines can be highly effective but need to be managed—nitrification monitoring/control plan
QUESTIONS?