Chloramination and Nitrification Part 1

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OTCO 58th Annual Water Workshop

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Agenda

- Brief history of chloramination
- Chloramine production and chemistry
- Forms of ammonia
- Chlorine to nitrogen ratios
- Example dosage calculations
- Complexities of combined chlorine
- Chloramine decay reactions

Brief History of Chloramines

- Discovered by Friedrich (Fritz) Raschig in 1907
  - Accidental discovery reacting analine with hypochlorite and ammonia
    - Produced yellow oily substance that he named “chloramine”
- Later chloramination developed for its germicidal effects in water
  - First chloramination - Ottawa, Canada 1916
  - First US facility - Denver, Colorado 1917

F. Raschig 1897

Brief History of Chloramines

- Popular disinfection method during 1920s and 1930s
  - 16% public water systems used chloramination in 1930s
  - Because of World War II, chloramination stopped 1940s since ammonia was difficult to obtain
    - Started using free chlorine disinfection
  - 1990s, DBP formation responsible for renewed interest in chloramination
    - Stage 2 D/DBP Rule THM reduced from 100 μg/L to 80 μg/L
    - Significantly reduced DBP formation
  - Today, about 20% of public water systems use chloramines
    - DBP control
    - More persistent residual maintenance

Chloramines

- Byproduct of reaction between chlorine and ammonia
  - Disinfecting capabilities
  - Longer lasting residual than free chlorine
  - Slower decay and decomposition than free chlorine
  - Lower DBP formation than free chlorine
    - 40% to 80% lower DBPs reported
- Most common practice in water treatment
  - Meet CT with free chlorine, then convert to chloramines with ammonia source
  - Equilibrium reaction, strongly favored to right

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

Chloramines

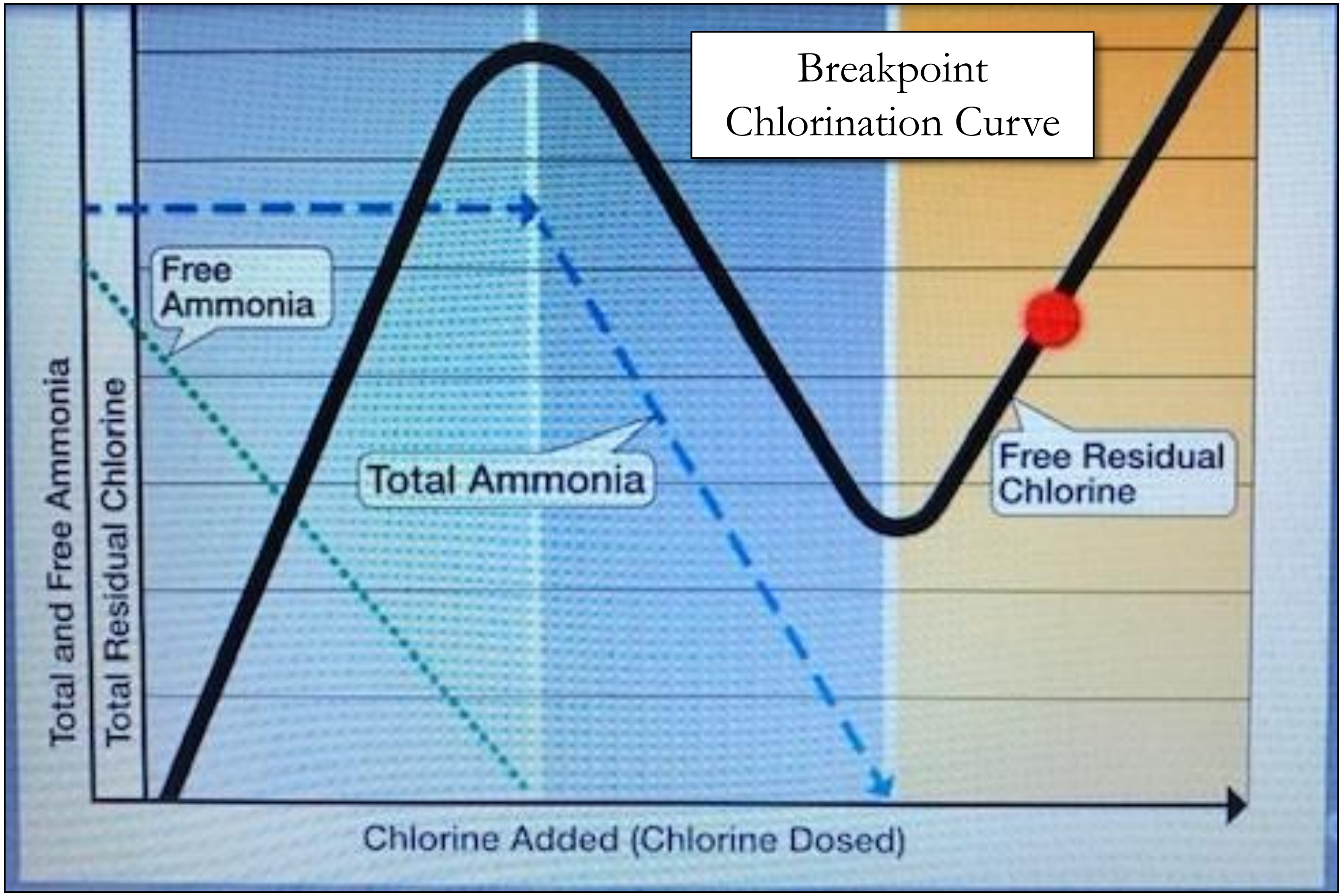
$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

