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Chloramine Conversion to Free Chlorine in a Combined System

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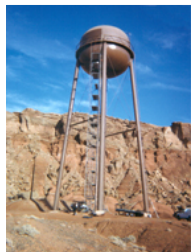


The Stage 2 D/DBP Rule Affects Treatment

- **More stringent limits for DBPs in the distribution system**
- **Chloramines are less reactive than free chlorine**
  - Form DBPs at a lower rate
  - Maintain a residual for a longer time
- **The use of chloramines for secondary disinfection is becoming more common**
  - Effective
  - But what happens in consecutive systems?

Chloramine Chemistry Can be Complicated

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2$$

OR

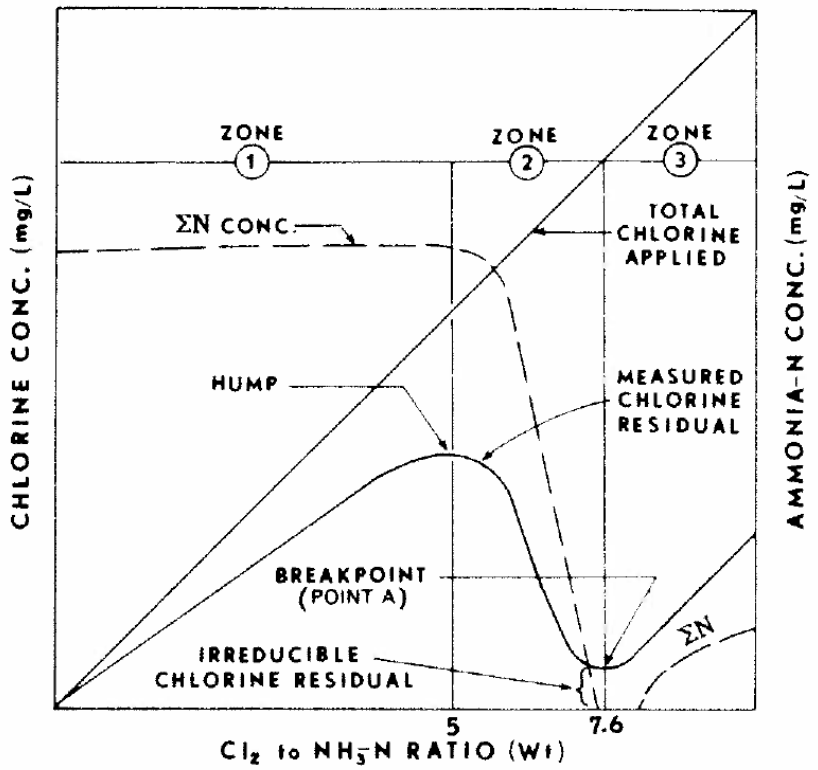
$$2NH_2Cl + Acid \longrightarrow NH_3 + NHCl_2 + Acid$$

$$x NHCl_2 + y HOCl \longrightarrow \text{nitrogen oxides, } N_2, \text{ and HCl}$$

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

Breakpoint Curve Provides a General Guide to Chloramine Chemistry

- **Primarily monochloramine to ≈ 5:1 Cl_2:N ratio**
  - **pH dependent**
- **At higher ratios, increasing dichloramine formation**
  - **Slower reaction**
  - **Fastest at pH ≈ 5**
- **Dichloramine decomposes in the presence of excess chlorine**
  - **Theoretical breakpoint at Cl_2:N ratio of 7.6:1**
  - **In practice, breakpoint often at higher Cl_2:N ratio**
- **Free chlorine residual past breakpoint**

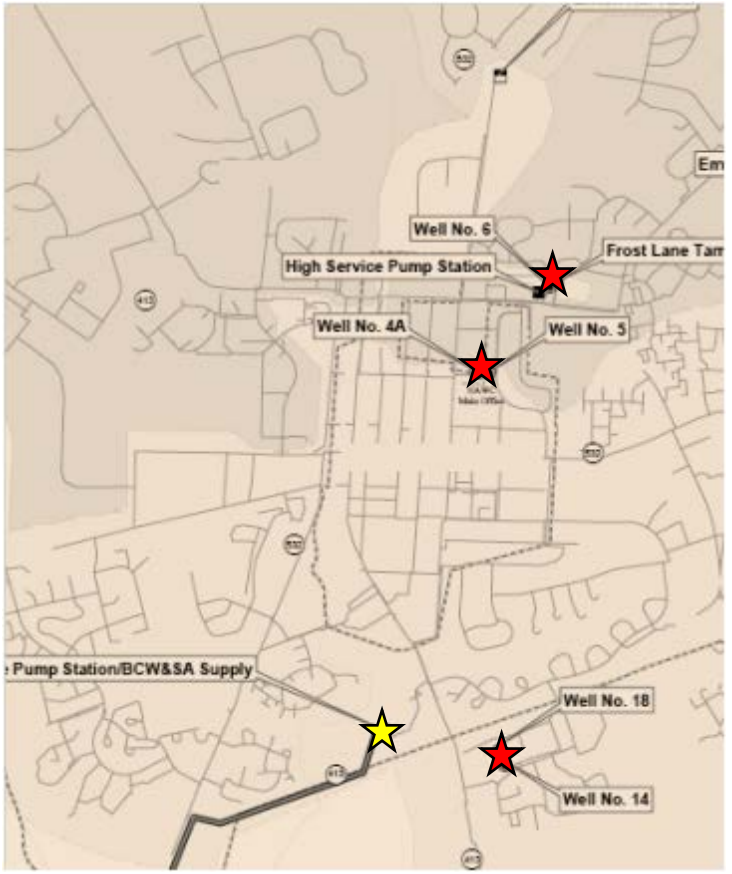


Theoretical Breakpoint Curve

From: *Handbook of Chlorination and Alternative Disinfectants: Fourth Edition* White, George Clifford; 1999.

