Outline

- History and extent of chloramination in Texas
- What is nitrification?
- History of nitrification in Texas
  - Case studies
  - 2005 Special Study
- Nitrification Action Plans (NAPs)
Take-home Message

• Nitrification can cause residual loss in chloraminated distribution systems.
  – And form nitrite (NO2-) & nitrate (NO3-)
• Texas water systems need chloramines to maintain residuals and meet disinfection byproduct (DBP) regulations.
• Nitrification can be detected and controlled using a NAP.
History / Extent of Chloramination in Texas
Texas has history of chloramine usage

- Historically, public water systems (PWSs) used chloramines to keep a stable residual.
  - Example--Austin started chloraminating in 1950s

- Later, systems started using chloramines for disinfection byproduct (DBP) control.
  - Total Trihalomethane Rule 1989
    - Most systems > 100,000 population converted
  - Stages 1 & 2 DBP Rules
    - 2002 for large
    - 2004 for small
    - Starting in 2013, LRAAs added stringency
      » Locational Running Annual Averages
About 1,200 of Texas’ 7,000 PWSs distribute chloramines

• Surface water ~1,200
  – About 90% of 350 PWSs with surface water treatment plants (SWTPs) chloraminate
  – ~850 PWSs purchase and redistribute chloraminated SW

• Ground water ~12
  – High-carbon groundwater in northeast Texas
  – High bromide water in coastal Texas
Chloramination clarification

• Chloramination *facts*:
  
  – **Chloramines smell fine** unless they are dosed or maintained wrong.
    
  
  – Experience proves that **chloramimes do not cause health issues**.
    
    – *Fiction*: Some web sites blame various symptoms on chloramines, but 25% of Americans are okay drinking chloraminated water
What is nitrification?
The chemicals of interest

• Normal chloramine reactions,
  • in the monochloramine zone:

  \[
  \text{HOCl} + \text{NH}_3 \leftrightharpoons \text{NH}_2\text{Cl} + \text{H}_2\text{O}
  \]

  \[
  2 \text{NH}_2\text{Cl} \leftrightharpoons \text{NHCl}_2 + \text{NH}_3
  \]

• Nitrification

  \[
  \text{NH}_3 + \text{O}_2 \rightarrow \text{AOB} \rightarrow \text{NO}_2^- + 3\text{H}^+ + 2\text{e}^-
  \]

  \[
  \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NOB} \rightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-
  \]
Nitrification in the environment

Nitrosomonas bacteria (AOB) uses up ammonia and makes NITRITE

Nitrobacter bacteria (NOB) uses nitrite to make NITRATE

AMMONIA

Wastewater effluent

Run off

Fish excreta and urine

NITRITE (NO₂⁻)

Gases

NITRATE (NO₃⁻)

NITRATE BUILD UP

PLANT FERTILIZER

Plant remnants
Nitrification in a pipe

Nitrosomonas bacteria (AOB) uses AMMONIA to produce NITRITE

Nitrobacter bacteria (NOB) uses NITRITE to produce NITRATE

Reactions happen in biofilm

Naturally occurring

Decomposition of chloramines

AMMONIA

NITRITE ($\text{NO}_2^-$)

NITRATE ($\text{NO}_3^-$)

NITRATE BUILD UP

Added

/reacts with fish to prevent death
Example: Without nitrification
Example: Nitrification
Nitrification in Texas
2003 Case study

- City with SWTP
  - Fish kill complaint
- Water quality:
  - Water temp 27 °C (Texas in May)
  - Nitrite: 1.56 mg/L
  - Monochloramine 1.5 mg/L
  - Ammonia 0.5 mg/L
- Other sites Ammonia ~ 1.75 mg/L
- We learned:
  - Nitrification can occur WITH good residual
  - Don’t ignore complaints about dead fish
2005 Summer—Special Study

• Sampled 1,029 ‘high-risk’ systems
  – Surface water, chloraminating, and their downstream consecutive purchasers
  – Sampled in distribution—at DBP sites
    • Nitrate,
    • Nitrite, and
    • Ammonia
2005 Summer—Special Study

continued

- Results—of 1,029 systems
  - 149 systems showed some evidence of nitrification
  - 11 systems exceeded 1 mg/L NO₂⁻
    - Highest NO₂: 2.08 mg/L (case study)
    - No NO₃⁻ over the MCL (10 mg/L) was found
  - 9 of those systems were identified as having issues
    - Case-by-case assistance was provided
• We learned:
  – Nitrification can happen under a range of conditions,
  – Approximately 10% of systems may experiencing nitrification, but apparently only 1% have extreme problems.
2007 Case study