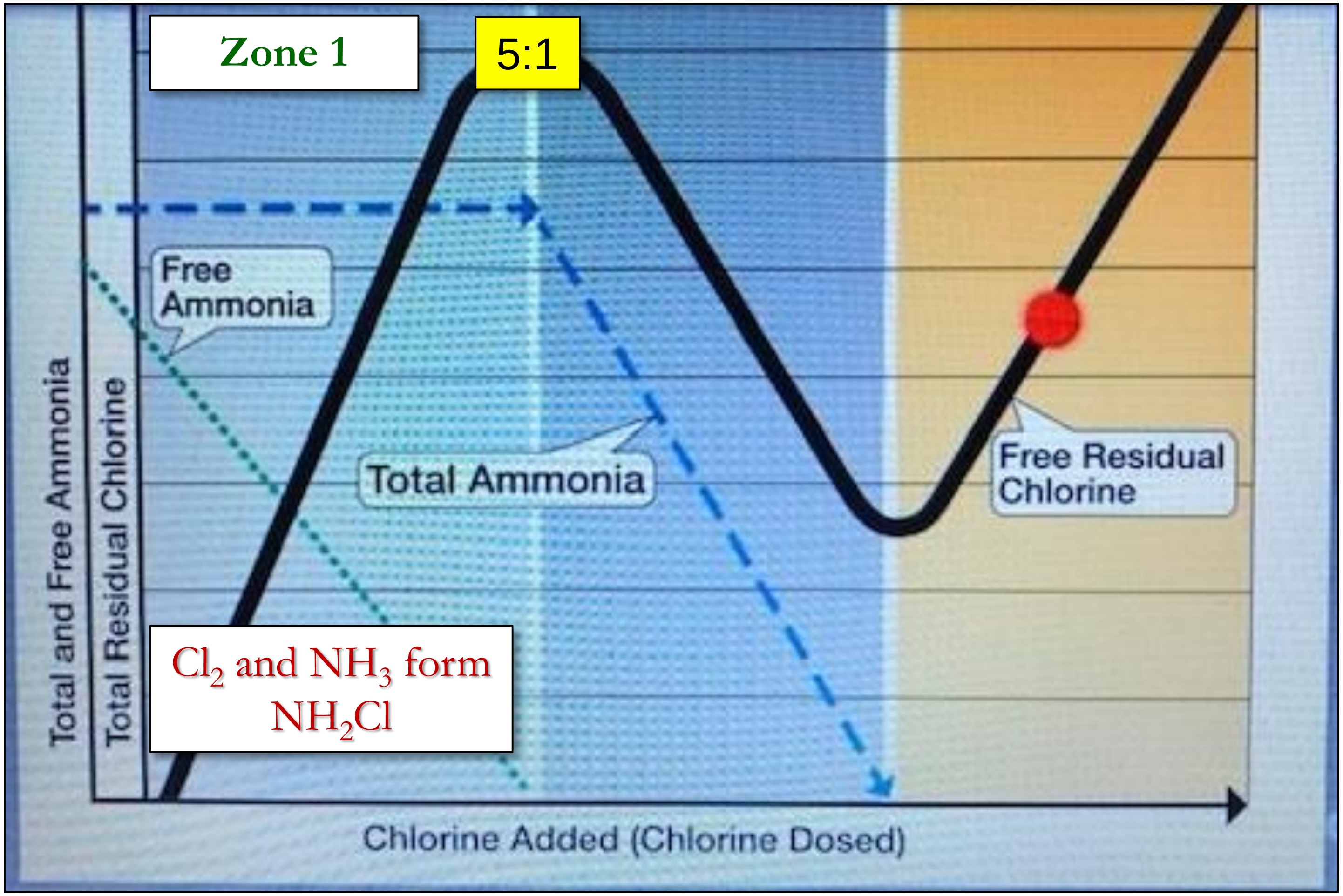
pH and temperature dependent

Chlorine/nitrogen ratio dependent

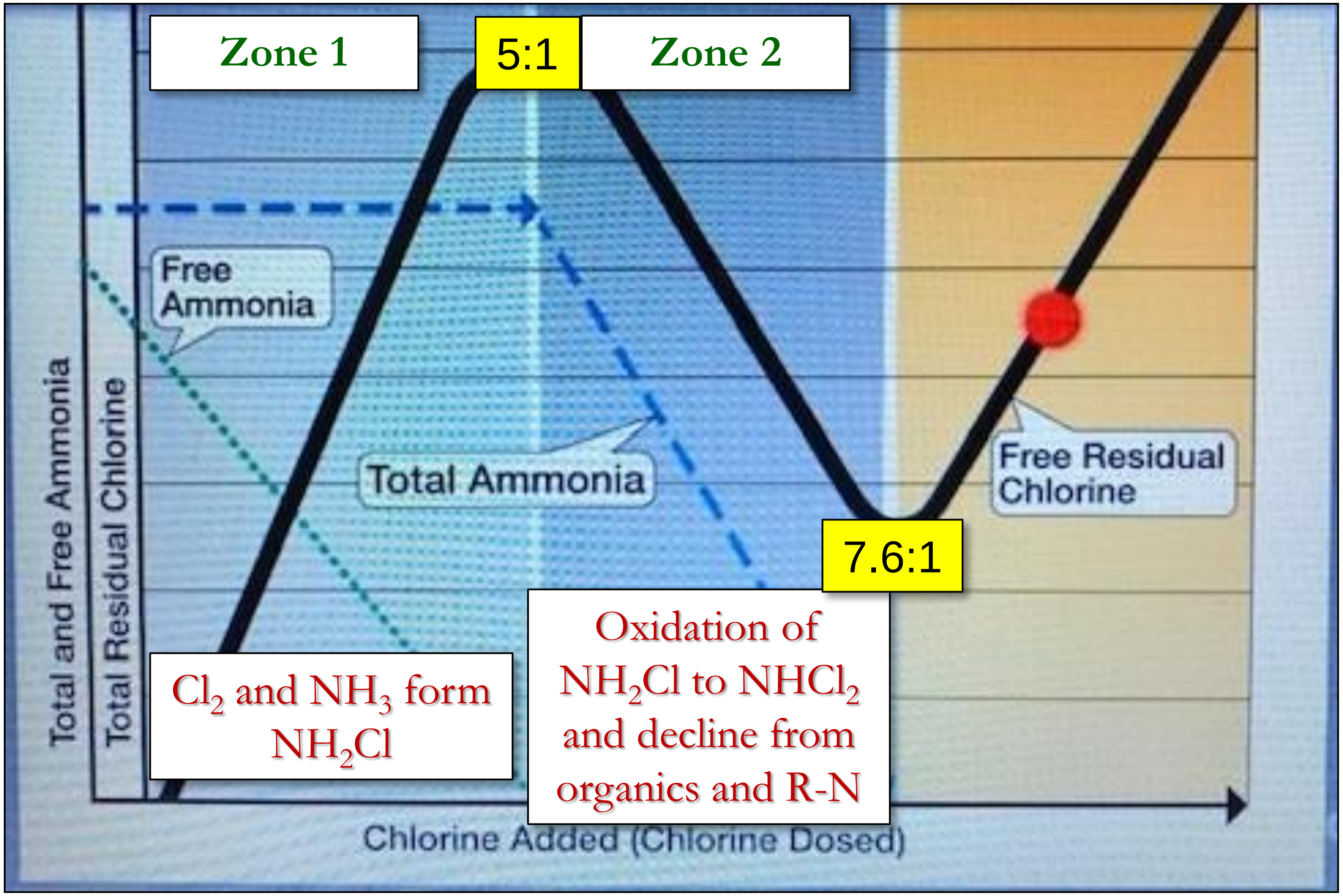
Chloramines



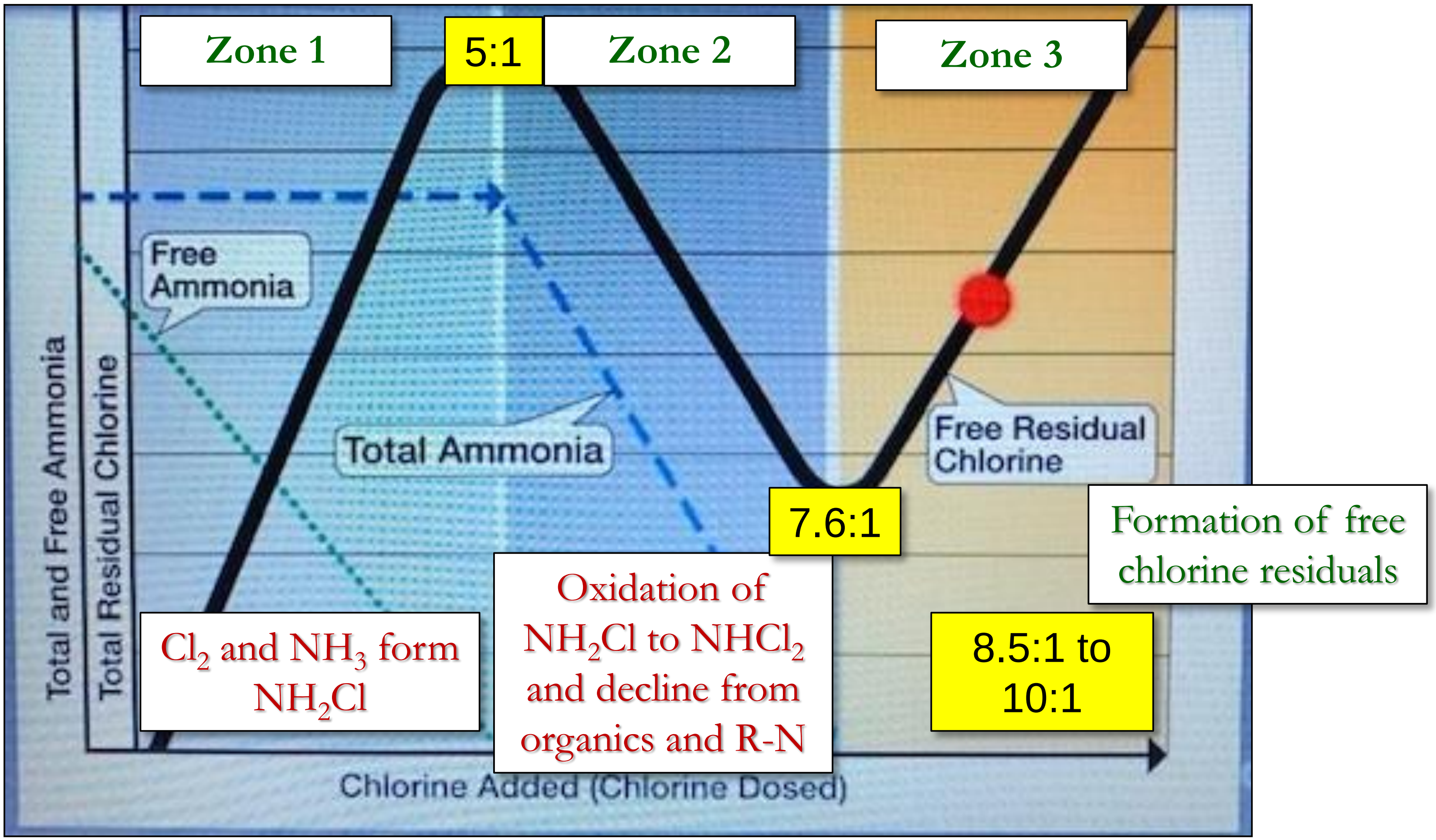
Chloramines



Chloramines



Chloramines



Chloramines

- Three forms exist
  - Monochloramine
  - Dichloramine
  - Trichloramine
- Cl_2:N ratio dependency
  - Monochloramine 5:1
  - Dichloramine 7.6:1
  - Trichloramine 15:1

Chlorine 70.7 MW
Nitrogen 14.01 MW
Cl_2:N ratio 5.05

Chloramines

Monochloramine

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O \quad (Cl_2{:}N \ \ 5{:}1)$$

Dichloramine

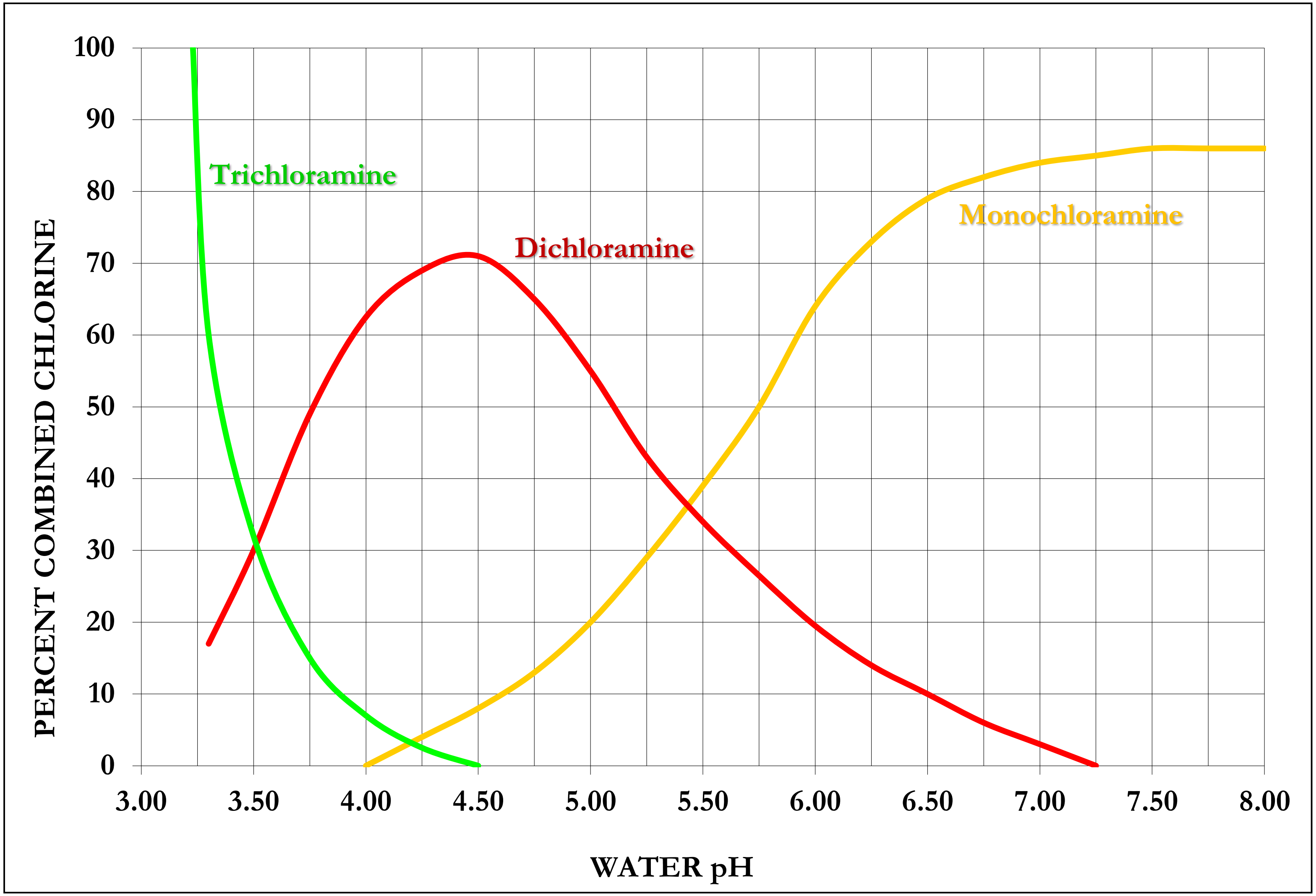
$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (Cl_2{:}N \ \ 7.6{:}1)$$

Trichloramine

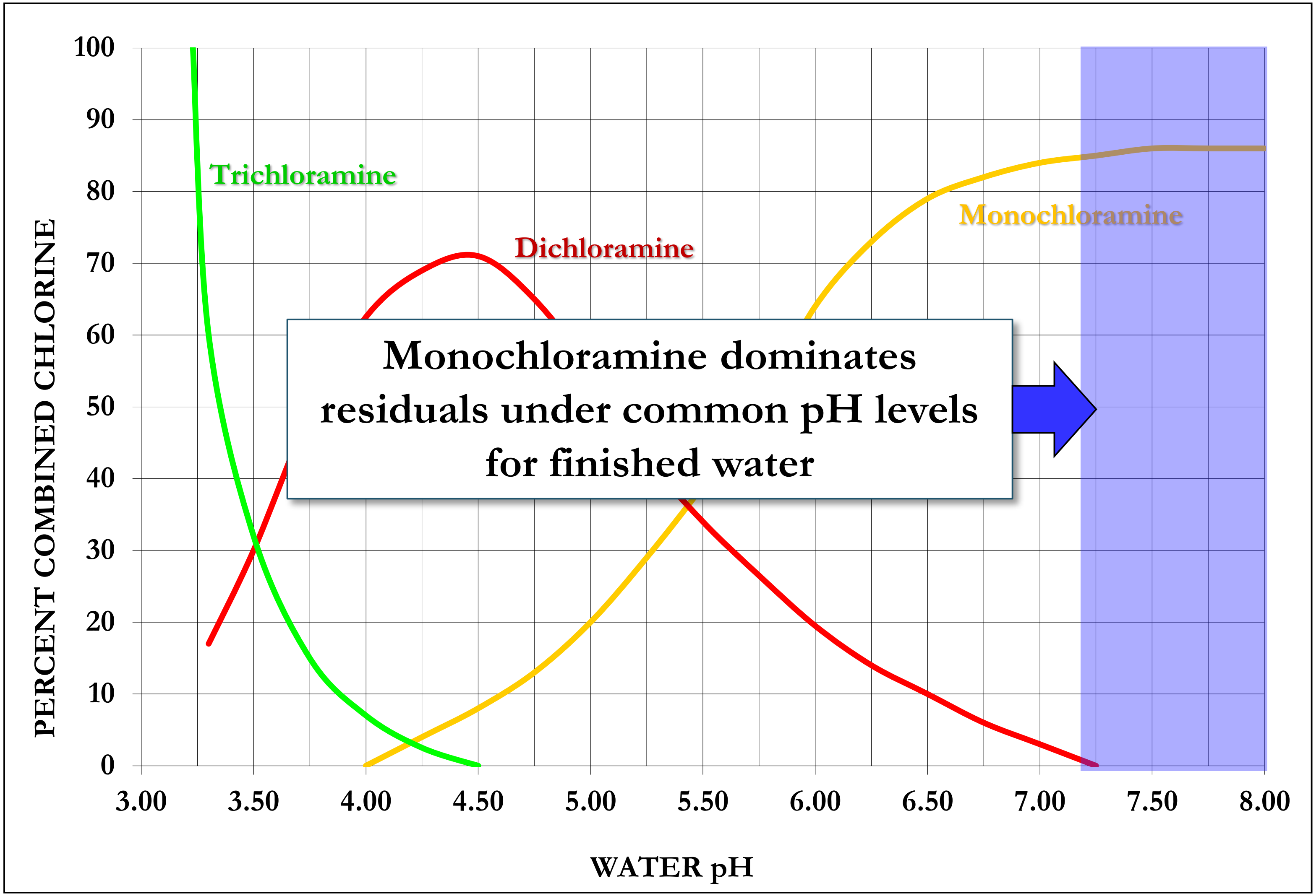
$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (Cl_2{:}N \ \ 15{:}1)$$

Avoid formation of di- and tri- species by maintaining proper Cl_2:N ratios and pH levels

Chloramines



Chloramines



Chloramines

- Equilibrium reverse reaction can lead to nitrification

$$NH_2Cl + H_2O \Leftrightarrow HOCl + NH_3$$

- Conversion to hydroxylamines - high pH conditions

$$NH_2Cl + OH^- \Rightarrow NH_2OH + Cl^-$$

Chloramines

- **Disinfecting Power**

Ozone	18,000,000
Hydrogen peroxide	347,000
Chlorine dioxide	263,000
Hypochlorous acid	10,000
Hypochlorite ion	100
Monochloramine	1.0
Fluorine	0.90
Bromine	0.63
Iodine	0.56

Chloramines

- Known chloramination byproducts
  - THMs
  - HAA5s
  - Haloketones
  - Halonitriles
  - Halonitroalkenes
  - Haloamides
  - Cyanogen chloride
  - Chloropycrin
  - Chlorophenols
  - Nitrosodimethylamine (NDMA)
  - Mono-, Di-, Tri-chloramines (residuals)
  - Free ammonia