A Case Study for Consecutive Systems

- **Five chlorinated well supplies**
  - Three locations
- **Chloraminated purchased water**
  - About 50-60% of the system supply



Chlorine in the Supplies is Adequate, but Coliform was Detected in Routine Samples

- **Free chlorine residual in well supplies 1.5 to2.5 mg/L**
- **Total chlorine in purchased water 1.8 to 2.4 mg/L**
- **Coliform detected in distribution system samples**
  - Detected in 1 to 3 of 30 samples several months in late 2009 and early 2010
  - No detection in check samples
  - Initial assumption was poor sampling

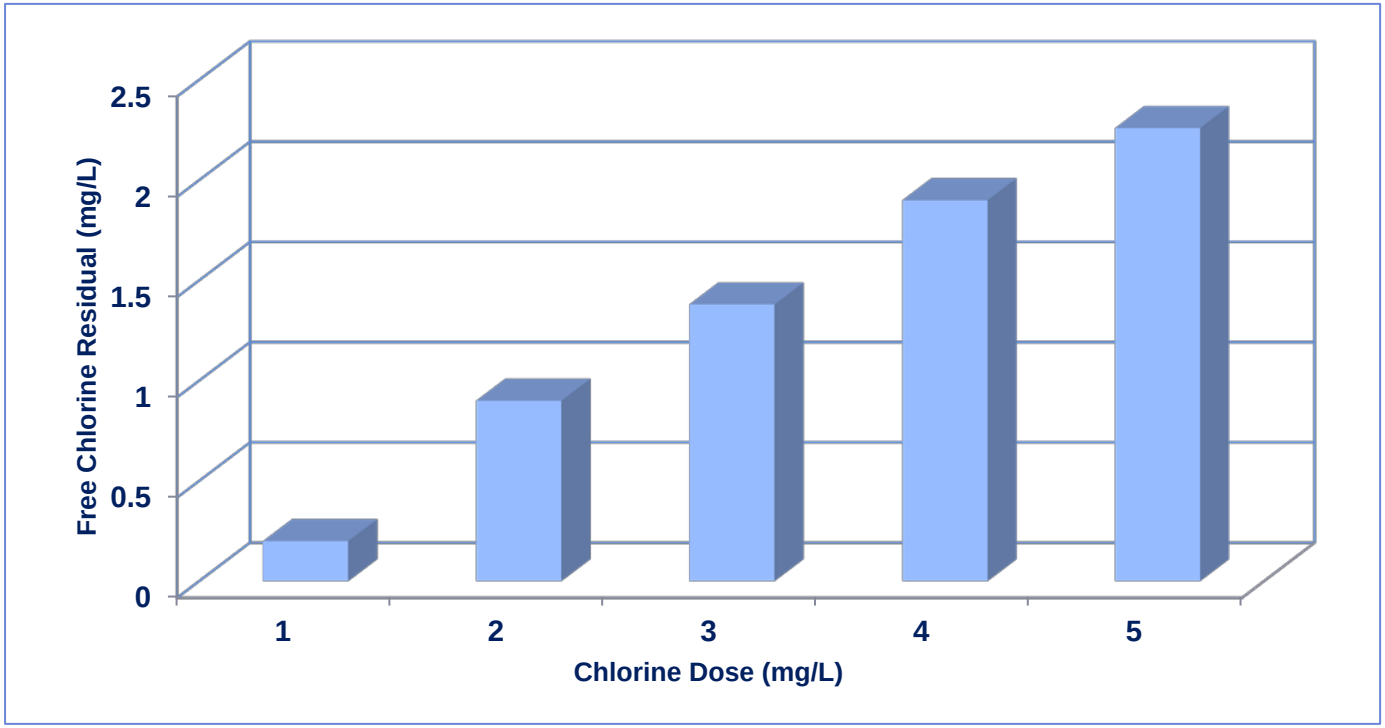
Multiple Supplies can Lead to Inadvertent Breakpoint Chemistry

- **So what happened?**
  - Low chlorine residual at multiple locations in the distribution system (<0.2 mg/L)
  - Coliform detected in areas with blended chloraminated and chlorinated source waters
- **Chloramines reacted with free chlorine in the distribution system and pushed the reaction to breakpoint**

Prevent Breakpoint Chemistry in Distribution System

- **Compared two alternatives:**
  - Adding ammonia to well sources to chloraminate
    - Not feasible because of the number of wells
    - May be the best choice for other systems
  - Adding free chlorine to purchased water supply to take advantage of breakpoint chlorination and maintain a free chlorine residual
    - Bench tested

