Regional Applied Research Efforts (RARE) Project – Region 6

Understanding the Impacts and Meaning of Maintaining Detectable Disinfection Residuals in Drinking Water Distribution Systems: Controlling Waterborne Pathogens, Disinfection Byproducts, Organic Chloramines, and Nitrification

Jonathan G. Pressman and David G. Wahman

December 5, 2017
Outline

- Project Specific Overview – Jonathan Pressman
- Detailed Technical Background – David Wahman
What is RARE?

Collaboration between the EPA Regions, States and EPA Office of Research and Development to conduct research projects of specific interest to those areas.

In this case – EPA Region 6 and Louisiana
Monitoring data shows challenges maintaining 0.5 mg/L Cl₂

More data correlating Cl₂ residual with pathogen occurrence and the potential for increased DBPs is needed

Disinfectant residual monitoring methods have known interferences from organic chloramines

Nitrification complicates matters
This project will provide data to better understand:

- *Legionella pneumophila*
- *Mycobacterium spp.*
- Other pathogenic microorganisms
- Disinfection Byproducts – THMs and HAA9s
- Organic Chloramines
Team Approach

- **EPA ORD:**
  - Jonathan Pressman, Ph.D., PE – Disinfection Process, Disinfection Byproducts,
  - David Wahman, Ph.D., PE – Disinfection Chemistry, Nitrification
  - Stacy Pfaller, Ph.D. – Microbiology, *Culture Analysis*
  - Jingrang Lu, Ph.D. – Microbiology, *DNA Analysis*

- **EPA OW:** Matthew Alexander, PE – Distribution System Optimization and Sampling

- **EPA Region 6:** Jatin Mistry, MPH – EPA Region 6 Technical Lead

- **LDHH:** Amanda Laughlin, PE – LDHH Lead w/ support from many field/district staff

- Utility Partners with us today!
Sampling Approach

- 4 Utilities in Region 6 – Specifically Louisiana
- 4 Sampling locations in each Utility
  - DS Entry Point site
  - Average residence time site
  - Maximum residence time site
  - Downstream of a storage tank site
- 4 Quarters/Seasons
- 64 total project samples across time/space for evaluation
## Project Schedule

<table>
<thead>
<tr>
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<th>2017</th>
<th>2018</th>
<th>2019</th>
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<td>Quality Assurance Project Plan preparation and approval</td>
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<td>Site Identification and Selection</td>
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<td>Sample collection</td>
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<td>Data analysis</td>
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<td>Present data at scientific venue</td>
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<td>Report/manuscript preparation and submission</td>
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Project Objectives

- Provide occurrence data to correlate drinking water pathogens and DBPs with various disinfection residual concentrations
- Evaluate organic chloramine formation and the resulting positive interferences on measuring disinfectant residuals
- Evaluate nitrification impacts on organic chloramine formation and residual demand
Technical Background
Project Objectives

- Provide occurrence data to correlate drinking water pathogens and DBPs with various disinfection residual concentrations
- Evaluate organic chloramine formation and the resulting positive interferences on measuring disinfectant residuals
- Evaluate nitrification impacts on organic chloramine formation and residual demand
First Introduced in the Surface Water Treatment Rule, 6/1989, 40 CFR 141.72 (b)(3)(i)

The residual disinfectant concentration in the distribution system, measured as total chlorine, combined chlorine, or chlorine dioxide...cannot be undetectable in more than 5 percent of the samples each month, for any two consecutive months...a heterotrophic bacteria concentration less than or equal to 500/ml...is deemed to have a detectable disinfectant residual...
Residual – Intent of Residual Regulation

- US regulatory requirement \(\rightarrow\) “detectable”
  - Surface water (SW)
  - Groundwater under direct influence (GWUDI) of SW
  - Heterotrophic plate count (HPC) < 500/mL \(\equiv \) “detectable”

- Intent behind regulations
  - Distribution system integrity
  - Proper system maintenance
  - Identify & limit outside contamination
  - Limit heterotrophic bacteria & *Legionella* growth
  - Provide quantifiable minimum target \(\rightarrow\) action
§903. Coliform Routine Compliance Monitoring.
- The monitoring plan shall include a minimum number of point of collection (POC) monitoring sites calculated by multiplying 1.5 times the minimum number of samples required to be routinely collected.

§367. Disinfectant Residual Monitoring and Record Keeping
- B. Disinfectant Residual Monitoring in Distribution System. A public water system shall measure the residual disinfectant concentration within the distribution system:
  1. by sampling at the same points in the distribution system and at the same times that samples for total coliforms are required to be collected by the public water system under this Part;
  2. by sampling at an additional number of sites calculated by multiplying 0.25 times the number of total coliform samples the public water system is required under this Part to take on a monthly or quarterly basis, rounding any mixed (fractional) number product up to the next whole number. These additional residual monitoring samples shall be taken from sites in low flow areas and extremities in the distribution system at regular time intervals throughout the applicable monthly or quarterly sampling period; and
  3. by sampling at the site that represents the maximum residence time (MRT) in the distribution system at least once per day.
Residual – Six–Year Review (SYR) Process

- 1996 Safe Drinking Water Act (SDWA) requirement
- Review primary drinking water regulations every six years
- Third Six–Year Review (SYR3) completed December 2016
  - Occurrence data (2006–2011)
  - Included Microbial and Disinfection By–Product (DBP) regulations
- Revision candidates
  - Chlorite
  - Cryptosporidium (under IESWTR, LT1)
  - Giardia Lamblia (under SWTR)
  - HAA5 & TTHM
  - HPC
  - Legionella
  - Viruses (under SWTR)