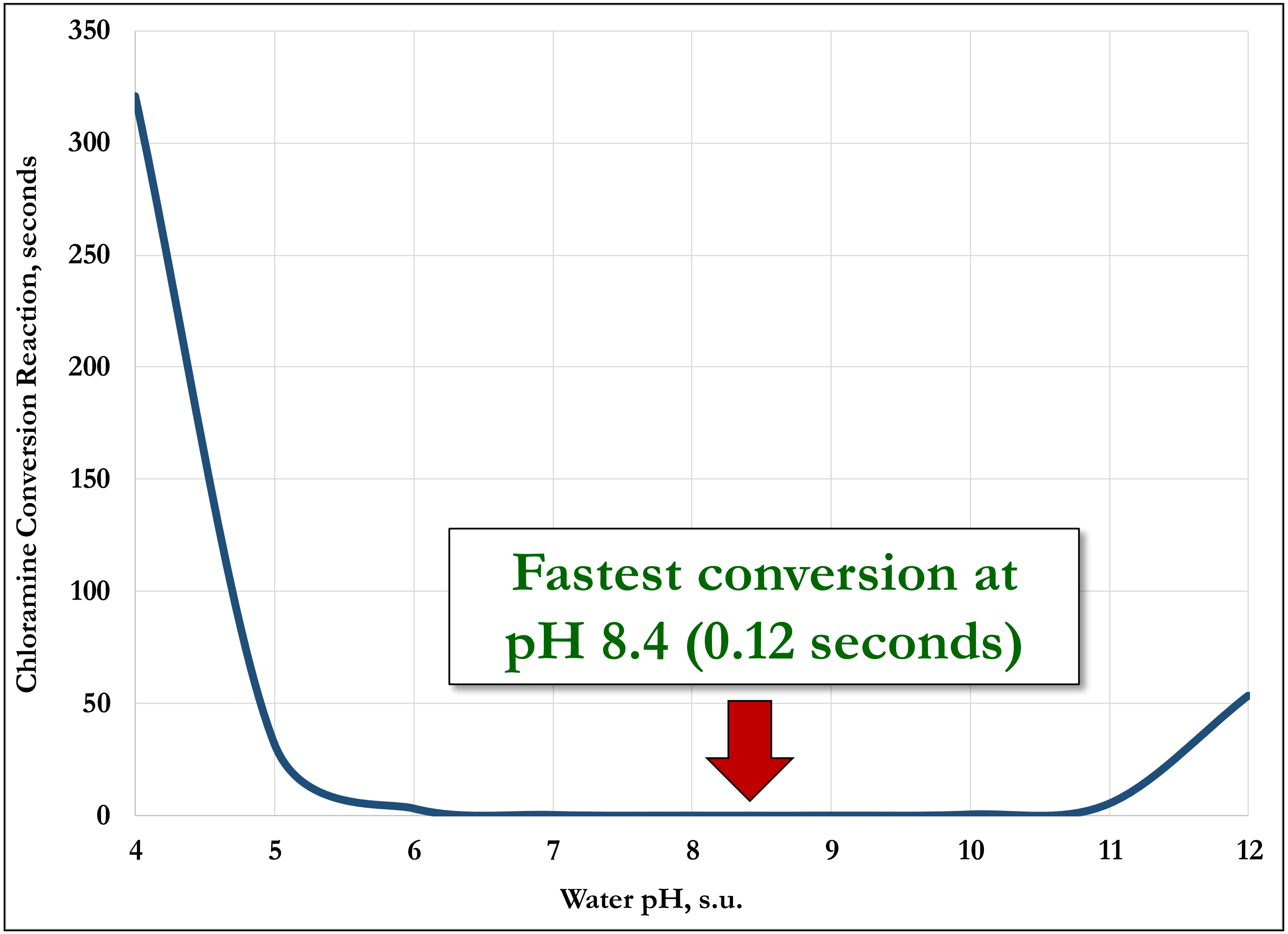
Chloramines

- Toxic to fish and amphibians
- Undesirable reactions with yeast in food manufacturing
  - Beer fermentation, musty taste
- Residuals difficult to remove from water
- WHO NOAEL
  - 9.4 mg/L based on human studies
- Common residuals from treatment
  - 2 mg/L to 5 mg/L
- Poor disinfectant for viruses and protozoa
  - CT requirements under SWTR

Chloramines

- Microbial destruction mechanisms
  - Electrochemical reaction with enzymes within microbial cell
  - Disruption of enzyme system fails to repair/grow cells
  - HOCl presence in NH_2Cl may increase disinfection capability
    - Biofilms tend to be resistant to chloramine disinfection once nitrification begins

Chloramines



Chloramines

- Can form non-germicidal residuals in reactions with certain organic compounds
  - Amino acids
  - Gelatin
  - Glycine
  - Cystine
  - Taurine
  - Uric acid
  - Uracil
  - Residuals often titrate as dichloramine false-positive values

Chloramines

- Control of monochloramine formation
  - Maintain proper chlorine to nitrogen ratios (Cl_2:N)
    - Target 4.5 to 5
  - Maintain pH at 8.4 or greater
    - Fastest conversion reaction time
    - Maintains equilibrium toward NH_2Cl and not reverse reaction
    - Reduces residual decay
  - Maintain free ammonia 0.05 mg/L or less
  - Reduce TOC from source water
    - Creates monochloramine demand and nitrification issues
    - Increases nutrient availability for biofilm growth (AOC)

Chloramines

- Control of taste and odor issues
  - Monochloramine residuals less than 5.0 mg/L
  - Dichloramine residuals less than 0.8 mg/L
  - Trichloramine residuals less than 0.02 mg/L

Ammonia Sources

- Natural source water levels (SW and GW)
  - Need to account for background NH_3 if not removed in treatment
- Anhydrous ammonia - gaseous
  - 99.95% NH_3
- Aqueous ammonia NH_4OH
  - 29.4% NH_3
- Liquid ammonium sulfate $(NH_4)_2SO_4$
  - Commonly LAS
  - 10% NH_3

Chlorine:Nitrogen Ratios

- Important to maximize monochloramine conversion and to minimize free ammonia residuals
- Cl_2:N target range
  - 4.5:1 to 5:1
- Common use of free chlorine for primary disinfection and CT compliance, then quench with ammonia source
  - Ammonia feed applied to convert free chlorine to monochloramine
  - Calculations important to prevent operating issues in distribution

Chlorine:Nitrogen Ratios

Example 1

- Free chlorine residual 2.3 mg/L
- Target Cl_2:N ratio 4.6
- Anhydrous ammonia applied (99.95% NH_3)

$$\frac{2.3\ mg/L}{4.6} = 0.5\frac{mg}{L}\ as\ N \qquad \frac{NH_3}{N} = \frac{17}{14} = 1.215$$

$$0.5\frac{mg}{L}\ as\ N\ * 1.215 = 0.61\frac{mg}{L}\ as\ NH_3$$

Chlorine:Nitrogen Ratios

Example 2

- Free chlorine residual 1.5 mg/L
- Target Cl_2:N ratio 5.0
- Aqueous ammonia applied (29.4% NH_3)

$$\frac{1.5\ mg/L}{5.0} = 0.3\frac{mg}{L}\ as\ N \qquad \frac{NH_3}{N} = \frac{17}{14} = 1.215$$

$$0.3\frac{mg}{L}\ as\ N\ * 1.215 = 0.365\frac{mg}{L}\ as\ NH_3$$

$$\frac{0.365\ mg/L}{0.294} = 1.24\frac{mg}{L}\ as\ NH_4OH$$

Chlorine:Nitrogen Ratios

Example 3

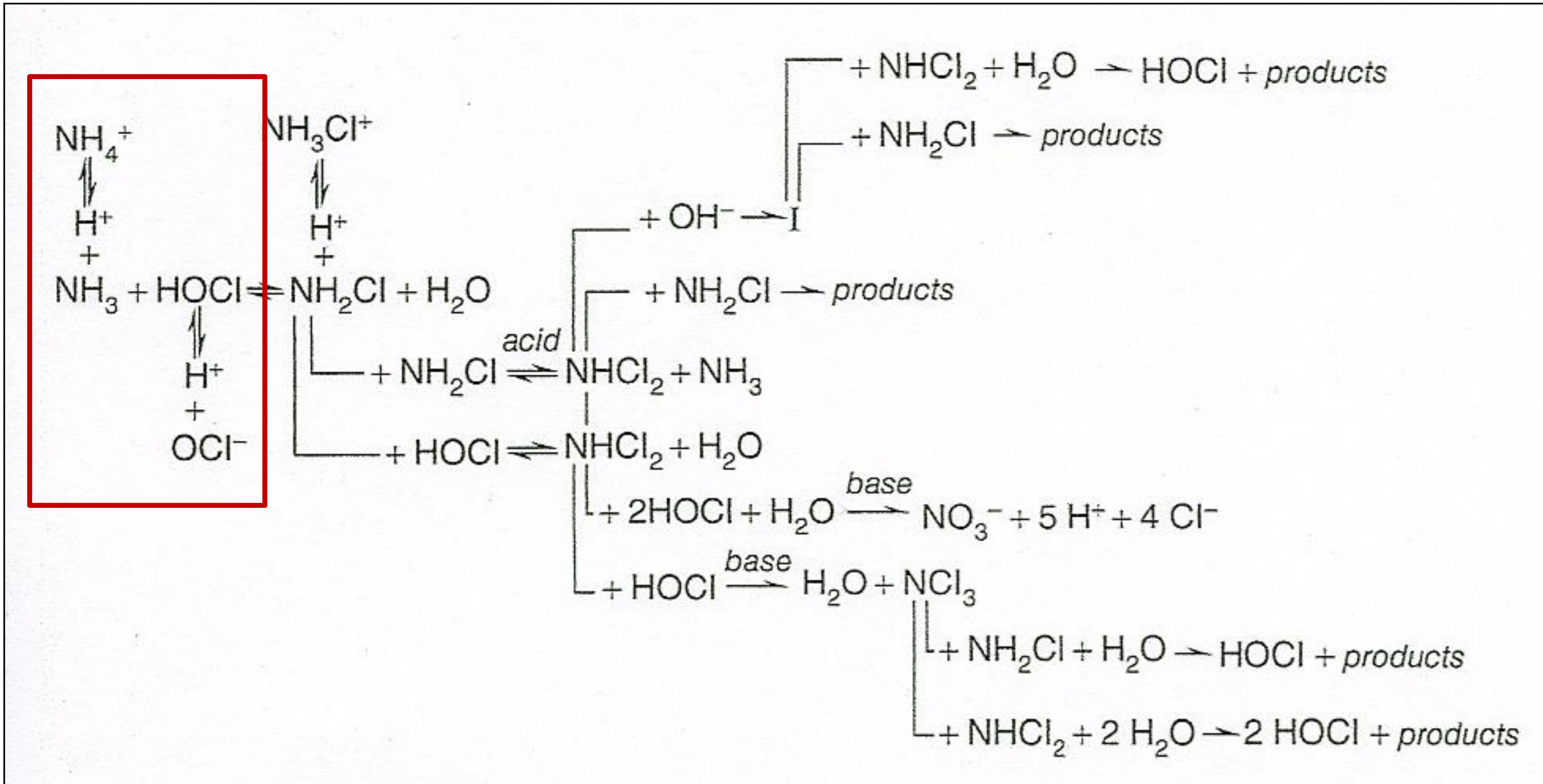
- Free chlorine residual 2.8 mg/L
- Target Cl_2:N ratio 4.8
- Liquid LAS applied (10% NH_3)

$$\frac{2.8\ mg/L}{4.8} = 0.58\frac{mg}{L}\ as\ N \qquad \frac{NH_3}{N} = \frac{17}{14} = 1.215$$

$$0.58\frac{mg}{L}\ as\ N\ * 1.215 = 0.70\frac{mg}{L}\ as\ NH_3$$

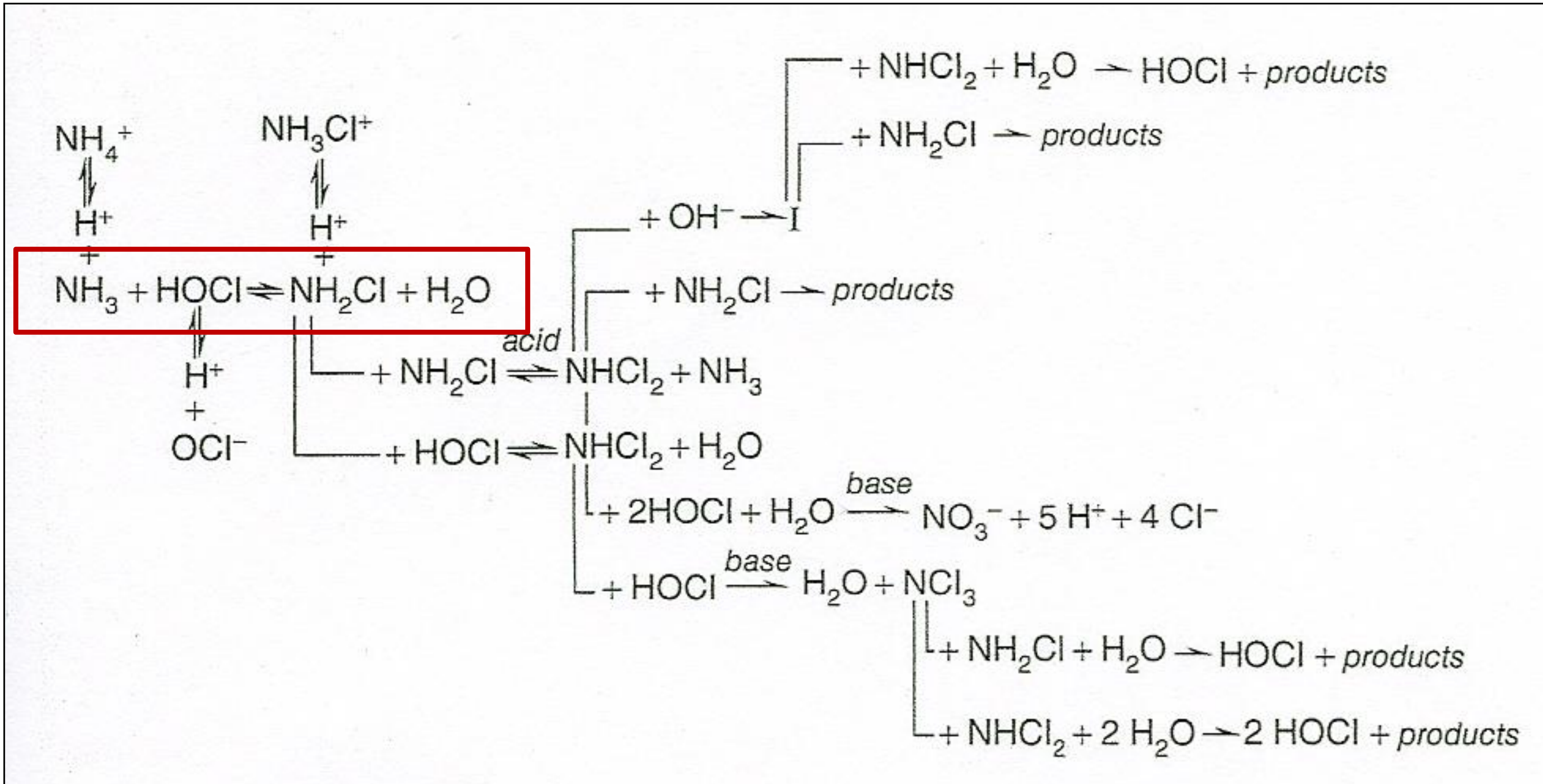
$$\frac{0.70\ mg/L}{0.10} = 7.0\frac{mg}{L}\ as\ (NH_4)_2SO_4$$