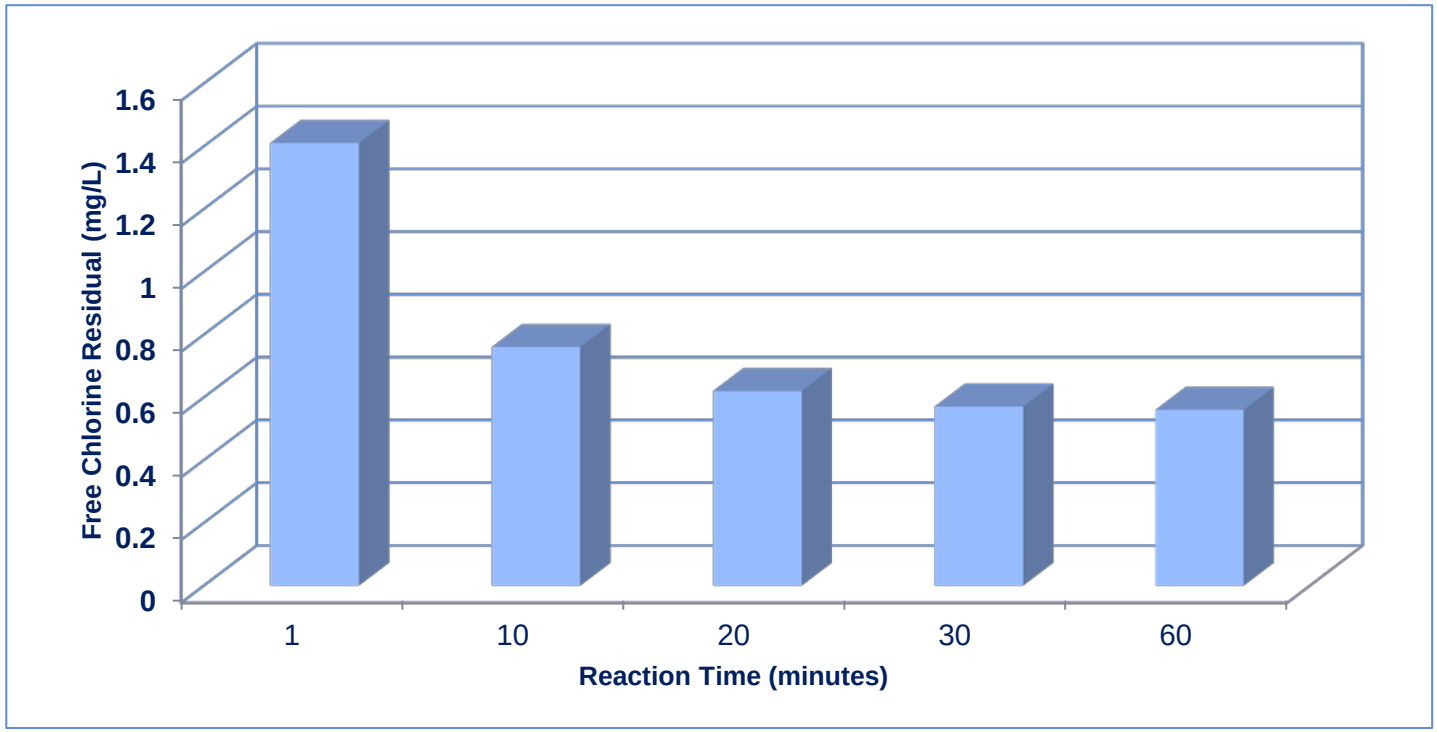
Bench Testing Showed Improved Free Chlorine Residual