- All Systems Free Chlorine Only (n = 1,167,919)
- All Systems Total Chlorine Only (n = 731,798)

- 0 mg/L
- > 0 to 0.2 mg/L
- > 0.2 to 0.5 mg/L
- > 0.5 to 1.0 mg/L
- > 1.0 mg/L
Chloramine Chemistry

- Chloramines
  - Free chlorine + free ammonia
  - 3 inorganic species
    - Monochloramine (NH₂Cl)
    - Dichloramine (NHCl₂)
    - Trichloramine (NCl₃)
  - Unified Model (Cl₂:N & pH)
- Monochloramine
  - Cl₂:N < 5:1
  - pH > 7
- Decay (Unified Model)
  - 3NH₂Cl → N₂ + NH₃ + 3Cl⁻ + 3H⁺
  - Major pathway

Unified Model

1. HOCl + NH₃ → NH₂Cl + H₂O
2. NH₂Cl + H₂O → HOCl + NH₃
3. HOCl + NH₂Cl → NHCl₂ + H₂O
4. NHCl₂ + H₂O → HOCl + NH₃
5. NH₂Cl + NH₂Cl → NHCl₂ + NH₃
6. NHCl₂ + NH₃ → NH₂Cl + NH₂Cl
7. NHCl₂ + H₂O → I
8. I + NHCl₂ → HOCl + products
9. I + NH₂Cl → products
10. NH₂Cl + NHCl₂ → products
11. HOCl + NHCl₂ → NCl₃ + H₂O
12. NHCl₂ + NCl₃ + 2H₂O → 2HOCl + products
13. NH₂Cl + NCl₃ + H₂O → HOCl + products
14. NHCl₂ + 2HOCl + H₂O → NO₃⁻ + 5H⁺ + 4Cl⁻

Source: Jafvert and Valentine (1992)
Natural organic matter (NOM)
\[ \text{NH}_2\text{Cl} + \text{NOM} \rightarrow \text{NOM}_{\text{ox}} + \text{NH}_4^+ + \text{Cl}^- \]

Cells
\[ 10\text{NH}_2\text{Cl} + C_5\text{H}_7\text{O}_2\text{N} + 9\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + \text{HCO}_3^- + 11\text{NH}_4^+ + 10\text{Cl}^- \]

Pipe surfaces
\[ \text{NH}_2\text{Cl} + 2\text{Fe}^{2+} + 6\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3(s) + \text{NH}_3 + \text{Cl}^- + 5\text{H}^+ \]

Nitrite
\[ \text{NH}_2\text{Cl} + \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NH}_4^+ + \text{Cl}^- \]

Organic Chloramines
\[ \text{RNH}_2 + \text{NH}_2\text{Cl} \rightarrow \text{RNHCl} + \text{NH}_3 \]
\[ \text{RNH}_2 + \text{HOCl} \rightarrow \text{RNHCl} + \text{H}_2\text{O} \]
Organic Chloramines – Issues

- Poor disinfectants
- Interfere with DPD
- Precursors in DS, formation over time
- Relatively stable (persist)
Organic Chloramines – Poor Disinfectants

Source: Westerhoff et al. (2010)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>EPA Compliance Approved?</th>
<th>Measures</th>
<th>Method Weakness</th>
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</thead>
<tbody>
<tr>
<td>Free Chlorine</td>
<td>DPD Free Chlorine</td>
<td>Yes</td>
<td>HOCl/OCl(^-) HOBr/OBr(^-)</td>
<td>NH(_2)Cl</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>DPD Total Chlorine</td>
<td>Yes</td>
<td>HOCl/OCl(^-) HOBr/OBr(^-) NH(_2)Cl, NHCl(_2), NCl(_3) Bromamines</td>
<td>Organic chloramines Organic bromamines</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>Hach 10200 Monochlor F</td>
<td>No</td>
<td>NH(_2)Cl</td>
<td>None related to free &amp; total chlorine</td>
</tr>
</tbody>
</table>
Organic Chloramines – Methods

Source: Lee et al. (2007)
Organic Chloramines – Methods

Source: Westerhoff et al. (2010)
Organic Chloramines – Formation

Source: Lee et al. (2007)
Organic Chloramines – Persistence

Source: Baribeau et al. (2005)

The graph shows the percent of total chlorine due to organic chloramines over different detention times for various materials:

- New Cement-Lined Ductile Iron
- New PVC
- Aged Cast Iron

At detention times of 3, 12, and 48 hours:

- Total Chlorine ≤ 0.2 mg Cl₂/L
- Total Chlorine ~ 1 mg Cl₂/L

The data indicates a significant increase in the percent of total chlorine due to organic chloramines over time and for different materials.
“Detectable” is horrible for prevention of nitrification

AWWA manual
- 1.5 mg/L everywhere
- 0.5 mg/L minimum

Whole series of issues on why nitrification is bad:
- Produces organics – SMPs which serve as food for HPC
- May not occur where monitoring for TC compliance
- Nitrification issues:
  - Support HPC growth
  - Remove remaining disinfectant (even while measuring organic chloramine)
  - Biological destabilization
Nitrification – Residual Impact

Source: Gomez-Alvarez et al. (2014)
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