Combined Chlorine Complexity

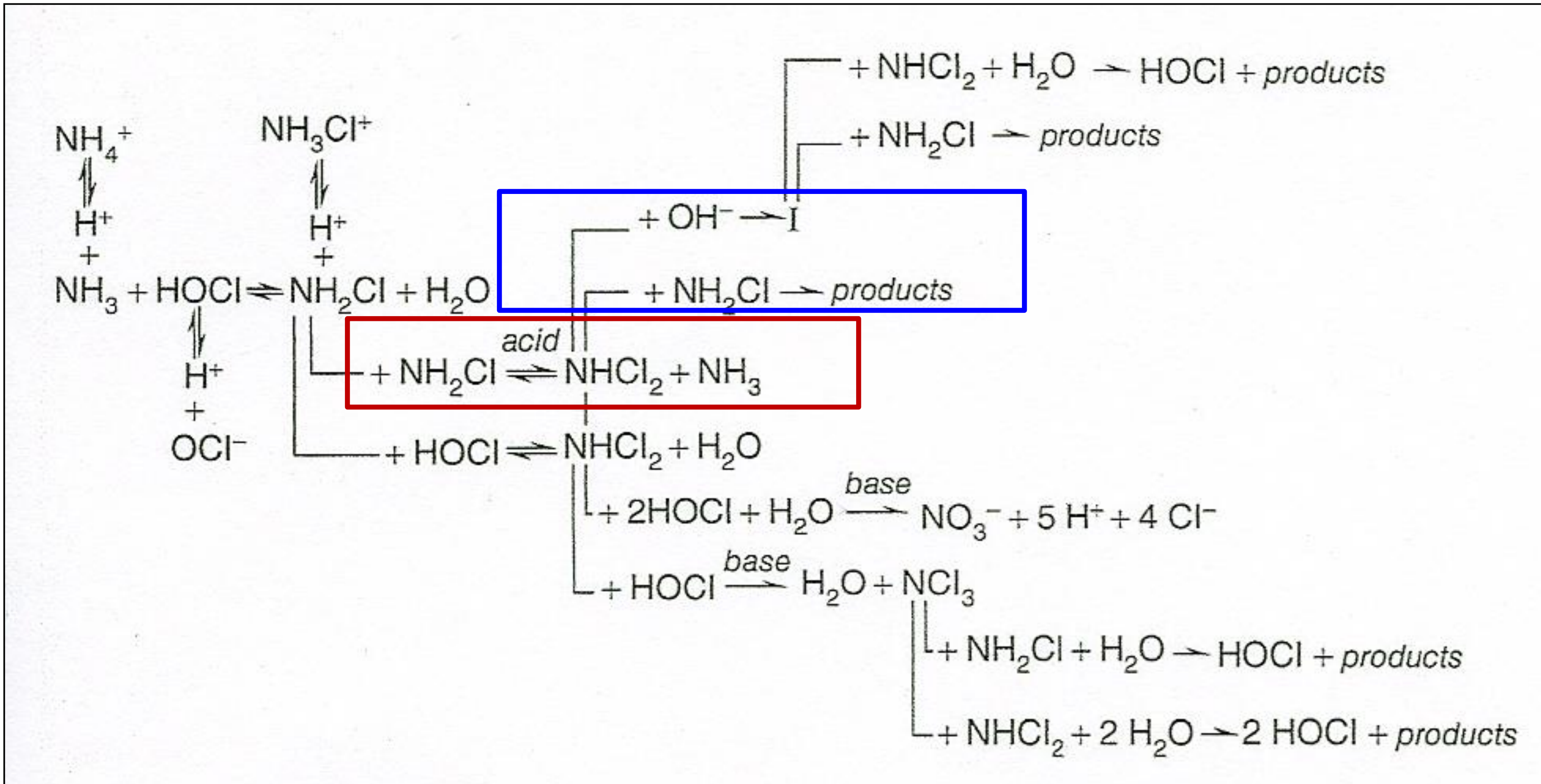


From "White's Handbook of Chlorination and Alternative Disinfectants"

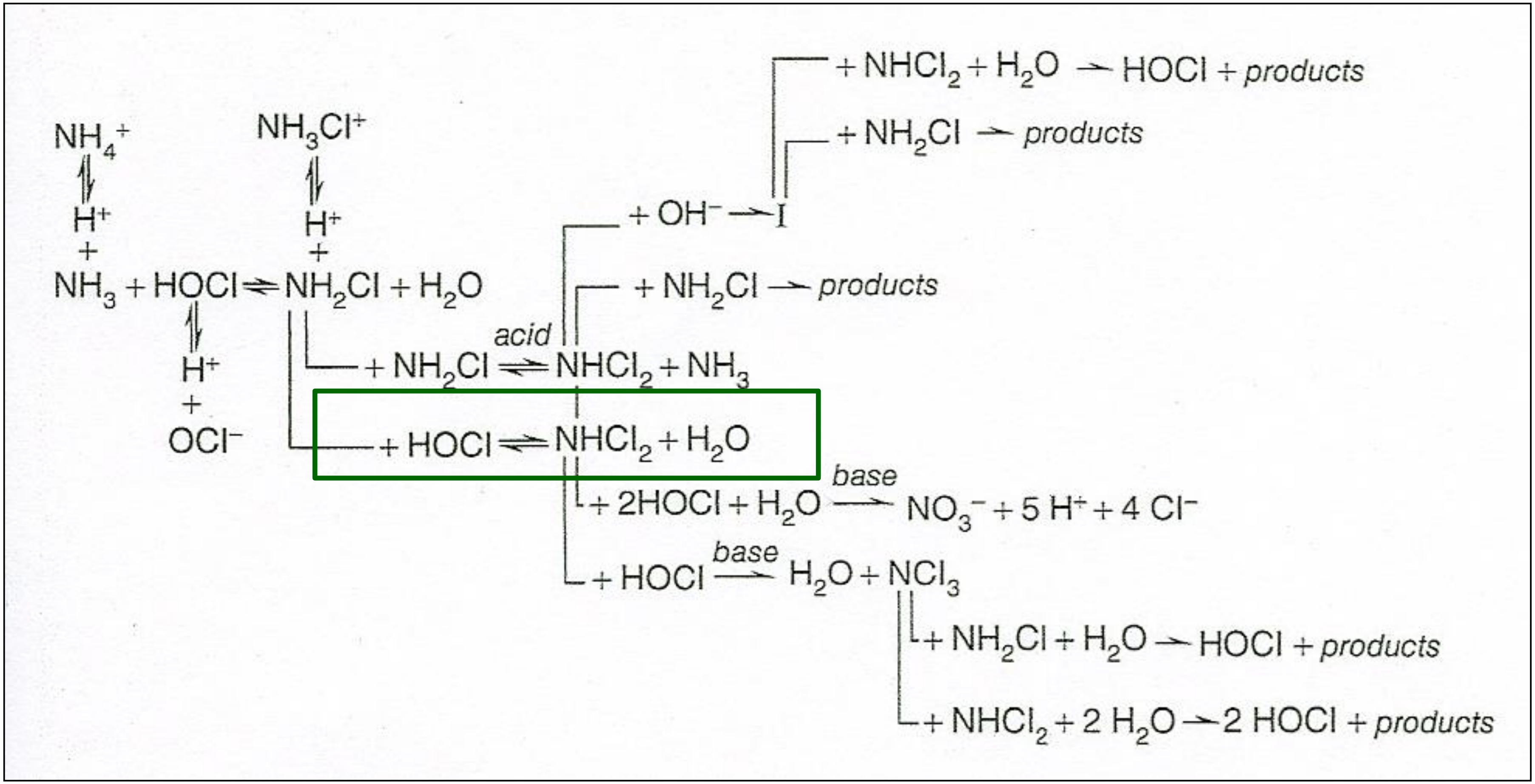
Combined Chlorine Complexity



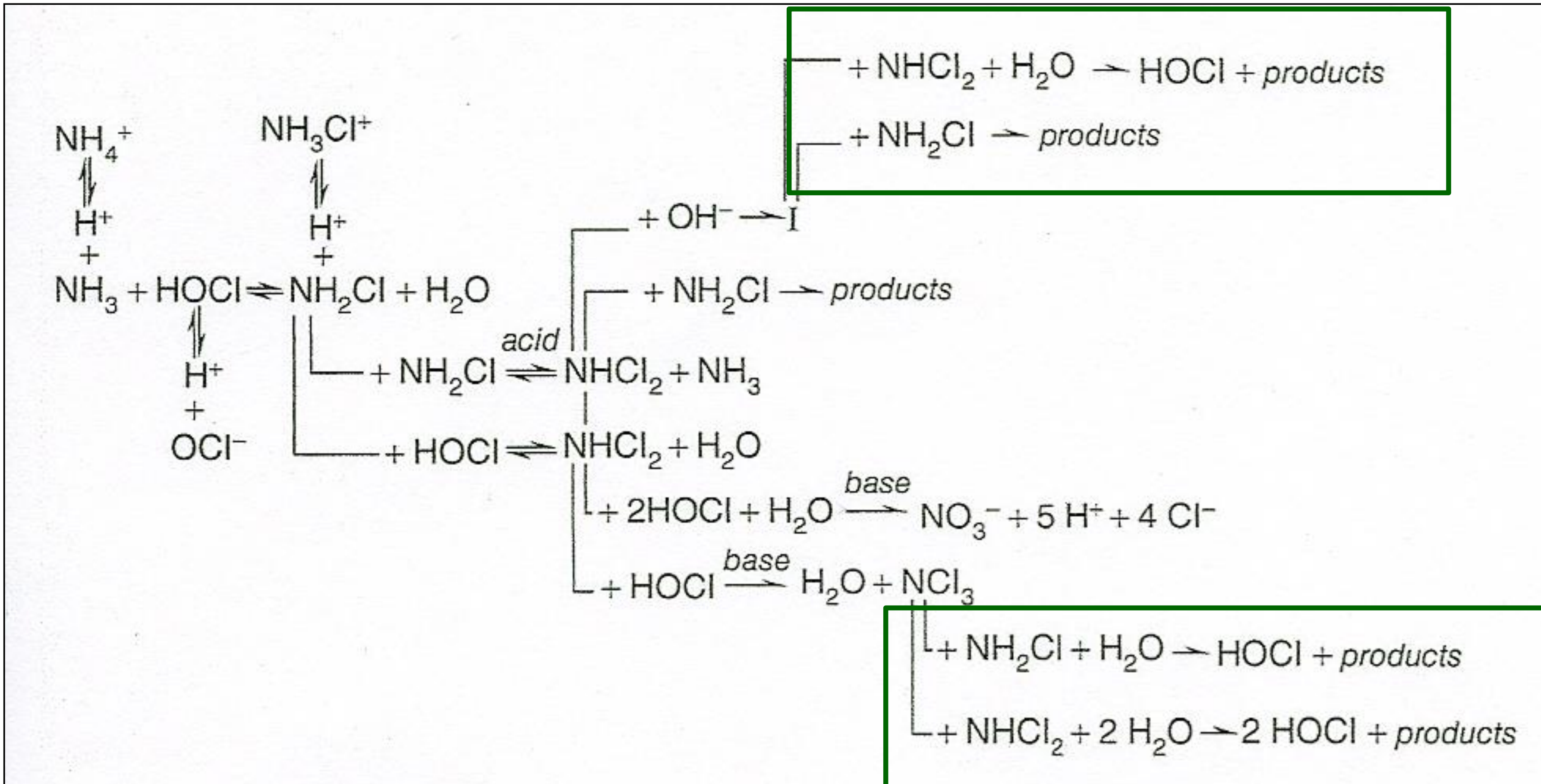
Combined Chlorine Complexity



Combined Chlorine Complexity



Combined Chlorine Complexity



Chloramine Decay

- Residual decay generally follows first order reaction

$$C_t = C_o e^{-kt}$$

C_t = concentration at time t

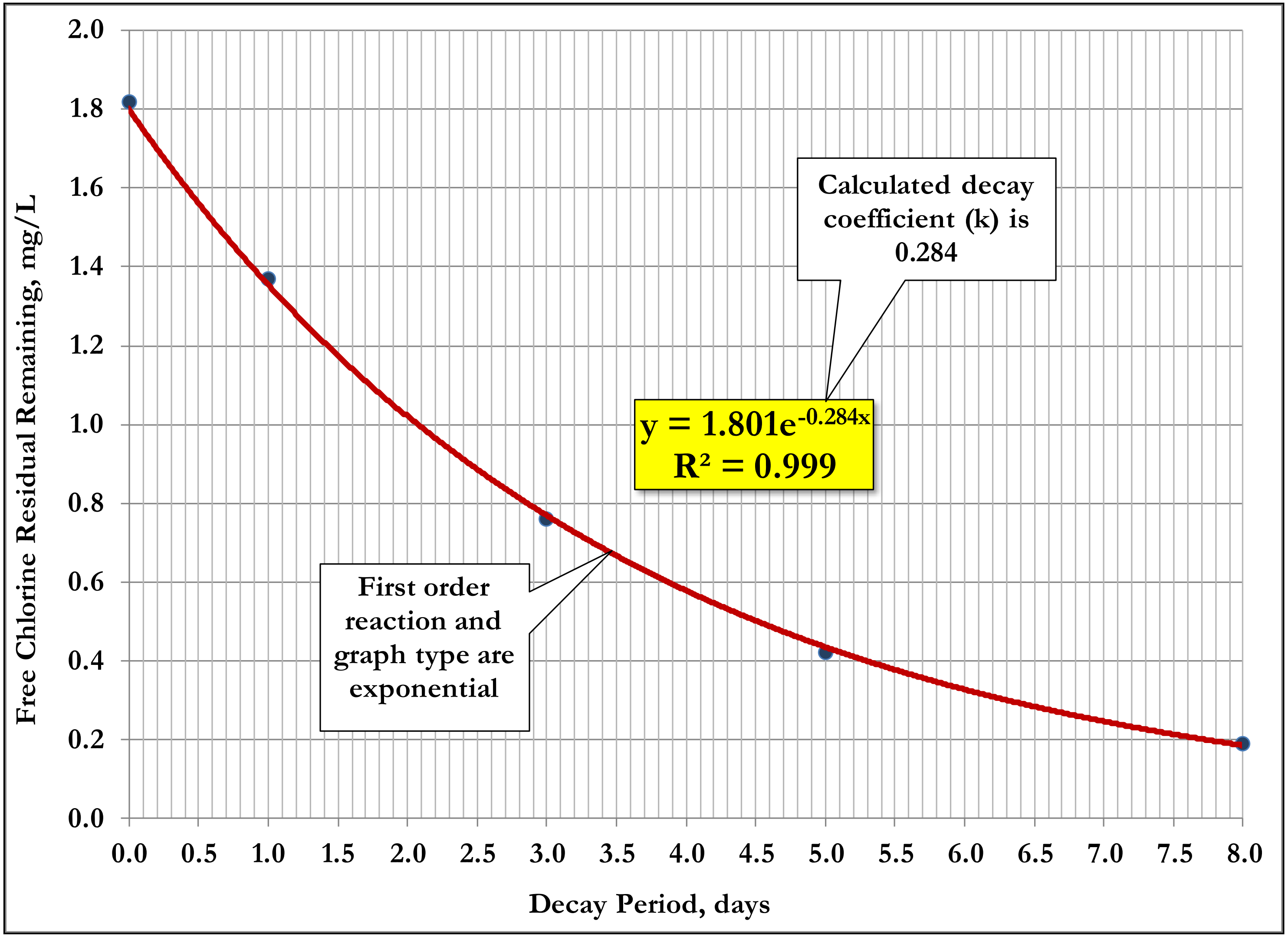
C_o = initial concentration

k = residual decay coefficient

t = decay time in days

- Calculate decay coefficient (k) from experimental data using reaction equation
  - Bulk water only based on experimental observations