Reaction Time: 1 minute

Initial Total Chlorine Residual: 1.65 mg/L

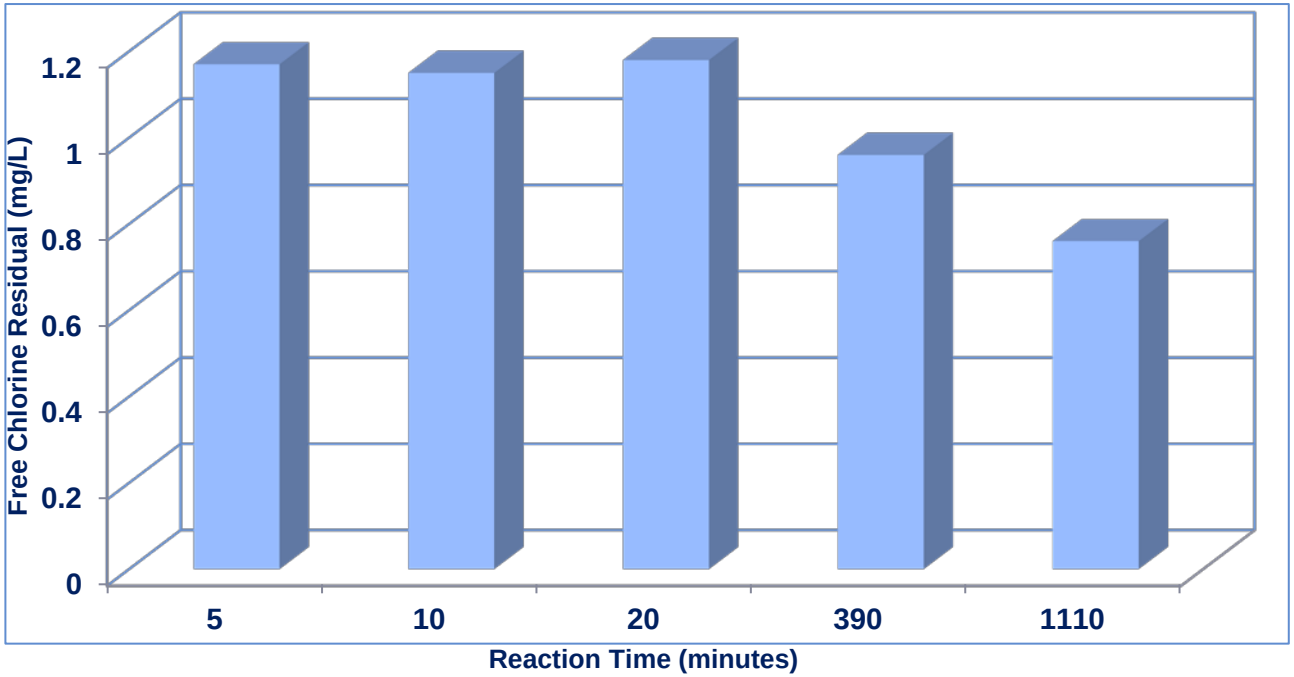
Chlorine/Chloramine Reaction is Slow



Chlorine Dose: 3 mg/L

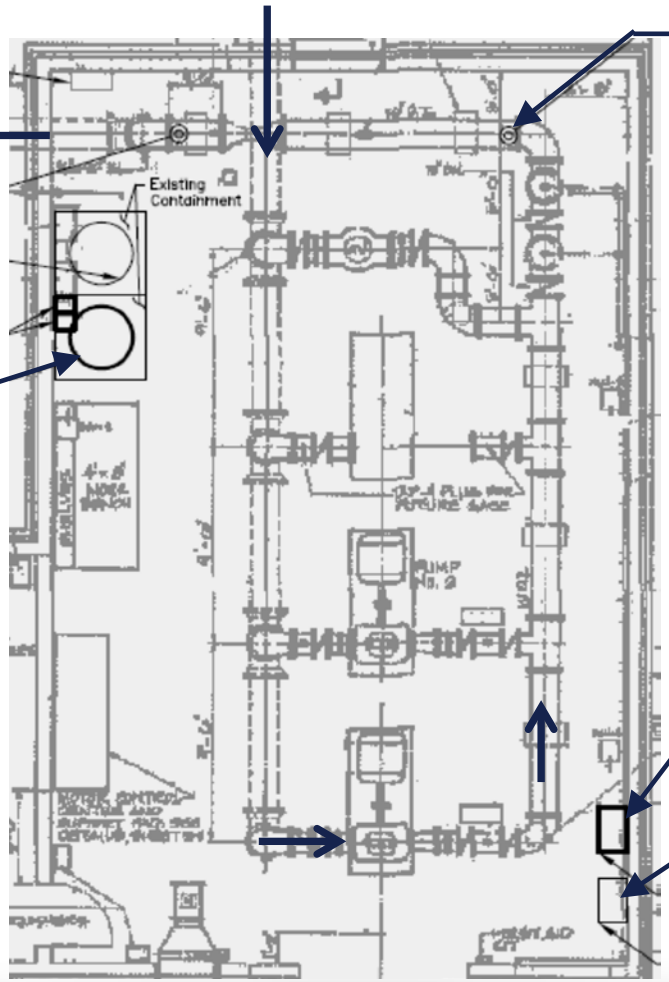
Initial Total Chlorine Residual: 1.65 mg/L

Converted Water Blended with Chlorinated Water Maintained a Stable Free Chlorine Residual



- 50/50 blend of converted water and well water
- Initial Chlorine Dose: 3 mg/L
- Initial Total Chlorine Residual: 1.65 mg/L
- Well Water Chlorine Residual: 2.70 mg/L