• City with SWTP
• Widespread residual loss
  – No existing flushing program
  – Positive bacteriological results
  – Boil water notice required
  – Extended free chlorine burn
• Resulted in innovative flushing and nitrification detection and response plan
  – Nitrification Action Plan
Nitrification Action Plan
Everyone Needs a NAP

Stop!
Check
Go!
A Nitrification Action Plan is like a Monitoring Plan

• It includes
  1. A sample site map,
  2. Sample schedules,
  3. Analytical methods,
  4. Site-specific goal/baselines and trigger levels, and
  5. Actions.
  6. *It should be documented and shared.*
1. NAP sites

- Distribution nitrification monitoring sites:
  - Should represent low, medium, and high water age.
  - Can be the same as coliform sites
    - But they don’t have to be.
- Critical control points
  - “A point where control can be applied and is essential to prevent or eliminate nitrification”
    - EG: Before booster chloramination
2. Routine NAP schedules

• NAP monitoring must be done weekly,
  – May be done more frequently.

• Small systems, <750 people or 250 cnx.
  – Monitor monochloramine and ammonia with every weekly total chlorine sample.

• Large systems, select CCPs at low, average and high water age for weekly sampling.
3. Analytical methods

- Total chlorine: Use EPA approved method (see 30 TAC 290.119)
- Monochloramine and ammonia:
  - EPA does not have approved methods.
  - Use methods that achieve the required accuracy
- Document on the Lab Approval Form
  - Attach to Monitoring Plan
4. Goals/baselines and trigger levels

- Nitrification is controlled by defining what “normal” is and looking for trends that are “abnormal.”
  - Therefore, initial data must be analyzed to define normal levels,
  - And additional data must be analyzed or hypothetical levels must be projected for levels that are a concern: trigger levels.
Chemicals that you need trigger levels for

– Total Chlorine & Monochloramine:
  • At least the regulatory minimum for Total PLUS a Safety Factor.

– Ammonia:
  • A little bit means you are in the right ‘zone.’
  • When it goes away – something is eating it.

– Nitrite & nitrate:
  • If distribution is more than baseline... Trigger!

– Also for pH, heterotrophic plate count if used.
Baseline (Green light – Go!)
Parameters in normal operating range – all systems ‘go’

Alert (Yellow flag-Act.)
Outside normal operating range – take precaution

Alarm! (Red flag-Act!!!)
Too far outside normal operating range - take immediate action!
5. Action!

- **Preventive action:**
  - Routine operating conditions
    - Do this even when your levels are ok

- **Corrective: Trigger 1**
  - Intermediate--Do this when levels are not quite ok

- **Corrective: Trigger 2**
  - Do this when nitrification is bad
Most preventive and corrective actions overlap

- Preventive and corrective actions:
  - Verify results.
  - Flush.
  - Dose chlorine and ammonia correctly.
  - Minimize water age.

- Operational corrective action:
  - Temporary conversion to free chlorine.
• Possible long-term corrective actions
  – Increase pH
    • Chloramine decays more slowly at higher pH
    • Con: Caustic feed
  – Feed chlorite
    • Low chlorite concentration can prevent nitrification
  – Permanent conversion to free chlorine
    • With aeration for trihalomethane (chloroform) removal.
• Those potential long-term corrective actions that require engineering should be considered only if the operational controls are unsuccessful.
  – Additional studies must be performed to evaluate their long-term, site-specific success at your PWS.
    • (One size does NOT fit all.)
NAP Actions: More sampling

• Monitoring: Additional monitoring should be done to
  – Verify results
    • After an ‘abnormal’ result is found, go back to that site and collect another sample to make sure the sample was accurate.
  – Determine where nitrification is happening
    • If the level is verified, collect samples nearby to see how far the abnormality extends.
NAP Actions: More flushing

• Routine flushing is required at every dead-end main.