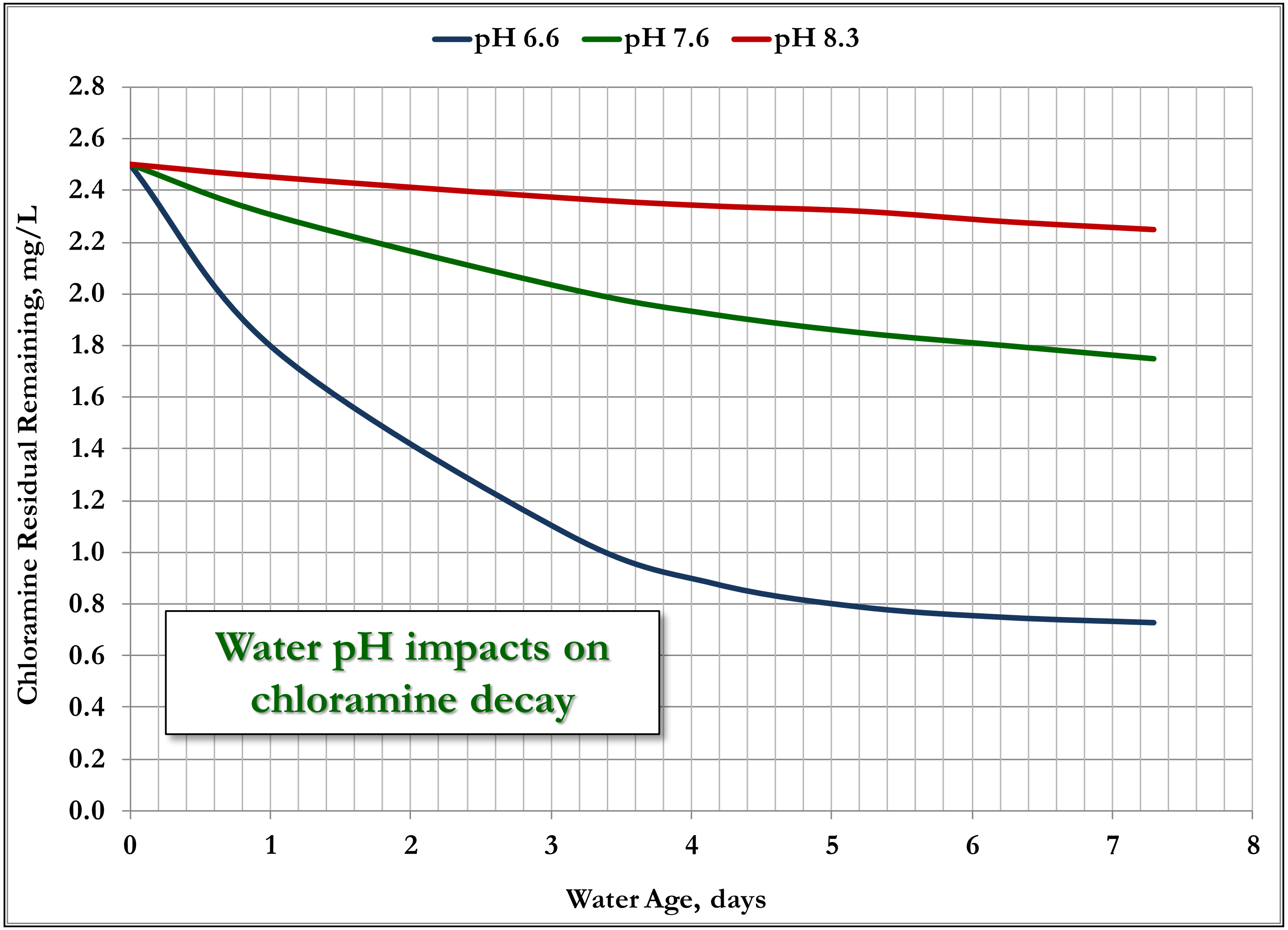
Chloramine Decay



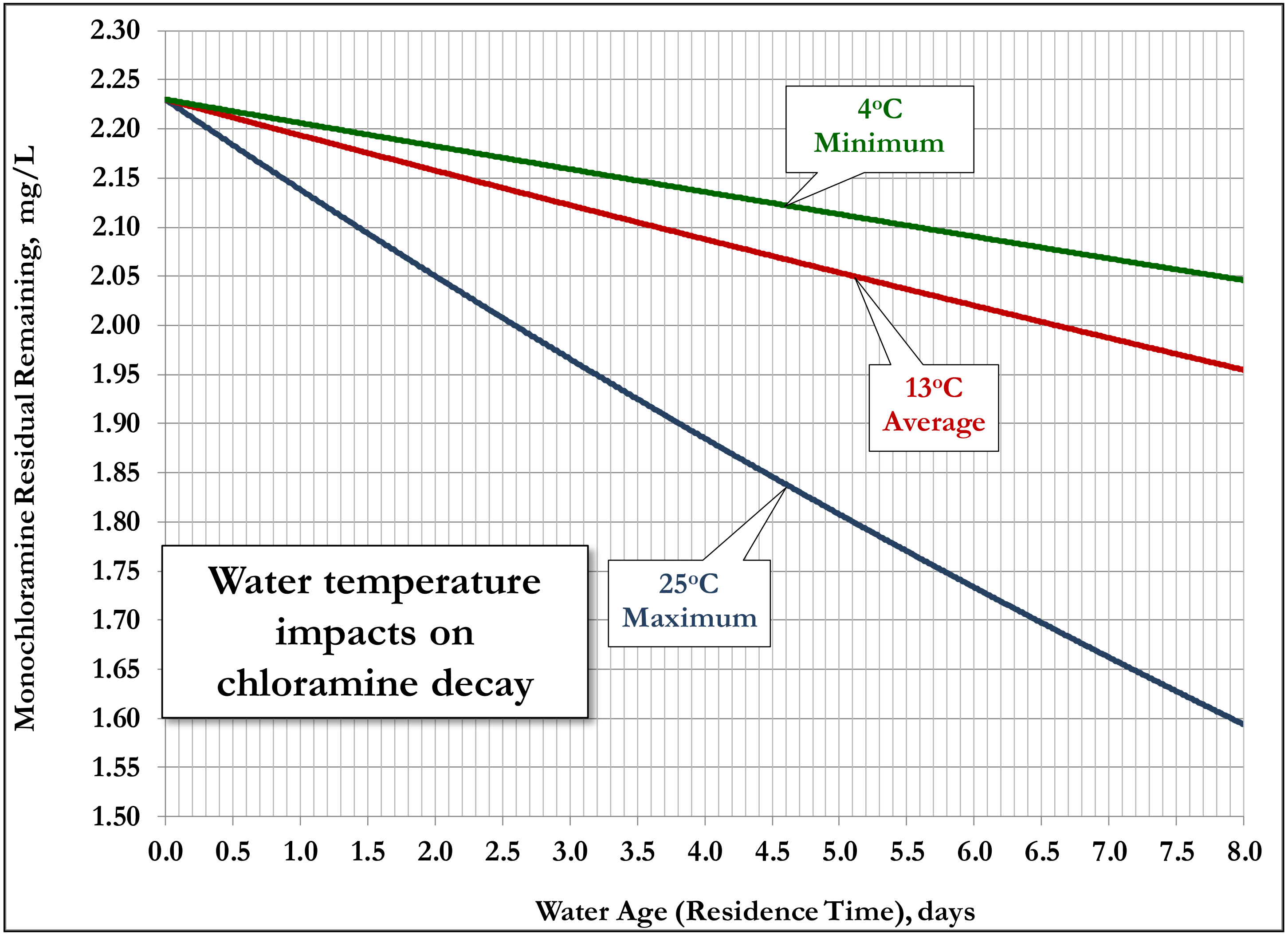
Chloramine Decay

- System decay coefficient (k) contains 2 components
  - $k_t = k_b + k_w$
  - k_w - decay coefficient pipe wall
  - k_b - decay coefficient bulk water
- k_w impacted by contact at pipe wall and presence of biofilms, deposits, corrosion materials
- k_b affected by demand-causing substances in distribution system (bulk water quality)
- k_t dependent on water quality and pipe conditions, site specific

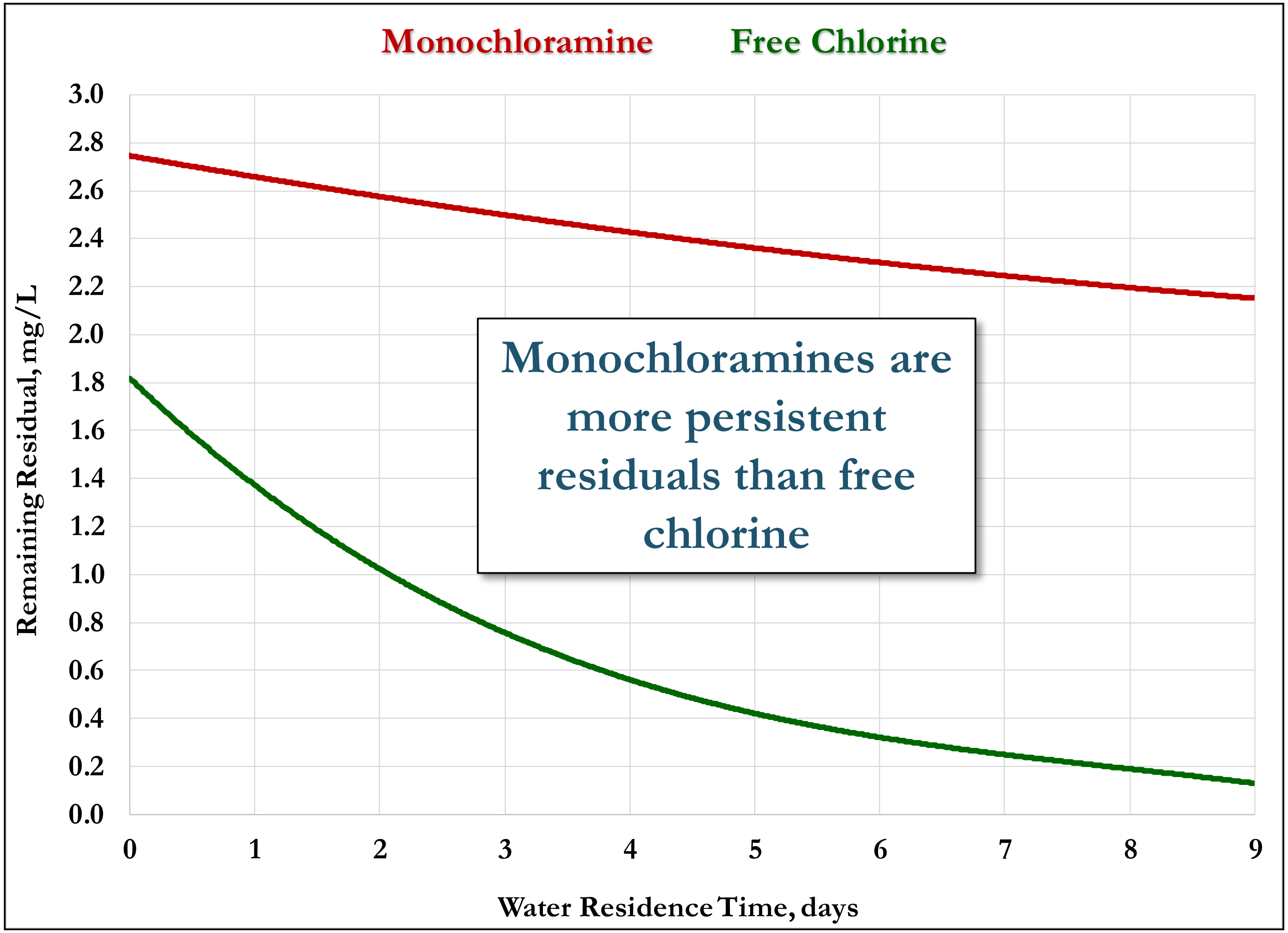
Chloramine Decay



Chloramine Decay



Chloramine Decay



Chloramine Decay Reactions

- Autodecomposition
- Reaction with corrosion byproducts (pipe surface)
- Excess ammonia and equilibrium reactions
- Oxidation of organic matter
- Nitrite reactions
- All decay reactions tend to reduce residuals resulting in potential nitrification occurrences