A Chlorine Feed System was Installed at the BPS



Sodium Hypochlorite
Application Point

Sodium Hypochlorite
Feed System

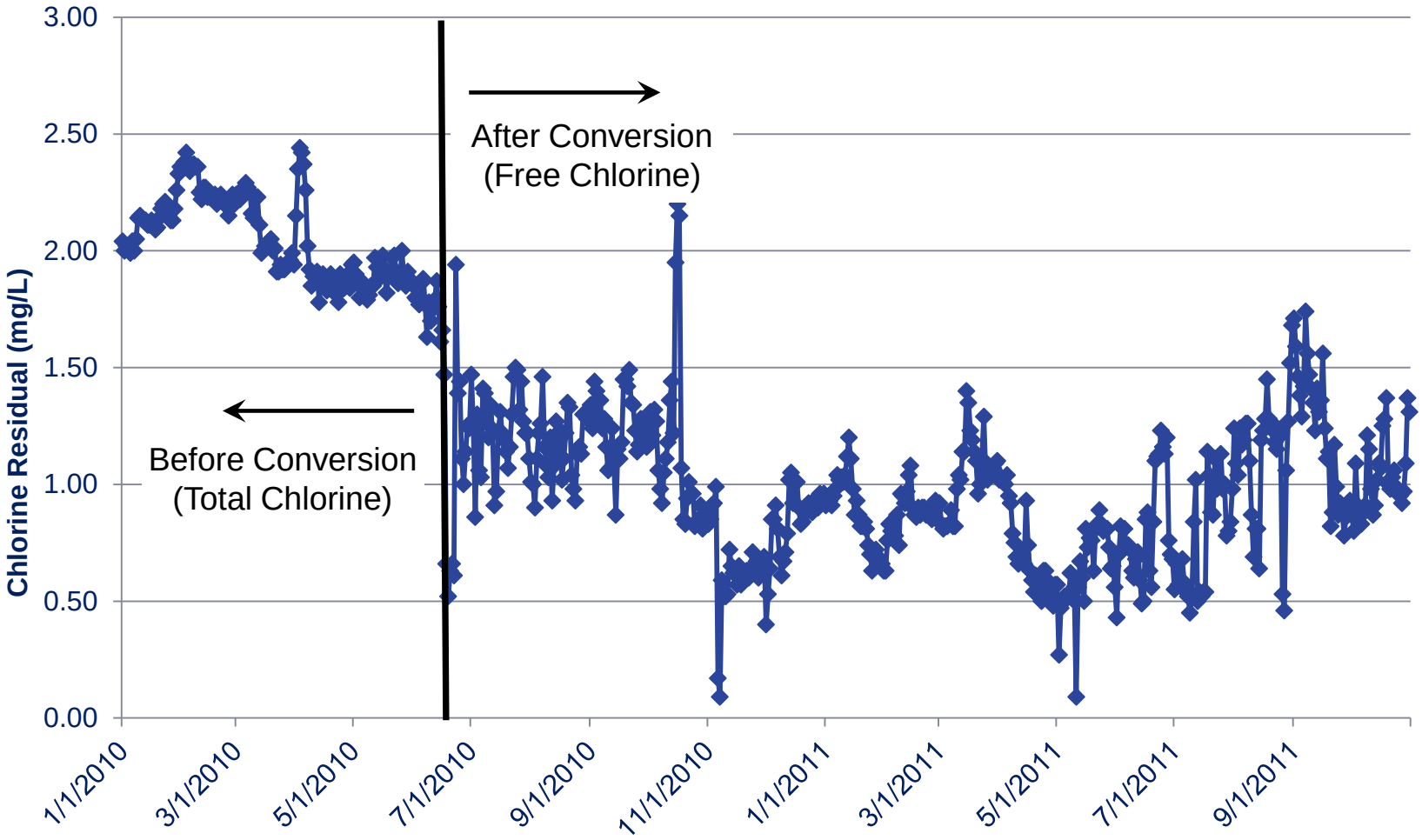
Free Chlorine
Residual Analyzer

Total Chlorine
Residual Analyzer

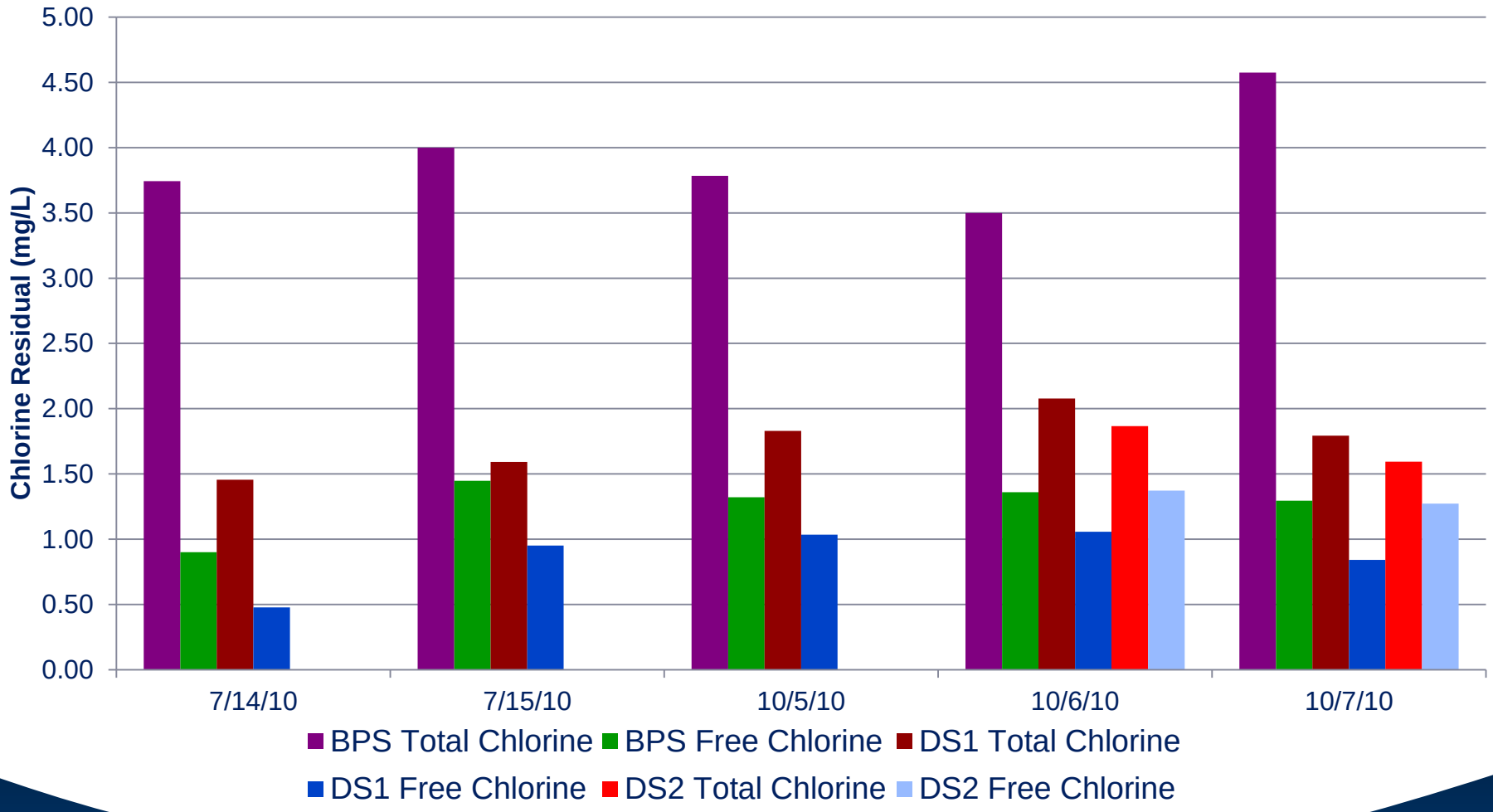
Free Chlorine Residuals Improved

Monthly Distribution System Samples	Summer 2009 – Before Conversion	Summer 2011 – After Conversion