• Additional flushing may be needed to bring fresh water with a high chloramine residual into an area that has nitrification.
NAP Actions:
Dose chemicals correctly

• For systems that operate water plants or booster stations, base the chemical dose on results of monitoring – not theoretical levels.
NAP Actions:
Increase total chlorine / decrease ammonia

• Ammonia
  – Minimize ammonia entering the distribution system – target of just detectable

• Total chlorine residual
  – Sources suggest over 2.0 is best
  – The lower the residual, the greater the risk
Order of addition, mixing

• Order of addition:
  – Source:
    • Chlorine first for dosing raw water
      – NOTE: SWTP can get exception to add ammonia first— with additional viral log inactivation.
  – Booster:
    • Add ammonia first to water with chloramines.
    • Add chlorine first to water with free chlorine.
Inject chlorine

Inject ammonia

Measure total chlorine, monochloramine ammonia

Base ammonia dose on measured chlorine residual

Measure chlorine

Ideal chloramination design: Source
Reality of chloramination design:

Inject chlorine
Inject ammonia

No room to measure chlorine
Ammonia dose is calculated based on chlorine dose

Measure total chlorine, monochloramine ammonia

Source
Ideal chloramination design: Booster

1. Measure total chlorine, monochloramine, ammonia
2. Inject ammonia (if needed)
3. Measure total, mono, ammonia
4. Inject chlorine
5. Measure total chlorine, monochloramine, ammonia

Base ammonia dose on desired monochloramine residual

Base chlorine dose on measured ammonia residual
NAP Actions: Minimize water age

• Routinely, exercise valves to ensure no unintended dead spots.

• Consider the impact of hydraulic dead-ends, where water goes back and forth,
  – Although the pipe may be continuous, water age may increase in these places.

• Prioritize flushing at higher water age locations.
NAP Actions: Free chlorine

• A temporary conversion to free chlorine will ‘starve’ the nitrifying bacteria that ‘eat’ ammonia.
  – Notify TCEQ before doing a temporary free chlorine conversion: DBP@tceq.texas.gov
    • We will delay disinfection byproduct monitoring for 4 weeks.

• Have a plan to flush the chlorine in then flush it out.
6. Share the NAP with all operators

- Document the plan (see next slide)
- Share it with the folks who work in distribution
## Nitrification Action Plan Example

### Chloramine-Effectiveness Sample Suite

<table>
<thead>
<tr>
<th>Site</th>
<th>Chemical</th>
<th>Goal</th>
<th>Yellow Flag</th>
<th>Red Flag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Trigger</td>
<td>Actions</td>
</tr>
<tr>
<td><strong>Entry Point</strong></td>
<td>Total / Mono</td>
<td>4.0</td>
<td>3.5</td>
<td>1) Verify results</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.1</td>
<td>0.2</td>
<td>2) Check and adjust dose</td>
</tr>
<tr>
<td><strong>Average Water Age</strong></td>
<td>Total / Mono</td>
<td>2.0</td>
<td>1.5</td>
<td>1) Verify results</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.5</td>
<td>+/- 20%</td>
<td>2) Measure nitrite and nitrate</td>
</tr>
<tr>
<td><strong>Far Reaches</strong></td>
<td>Total / Mono</td>
<td>1.0</td>
<td>0.7</td>
<td>3) Adjust dose</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.9</td>
<td>+/- 20%</td>
<td>4) Identify affected area</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(check upstream and downstream)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5) Flush area</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6) Flush dead ends</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>→ Till levels return to normal</strong></td>
</tr>
</tbody>
</table>

### Nitrite/Nitrate

<table>
<thead>
<tr>
<th>Site</th>
<th>Chemical</th>
<th>Baseline</th>
<th>Yellow Flag</th>
<th>Red Flag</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Trigger</td>
<td>Actions</td>
</tr>
<tr>
<td><strong>All Sites</strong></td>
<td>Nitrite</td>
<td>1.23</td>
<td>&gt; 1.5</td>
<td>1) Verify results</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>0.12</td>
<td>+/- 20%</td>
<td>2) Identify source changes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IF confirmed-modify BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3) Identify area,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4) Flush area</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>→ Till levels return to normal</strong></td>
</tr>
</tbody>
</table>
Take-home Message
Take-home Message

• Chloramines are an important tool.
  – They can help maintain residuals, and
  – Avoid unwanted disinfection byproducts.

• Nitrification is a potential risk of chloramination.

• Nitrification can be detected and controlled using a Nitrification Action Plan