Chloramine Decay Reactions

- Autodecomposition
  - Chloramine acting on itself

$$4NH_2Cl + 3H_2O \rightarrow 3NH_3 + NO_3^- + 5Cl^- + 5H^+ (major)$$

$$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+ (minor)$$

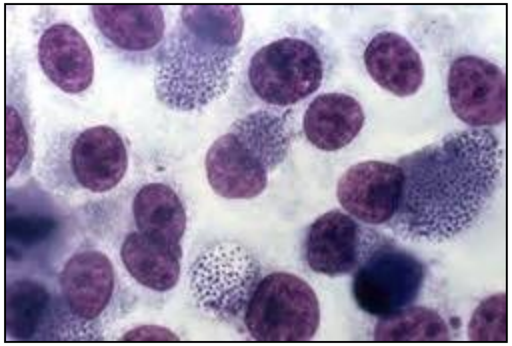
  - Impacted by water temperature, pH, and water age
    - Temperature affects reaction rates two-fold for every 10°C change
    - Low pH tends to increase NH_2CL decomposition and degradation
  - Hydrogen reaction byproduct consumes alkalinity and reduces pH

Chloramine Decay Reactions

- Pipe surface impacts (corrosion byproducts)

$$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$$

  - Release of ammonia adds food for microbial growth
  - Reaction depletes chloramine residuals
  - Acid addition lowers water pH and may impact lead solubility



Chloramine Decay Reactions

- Excess ammonia (imbalance of Cl2:N ratio)

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$

  - Ammonia oxidizes to nitrite (adds decay component)
  - Reaction depletes chloramine residuals
  - Hydrogen ion release produces acids and lowers pH

Chloramine Decay Reactions

- Oxidation of organic matter

$$C_5H_7O_2N + NH_2Cl + H_2O \rightarrow CO_2 + HCO_3^- + NH_4^+ + Cl^-$$

  - Ammonium ion byproduct release ammonia (add decay component)
  - CO_2 alters pH and consumes alkalinity, may impact lead solubility
  - Chloride alters water quality and may impact lead solubility

Chloramine Decay Reactions

- Oxidation of nitrite

$$NH_2Cl + NO_2^- + H_2O \rightarrow NH_3 + NO_2^- + HCl$$

  - Reaction releases ammonia adds food for microbial growth
  - Nitrite creates chloramine demand reducing residuals
  - Acid alters water chemistry and may impact lead solubility
    - Not uncommon to see reductions in pH of 1.0 s.u. or more
    - Not uncommon to see alkalinity reductions of 20 mg/L or more

Part 1

Questions

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Chloramination and Nitrification Part 2

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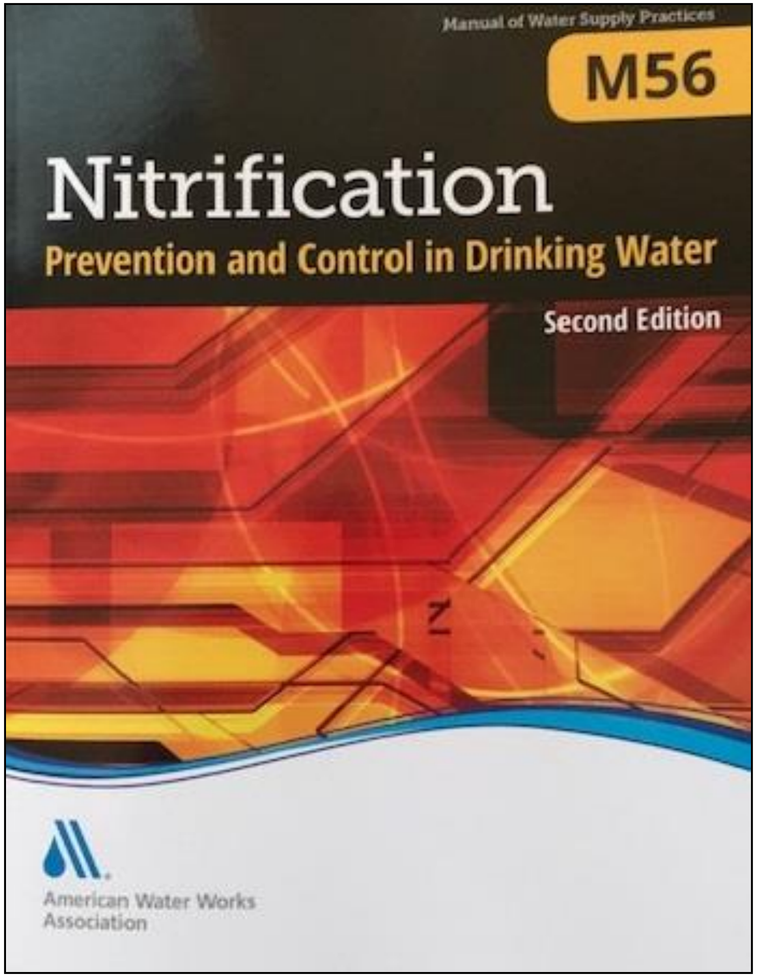
OTCO Water Workshop

March 10, 2020

Agenda

- Nitrification and its causes
- Symptoms of nitrification
- Steps to avoid nitrification
- Nitrification occurrences
- Distribution monitoring plans
- Nitrification mitigation requirements
- Prevention using chlorite ion
- Nitrification case study 2019

Nitrification



- AWWA M56 - Nitrification Prevention and Control in Drinking Water
  - Second Edition 2013
  - Excellent reference related to nitrification issues
  - Causes, symptoms, mitigation, monitoring programs, response plans

Nitrification

- Natural decay or decomposition of chloramines resulting in ammonia release and residual decline
  - Primary cause elevated water temperature >18°C
    - Can be highest in distribution storage tanks (>38°C observed in field)
  - Low DO and high water age contribute to decay
  - Chloramine demands produce NH_3, NH_4^+ or NO_2^- feeding biofilm microorganisms
  - Excess free ammonia metabolizes biofilms
    - Biofilms resistant to chloramines and are protected in biofilm mass
    - Proliferate in high water age areas particularly with low DO and elevated temperatures
  - HPC increases as chloramine residuals decline

Nitrification

- Non-coliform bacteria always present in distribution systems
  - Free chlorine or chloramine residual maintenance typically control populations to background counts
    - HPC bacteria range typically from <1 to about 20 colonies per mL
- Nitrosomonas and Nitrobacter species are common in biofilms (non-coliform species)
  - Contribute significantly to nitrification events
  - Nutrient availability and temperature affect biolfilm growth
  - Exponential population growth exacerbates nitrification events

Nitrification

- Chloramine decay pathways
  - Autodecomposition
  - Chloramine demand

- System demands for chloramines
  - NOM (AOC) - food source
  - Free ammonia – nutrient source
  - Biofilms (cometabolism accounts for 30% to 60% chloramine decay)
    - Ammonia-Oxidizing Bacteria – AOB
    - Nitrite-Oxidizing Bacteria – NOB
  - Pipe corrosion byproducts and inhibitors provide strata for biofilms
  - Nitrification events where NO_2^- creates chloramine demand

Nitrification

- AOB and Nitrosomonas species
  - Ammonia-oxidizing bacteria
  - Optimum pH for increased growth rate 6 to 9
    - pH >9 less favorable for cell division
  - Optimum water temperature 25°C to 35°C
    - Cell metabolism maximizes if food and nutrients available
    - Increases thermal stratification in unmixed storage tanks
    - Increases NH_2Cl decay and decomposition leading to free NH_3 release
  - Resistant to NH_2Cl, but easily inactivated with free chlorine
  - Use free NH_3 for metabolism and growth
    - NO_2^- reaction byproducts further degrade NH_2Cl releasing more NH_3
    - NO_2^- simple detection trigger that indicates nitrification is occurring

Nitrification

- NOB and Nitrobacter species
  - Nitrite-oxidizing bacteria
    - NO_3^- reaction byproducts produced
    - NO_2- and NO_3^- detection triggers that nitrification is occurring
  - Optimum pH for increased growth rate 7.5 to 8.0
    - pH >8 less favorable for cell division
  - Optimum water temperature 25°C to 35°C
    - Cell metabolism maximizes if food and nutrients available
    - Increased thermal stratification in unmixed storage tanks
  - Resistant to NH_2Cl, but easily inactivated with free chlorine
  - Use NO_2^- for metabolism and growth

Nitrification

- Two-step microbiological process
  - AOB metabolize NH_3 oxidizing to NO_2^-
  - NOB metabolize NO_2^- oxidizing to NO_3^-
  - Increases in nitrite (NO_2^-) are early warning sign that nitrification is occurring
- Generally begins at elevated temperatures (>18°C), in low DO water, with highest water age
- NOM/TOC/AOC/free NH_3 can trigger metabolic growth of biofilms acting as nutrient at pipe wall
  - Nitrosomonas species
  - Nitrobacter species
  - Metabolic reactions release NH_3 from NH_2Cl residuals

Symptoms of Nitrification

- Declining chloramine residuals
  - Particularly in high water age locations due to NH_3 release
- Decreasing pH levels
  - Due to H^+ and CO_2 byproduct formations from nitrification reactions
  - Acid formation increases NH_2Cl decomposition
- Decreasing alkalinity concentrations
  - Due to increased acidity from nitrification byproducts

Symptoms of Nitrification

- Significant decline in chloramine residuals
  - Commonly reduced to less than 50% of normal residual levels
- Reductions in water pH
  - Common reductions of about 1.0 s.u. or more have been recorded
- Reduced alkalinity levels
  - Common reductions of 20 mg/L or more have been recorded
- Changes in water quality may impact lead solubility

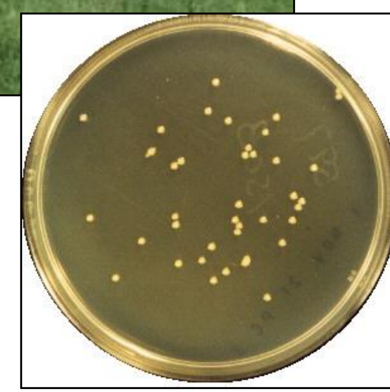
Flushing often pushes AOB and NOB into other non-affected areas of the system

Symptoms of Nitrification

- Presence of NO_2^- in distribution samples
  - NO_2^- greater than 0.02 mg/L signifies nitrification is occurring
  - NO_2^- can increase to 0.5 mg/L or more
- Increased HPC bacteria
  - Well above normal background, > 500 per mL
- Actual detection of AOB/NOB (not common)

Symptoms of Nitrification

- Reduction in dissolved oxygen (DO)
  - Consumed in nitrification reactions
  - Low levels in elevated water temperatures
- Elevated water temperatures
  - Optimal microbial growth at 25°C to 30°C
  - Temperatures can reach near 40°C in elevated storage tanks



Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Maintain Cl_2:N ratios in treatment above 4.5
    - Proper ratio assures complete conversion to chloramines and minimizes free ammonia
      - Account for actual free chlorine residual at ammonia application point
    - Produces low free ammonia residuals

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Maintain water pH at 8.5 or greater
    - Maximizes chloramine conversion rate
    - Minimizes autodecomposition of chloramines
    - Inhibits microbial growth and nitrification reactions

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Minimize free ammonia in finished water
    - Target 0.05 mg/L or less
    - Excess free ammonia becomes food for microbial growth
      - Primary result of improper Cl_2:N ratio in treatment
      - Can spark nitrification event
    - Establish 0.075 mg/L trigger to force adjustments in Cl_2:N ratio

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Maintain system chloramine residuals between 2 mg/L and 3 mg/L
    - Proper residual maintenance inhibits microbial growth by controlling biofilm populations
  - Avoid mixing chloraminated and chlorinated water in the system
    - Water chemistry issues and taste and odor issues
  - Install booster chloramination (chlorine and ammonia application)

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Minimize organic matter
    - Establish target TOC/DOC level to minimize DBP formation
    - Maintain normal TOC/DOC levels in the finished water
      - Adjust organics removal based on source water levels
    - Increases of 0.3 mg/L or greater in TOC levels can provide nutrients for microbial growth

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Control water age
    - Routine system flushing
    - Install tank mixing
    - Valve exercising to ensure system flow patterns
    - Maximize storage tank turnover
    - Take storage offline
  - Control booster pumping operations

Avoiding Nitrification

- Steps to help avoid nitrification in distribution systems
  - Establish routine Water Quality monitoring programs
    - Define parameters that signal water quality degradation
    - Increase monitoring frequency when water temperature >18°C
    - Define critical water quality parameters affected by nitrification events
    - Sample at bacteria monitoring sites
    - Help ensure water quality degradation does not initiate nitrification event

Nitrification Occurrences

- Steps to take once nitrification occurs
  - Stop flushing hydrants
    - Only pushes AOB and NOB to other areas of system starting nitrification reactions in those areas
  - Notify Ohio EPA of possible nitrification and current water quality results
    - Confirm nitrification is occurring
    - Initiate conversations for next steps
    - Discuss public notification requirements and public notice language

Nitrification Occurrences

- Steps to take once nitrification occurs
  - Conduct public notification for free chlorine burn period
    - Why, when, how long
    - Usually takes two to three weeks to complete the burn period
    - Possible taste and odor occurrences when free chlorine and chloramines combine
    - Who to contact with questions

Nitrification Occurrences

- Steps to take once nitrification occurs
  - Initiate the burn period
    - Define target residuals and water pH levels
      - – Research states 1.8 mg/L sustained free residual can inactivate AOB and NOB relatively easily
    - Terminate ammonia feed
    - Adjust finished water free chlorine to target residual level (2.5 mg/L or greater may ne needed depending on decay)
    - Continue system water quality monitoring
      - – Maintain burn period until water pH is re-established, NO_2^- reduces to 0.02 mg/L, and free chlorine residual persists