Median Free Chlorine Residual	0.10 mg/L	0.82 mg/L
Percent of Samples less than 0.1 mg/L	45%	4%

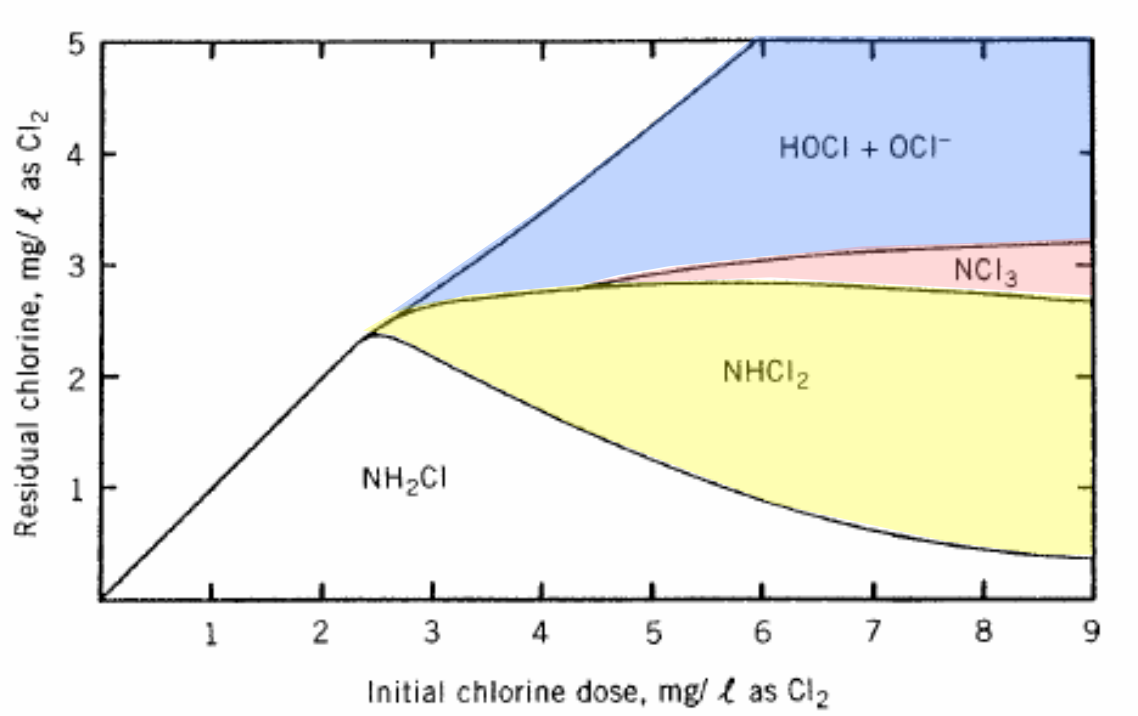
Free Chlorine Residual is Maintained in the BPS Discharge



The Conversion Reaction is Not Immediate



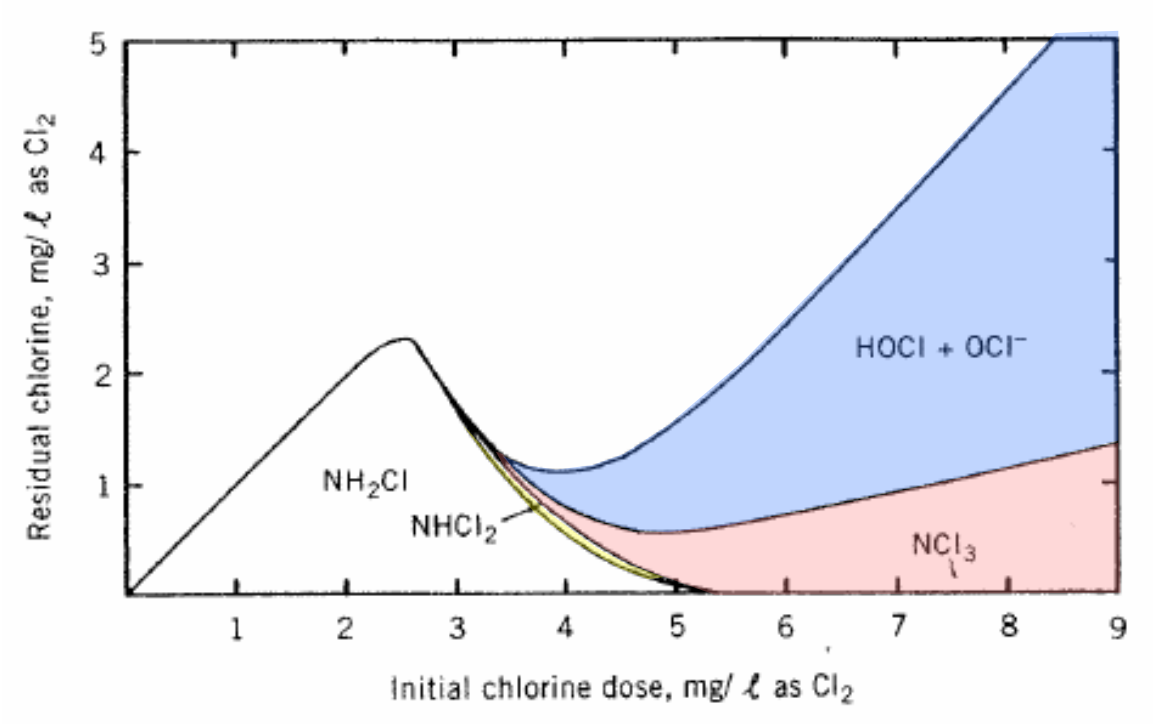
Chloramine Conversion Incomplete after Short Contact Time



Predicted chlorine residual curves after 2.5 minutes contact time ($pH = 7.4$, NH_3-N = 0.5 mg/L, 15°C)

From: *Handbook of Chlorination and Alternative Disinfectants: Fourth Edition*
White, George Clifford; 1999.

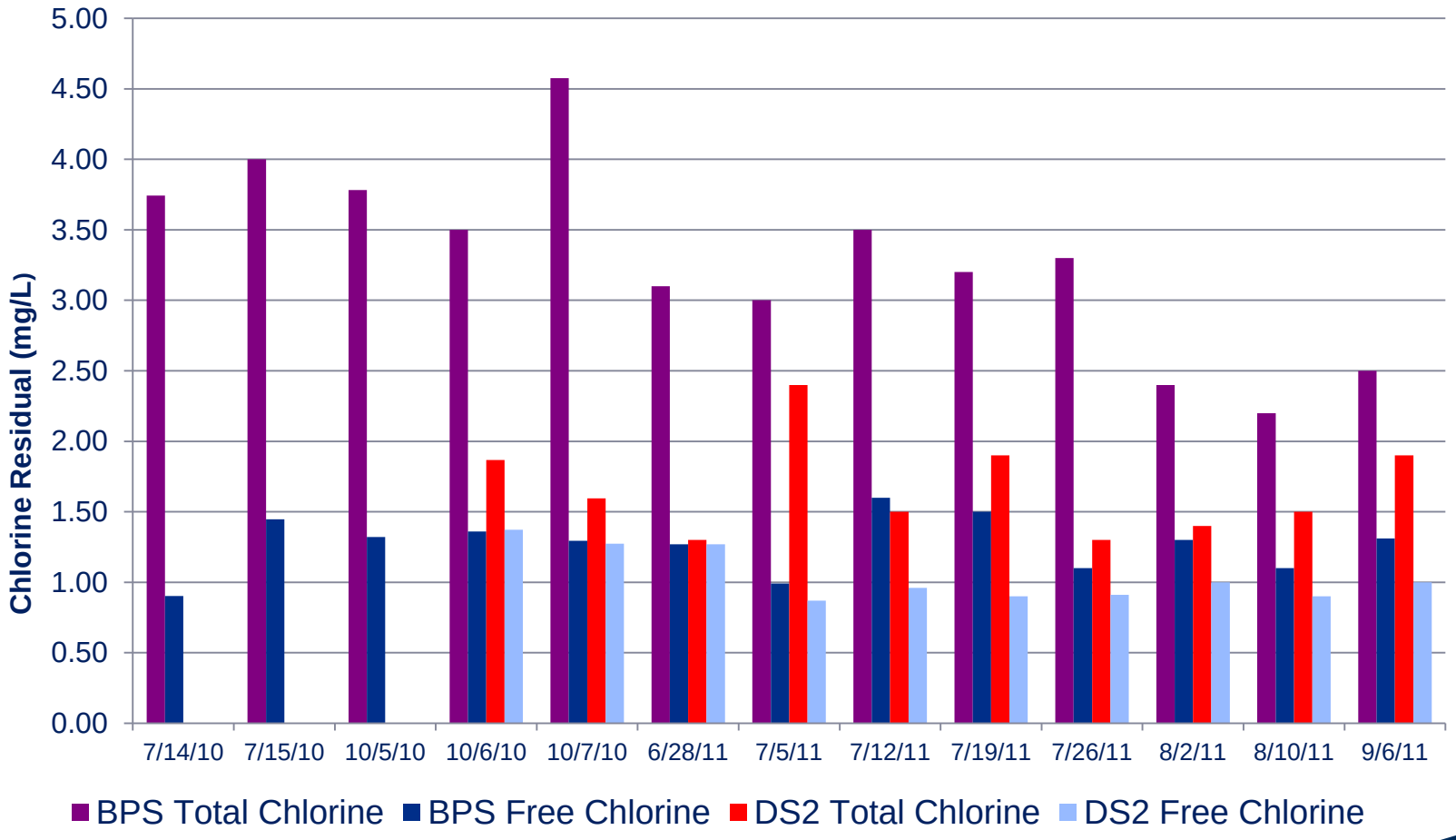
Chloramine Conversion Nearly Complete After More Contact Time