Nitrification Occurrences

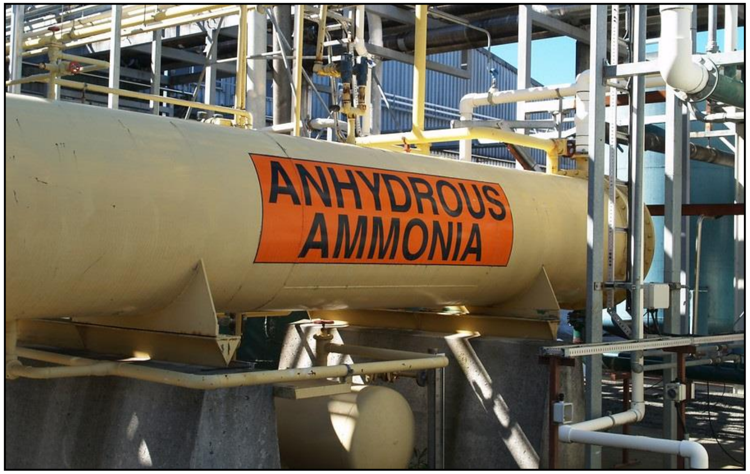
- Steps to take <u>once nitrification occurs</u>
  - Continue frequent monitoring of water quality
    - Water pH, alkalinity, NO_2^- levels, chlorine residuals, free ammonia, DO
  - Initiate flushing once free chlorine residuals established
    - Moves free chlorine more rapidly through distribution piping systems and inactivates AOB/NOB more quickly

Nitrification Occurrences

- Steps to take once nitrification occurs
  - Work with OEPA on steps to return to chloramination
  - Conduct public notification related to return to chloramination
    - When, how long to return to normal
    - Possible taste and odor occurrences when free chlorine and chloramines combine
    - Usually takes about two weeks to convert back to chloramines after burn period depending on system size and hydraulics

Nitrification Occurrences

- Steps to take once nitrification occurs
  - Implement ammonia feed and frequent water quality monitoring
    - Maintain minimum 4.5 Cl_2:N ratio for dosing
    - Maintain pH levels greater than 8.5
  - Continue flushing to move ammonia into free chlorine residual areas
    - SOP should be developed for next event
  - Consider more permanent means to reduce high water age areas



Distribution Monitoring Plans

- Specific water quality parameters either to deter or to confirm nitrification events
- Increase sampling frequencies based on water temperature and/or increased trigger values
- Routine and increased monitoring carefully planned with sample locations, test parameters, triggers, and written SOP to manage the program
  - Include indicators that confirm whether nitrification is occurring
  - Include nitrification response plan outlining activities if nitrification occurs
  - Include public notification procedures and language for public notices

Distribution Monitoring Plans

- Water quality parameters
  - Water temperature and pH
  - Residual concentrations
  - Cl_2:N feed ratios
  - Free ammonia concentration
  - Total alkalinity levels
  - Finished water TOC and SUVA
  - NO_2^- ion concentrations
  - Dissolved oxygen
  - HPC bacteria
  - Water residence time or age
  - Tank turnover rates

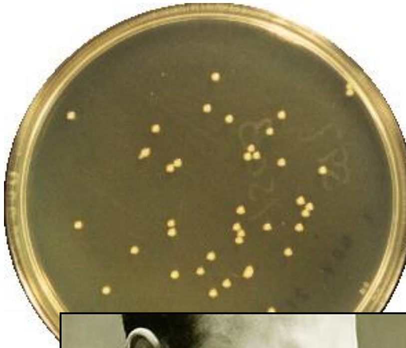
Routine monitoring should be conducted monthly

Increase frequency to biweekly once water temperature greater than 18°C

Increase frequency to at least 3 times per week if NO_2^- increase above 0.05 mg/L

Reverse frequency based on declining water temperature or when chlorine burn completed

Mitigation Requirements



- Nitrification can create serious health concerns if not contained or mitigated in distribution systems
  - Significantly reduced chloramine residuals resulting in increased microbial activity
    - Potential coliform regrowth due to nitrification events
    - Potential growth of opportunistic microbes like Legionella
  - Increased disinfection byproducts concentrations
  - Potentially higher lead solubility
  - Increased metals uptake from corrosion reactions
  - Pipe damage

Mitigation Requirements

- Nitrification can get out of control if not mitigated or eliminated
- May require "free chlorine burn" period to kill off Nitrosomonas and Nitrobacter populations
- 1.8 mg/L sustained free chlorine residual will inactivate AOB and NOB (literature)
  - Feed rates may be higher due to free chlorine decay and mixtures of chloramines and free chlorine
  - 3.0 mg/L or higher may be needed in finished water to obtain 1.8 mg/L in some areas of distribution
    - Hydraulics and dead ends can produce problems obtaining residuals

Mitigation Requirements

- Burn period may require public notification
  - Check with state regulatory agency (Ohio EPA)
- Burn must be long enough to rid the system of AOB and NOB while sustaining free chlorine residual throughout
  - May need two to four weeks of sustained free residuals depending on system hydraulics and microbial populations

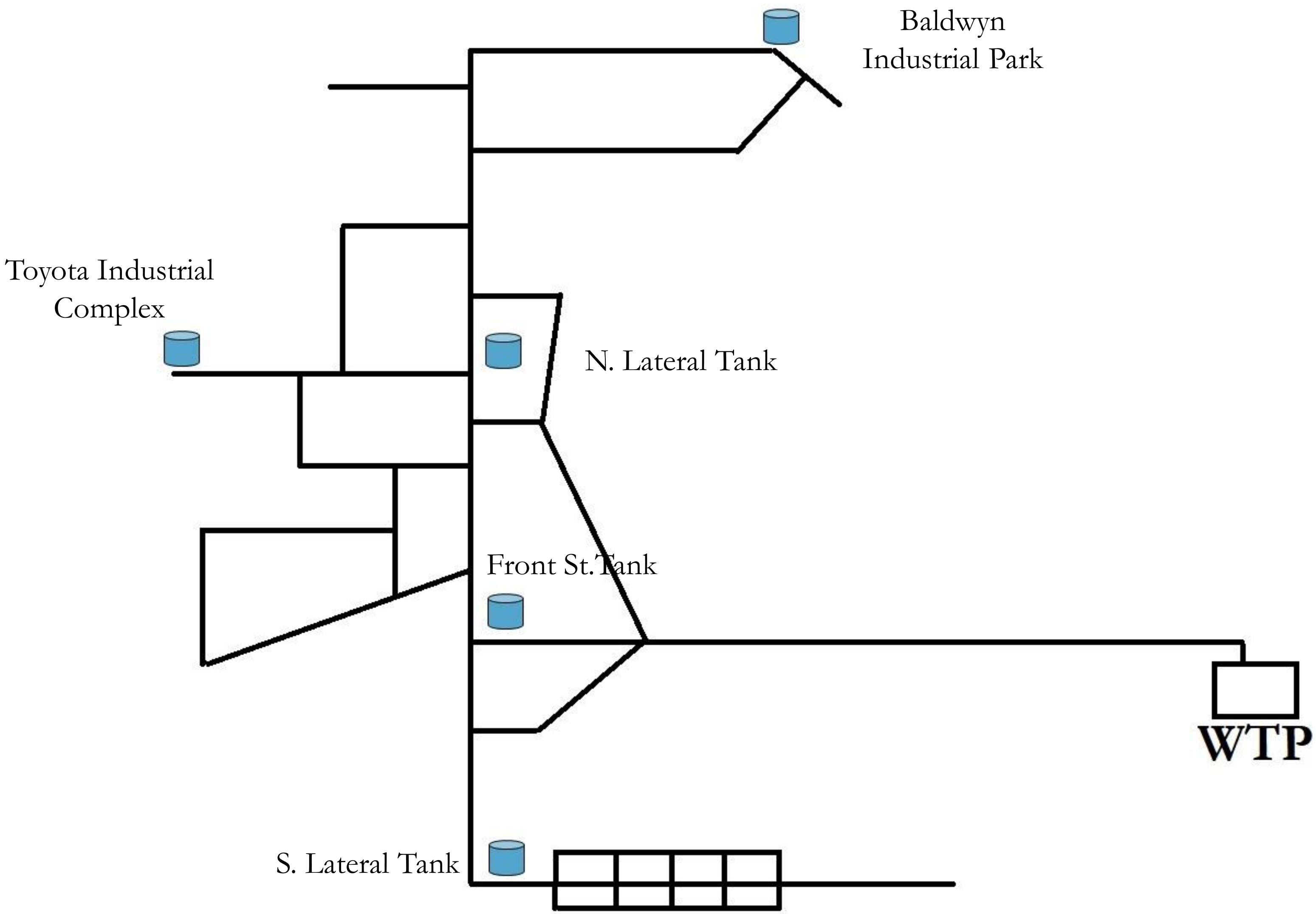
Prevention using Chlorite Ion

- Chlorite ion has proven to help prevent nitrification in some water systems
  - ClO_2^- toxic to AOB, does not allow prolific growth
  - ClO_2^- also a regulated disinfection byproduct
    - MCLG 0.8 mg/L
    - MCL 1.0 mg/L
- Key to prevent growth of AOB before it really begins
  - ClO_2^- not effective once nitrification starts
  - Target dosages generally 0.2 mg/L to 0.6 mg/L
  - Application of sodium chlorite to finished water
    - Used in onsite production of chlorine dioxide
  - Maintains NH_2Cl residuals by preventing nitrification
  - Monitor chlorite ion frequently if applied

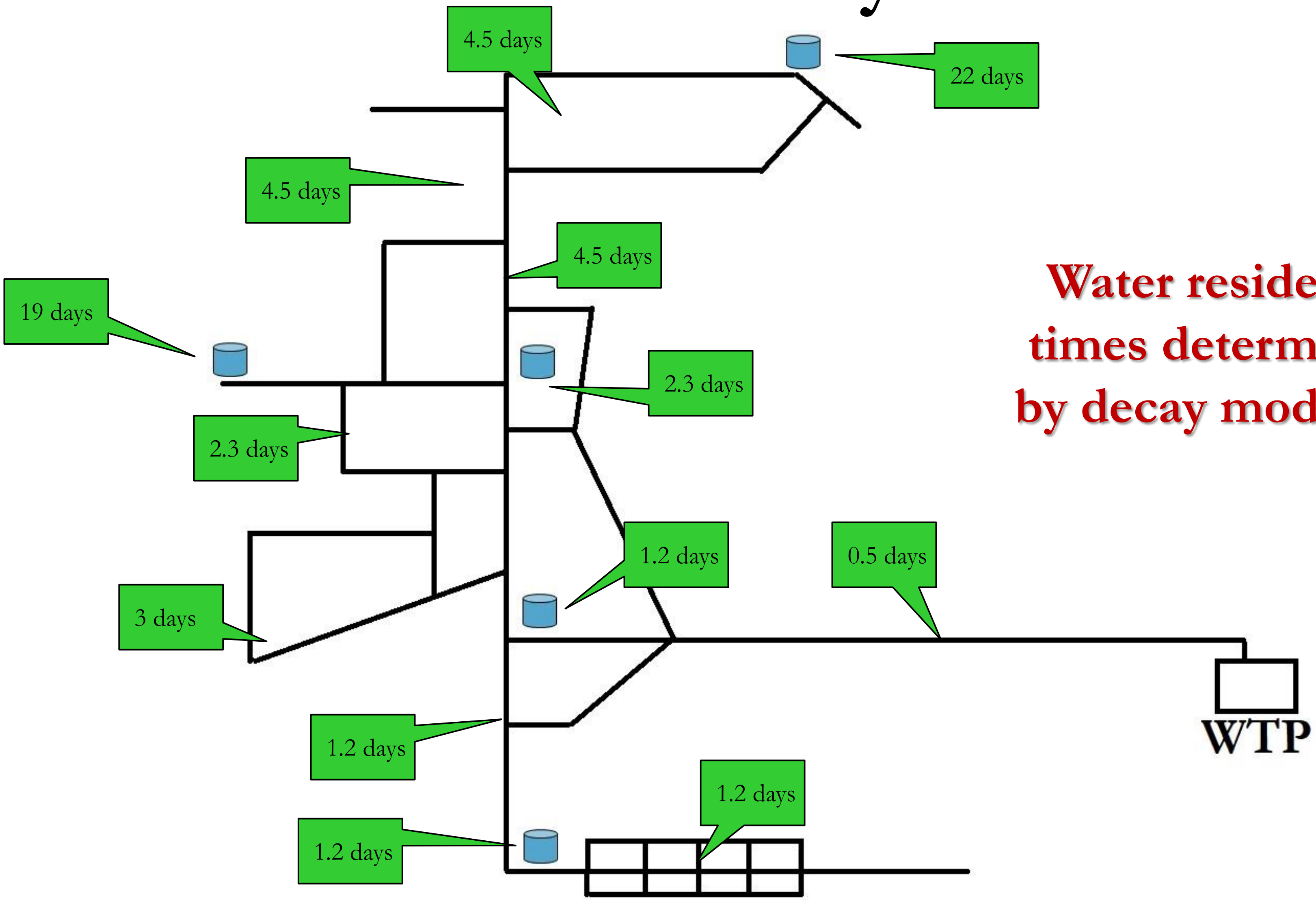
Nitrification Case Study

- Northeastern Mississippi
  - Chloramination practiced since 2004
    - NH_3 fed after CT compliance
  - Cl_2:N ratio generally 4.0
  - Free ammonia variable from 0.02 mg/L to 0.12 mg/L
  - Water pH 8.34 ±
  - Alkalinity averages 45 mg/L
  - Finished TOC averages 1.9 mg/L
  - Max water temperature generally 29°C in summer months
  - Very large distribution system serving multiple consecutive systems

Nitrification Case Study



Nitrification Case Study



Water residence times determined by decay modeling

Nitrification Case Study

NE Mississippi Regional Water Supply District
Tupelo, MS
Total Chlorine Decay Model