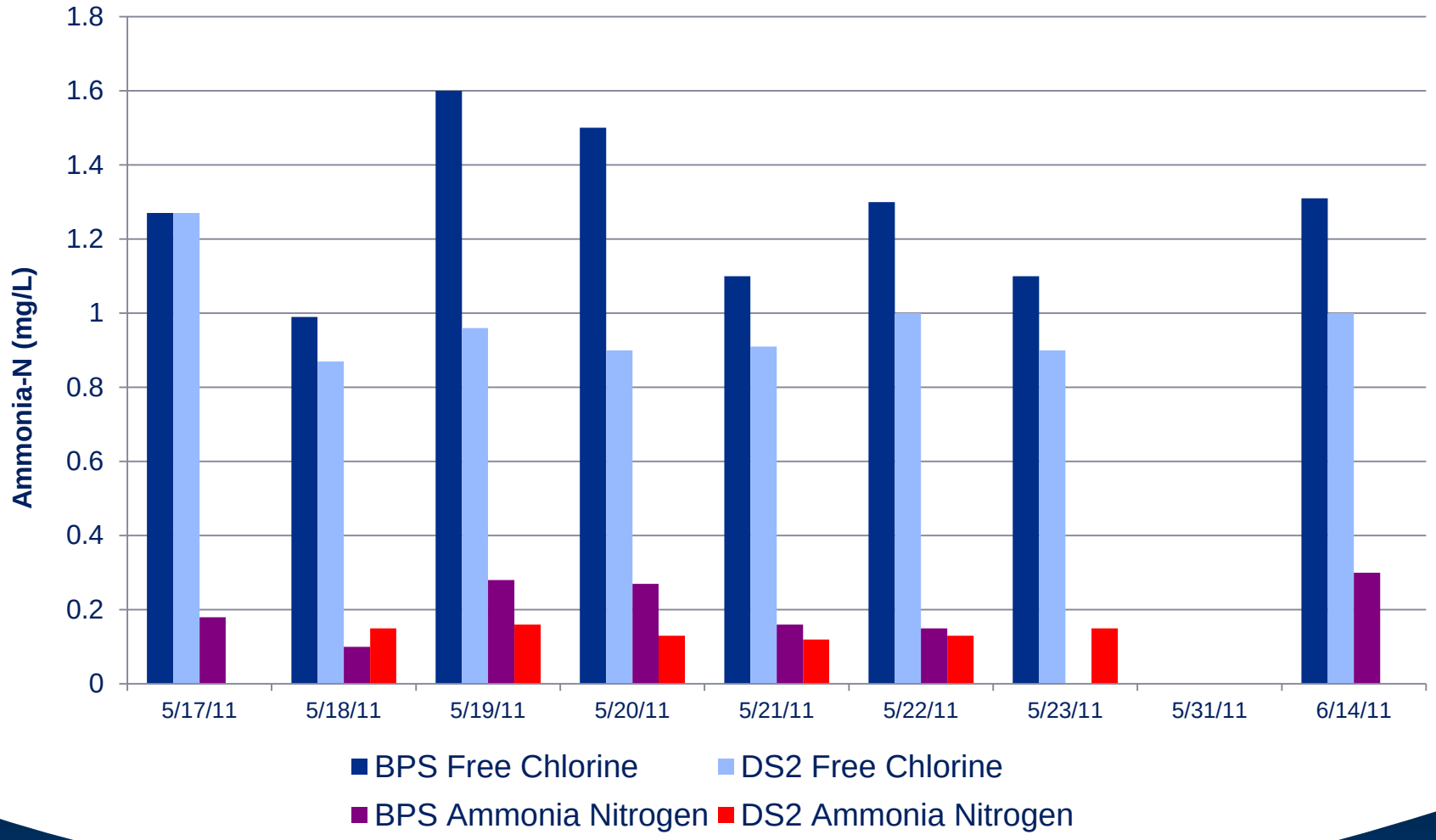
Predicted chlorine residual curves after 20 minutes contact time (pH = 7.4, NH_3-N = 0.5 mg/L, 15°C)

From: *Handbook of Chlorination and Alternative Disinfectants: Fourth Edition*
White, George Clifford; 1999.

Conversion Nears Completion in the Distribution System



Low Levels of Free Ammonia Are Present



Chlorine Residuals Have Improved, but Fine Tuning May be Needed

- **Still having some localized low chlorine residuals**
- **Total coliform has been detected in several samples since the conversion**
- **Taste and odor complaints have increased**
  - Due to higher free chlorine residuals?
  - Or could be intermediate trichloramine formation

Chloramines For Secondary Disinfection Can have Unintended Consequences

- **More systems are using chloramines for secondary disinfection**
  - Reduce DBP formation
  - Maintain a residual more easily
- **Combining a chloraminated source water with a chlorinated source water can lead to a loss of chlorine residual**

Preventing Breakpoint Chemistry in the Distribution System is Essential

- **Convert the free chlorine into chloramines**
  - For systems with many sources, this may not be feasible
  - Can be difficult to ensure the optimum Cl2:N ratio
- **Add free chlorine for controlled breakpoint chemistry and form a free chlorine residual**
  - Consider reaction times
  - DBPs may be a concern for some systems

Thank You!

Thanks also to:

Stephanie Posse
Jamie Shambaugh

Any Questions?

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