Chloramine Decay Model Predictions

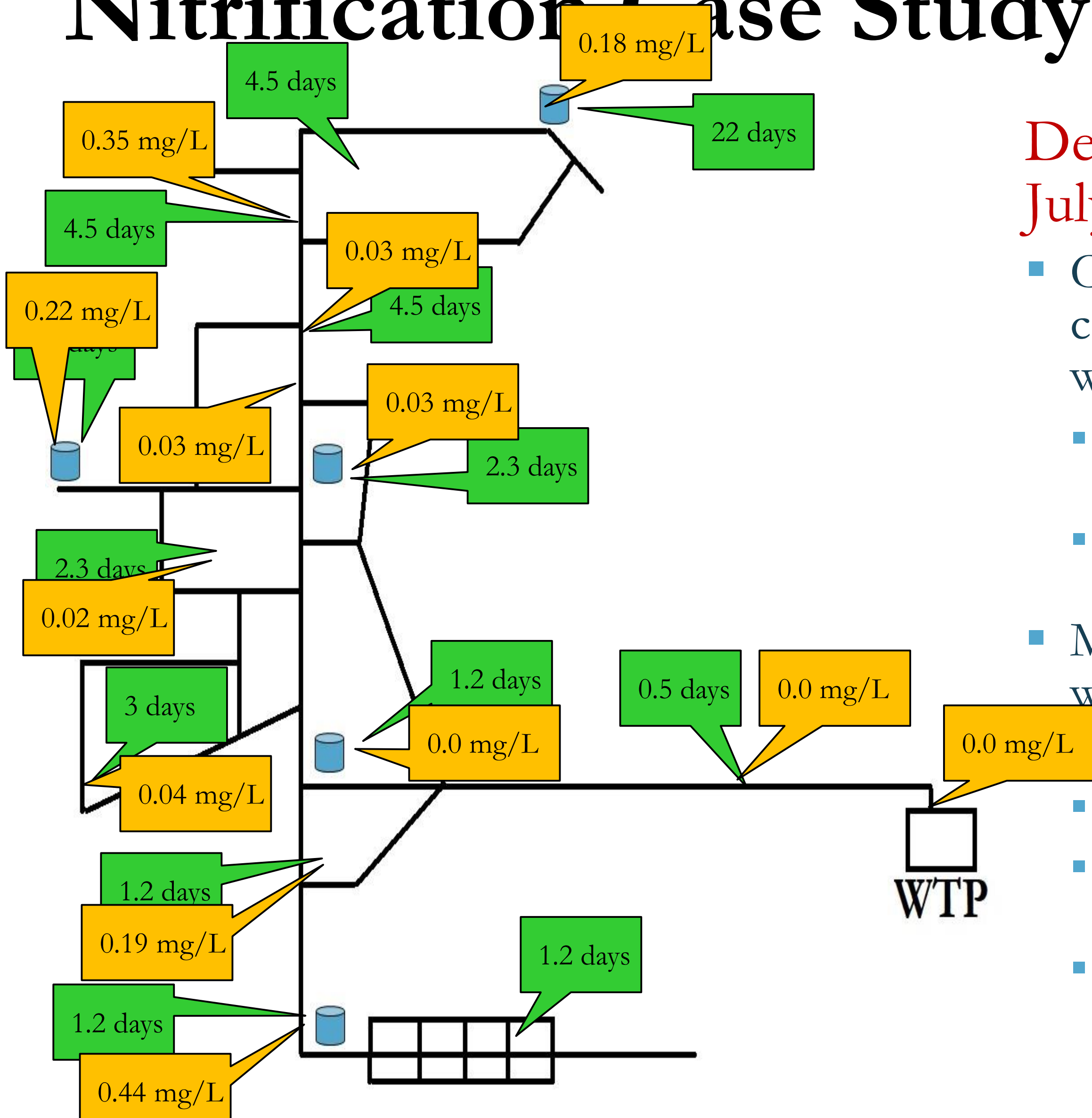
Temp **35** °C (temp varies 7°C to 29°C)

k **0.0734**

Initial Total Cl_2 mg/L

Days	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	3.80	3.53	3.28	3.05	2.83	2.63	2.45	2.27	2.11	1.96	1.82	1.69	1.57	1.46	1.36	1.26	1.17	1.09	1.01	0.94	0.88	0.81
	3.70	3.44	3.19	2.97	2.76	2.56	2.38	2.21	2.06	1.91	1.78	1.65	1.53	1.42	1.32	1.23	1.14	1.06	0.99	0.92	0.85	0.79
	3.60	3.35	3.11	2.89	2.68	2.49	2.32	2.15	2.00	1.86	1.73	1.61	1.49	1.39	1.29	1.20	1.11	1.03	0.96	0.89	0.83	0.77
	3.50	3.25	3.02	2.81	2.61	2.42	2.25	2.09	1.95	1.81	1.68	1.56	1.45	1.35	1.25	1.16	1.08	1.00	0.93	0.87	0.81	0.75
	3.40	3.16	2.94	2.73	2.53	2.36	2.19	2.03	1.89	1.76	1.63	1.52	1.41	1.31	1.22	1.13	1.05	0.98	0.91	0.84	0.78	0.73
	3.30	3.07	2.85	2.65	2.46	2.29	2.12	1.97	1.83	1.70	1.58	1.47	1.37	1.27	1.18	1.10	1.02	0.95	0.88	0.82	0.76	0.71
	3.20	2.97	2.76	2.57	2.39	2.22	2.06	1.91	1.78	1.65	1.54	1.43	1.33	1.23	1.14	1.06	0.99	0.92	0.85	0.79	0.74	0.68
	3.10	2.88	2.68	2.49	2.31	2.15	2.00	1.85	1.72	1.60	1.49	1.38	1.28	1.19	1.11	1.03	0.96	0.89	0.83	0.77	0.71	0.66
	3.00	2.79	2.59	2.41	2.24	2.08	1.93	1.79	1.67	1.55	1.44	1.34	1.24	1.15	1.07	1.00	0.93	0.86	0.80	0.74	0.69	0.64
	2.90	2.69	2.50	2.33	2.16	2.01	1.87	1.73	1.61	1.50	1.39	1.29	1.20	1.12	1.04	0.96	0.90	0.83	0.77	0.72	0.67	0.62
	2.80	2.60	2.42	2.25	2.09	1.94	1.80	1.67	1.56	1.45	1.34	1.25	1.16	1.08	1.00	0.93	0.86	0.80	0.75	0.69	0.64	0.60
	2.70	2.51	2.33	2.17	2.01	1.87	1.74	1.61	1.50	1.39	1.30	1.20	1.12	1.04	0.97	0.90	0.83	0.77	0.72	0.67	0.62	0.58
	2.60	2.42	2.24	2.09	1.94	1.80	1.67	1.56	1.45	1.34	1.25	1.16	1.08	1.00	0.93	0.86	0.80	0.75	0.69	0.64	0.60	0.56
	2.50	2.32	2.16	2.01	1.86	1.73	1.61	1.50	1.39	1.29	1.20	1.11	1.04	0.96	0.89	0.83	0.77	0.72	0.67	0.62	0.58	0.53
	2.40	2.23	2.07	1.93	1.79	1.66	1.54	1.44	1.33	1.24	1.15	1.07	0.99	0.92	0.86	0.80	0.74	0.69	0.64	0.59	0.55	0.51
	2.30	2.14	1.99	1.85	1.71	1.59	1.48	1.38	1.28	1.19	1.10	1.03	0.95	0.89	0.82	0.76	0.71	0.66	0.61	0.57	0.53	0.49
	2.20	2.04	1.90	1.77	1.64	1.52	1.42	1.32	1.22	1.14	1.06	0.98	0.91	0.85	0.79	0.73	0.68	0.63	0.59	0.55	0.51	0.47
	2.10	1.95	1.81	1.68	1.57	1.45	1.35	1.26	1.17	1.08	1.01	0.94	0.87	0.81	0.75	0.70	0.65	0.60	0.56	0.52	0.48	0.45
	2.00	1.86	1.73	1.60	1.49	1.39	1.29	1.20	1.11	1.03	0.96	0.89	0.83	0.77	0.72	0.66	0.62	0.57	0.53	0.50	0.46	0.43
	1.90	1.77	1.64	1.52	1.42	1.32	1.22	1.14	1.06	0.98	0.91	0.85	0.79	0.73	0.68	0.63	0.59	0.55	0.51	0.47	0.44	0.41
	1.80	1.67	1.55	1.44	1.34	1.25	1.16	1.08	1.00	0.93	0.86	0.80	0.75	0.69	0.64	0.60	0.56	0.52	0.48	0.45	0.41	0.39
	1.70	1.58	1.47	1.36	1.27	1.18	1.09	1.02	0.94	0.88	0.82	0.76	0.70	0.65	0.61	0.57	0.53	0.49	0.45	0.42	0.39	0.36
	1.60	1.49	1.38	1.28	1.19	1.11	1.03	0.96	0.89	0.83	0.77	0.71	0.66	0.62	0.57	0.53	0.49	0.46	0.43	0.40	0.37	0.34
	1.50	1.39	1.30	1.20	1.12	1.04	0.97	0.90	0.83	0.77	0.72	0.67	0.62	0.58	0.54	0.50	0.46	0.43	0.40	0.37	0.35	0.32
	1.40	1.30	1.21	1.12	1.04	0.97	0.90	0.84	0.78	0.72	0.67	0.62	0.58	0.54	0.50	0.47	0.43	0.40	0.37	0.35	0.32	0.30
	1.30	1.21	1.12	1.04	0.97	0.90	0.84	0.78	0.72	0.67	0.62	0.58	0.54	0.50	0.47	0.43	0.40	0.37	0.35	0.32	0.30	0.28
	1.20	1.12	1.04	0.96	0.89	0.83	0.77	0.72	0.67	0.62	0.58	0.54	0.50	0.46	0.43	0.40	0.37	0.34	0.32	0.30	0.28	0.26
	1.10	1.02	0.95	0.88	0.82	0.76	0.71	0.66	0.61	0.57	0.53	0.49	0.46	0.42	0.39	0.37	0.34	0.32	0.29	0.27	0.25	0.24
	1.00	0.93	0.86	0.80	0.75	0.69	0.64	0.60	0.56	0.52	0.48	0.45	0.41	0.38	0.36	0.33	0.31	0.29	0.27	0.25	0.23	0.21

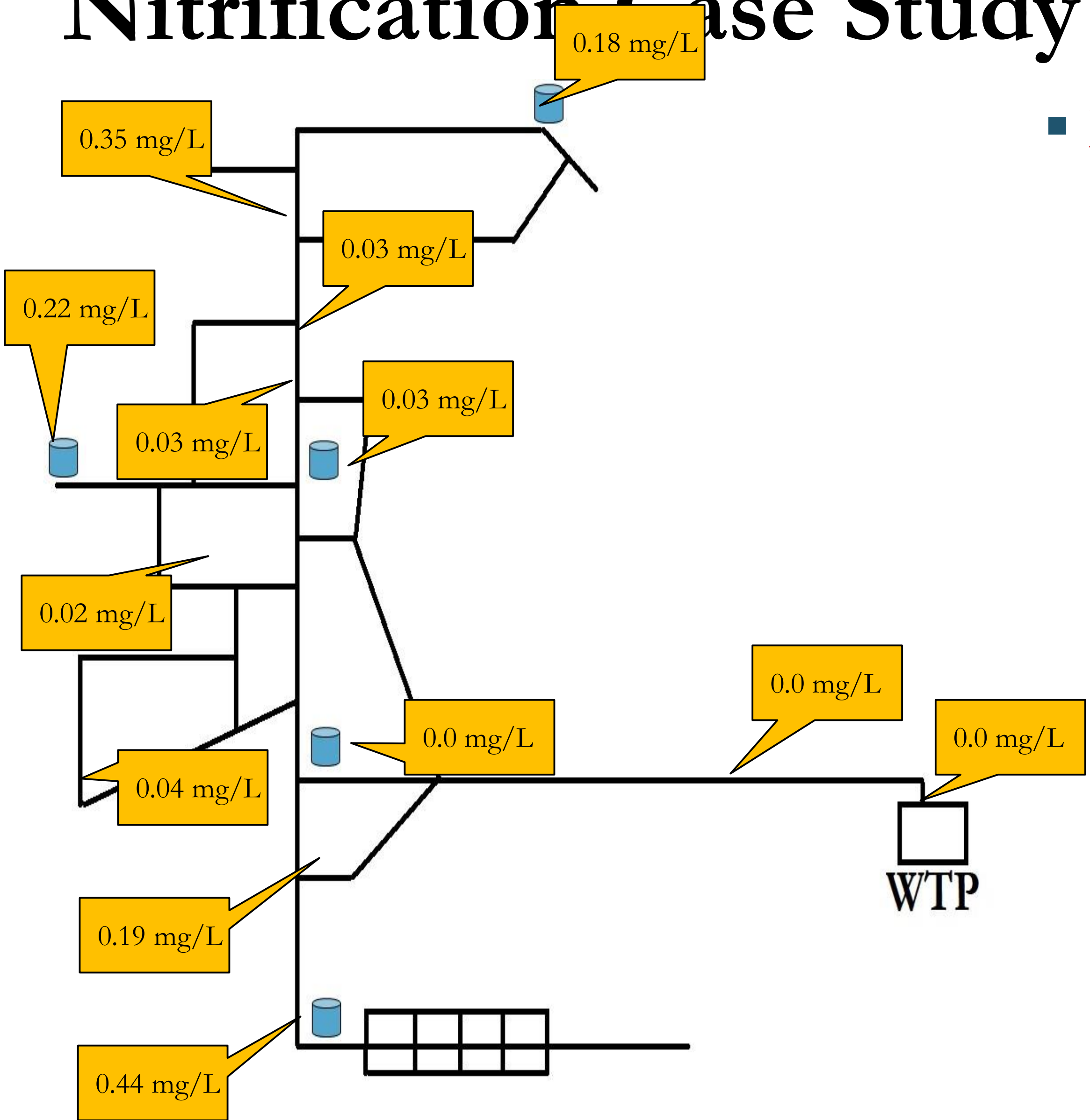
Nitrification Case Study



Declining chloramine residuals July 2019

- Chloramine decay modeling conducted in 2015 with predicted water ages
  - Identified issues on north end tank and mixer installed
  - Declining residuals more than usual in 2019
- Modeling defined more than just water temperature and decay issues
  - Nitrification confirmed late July
  - Communications with State DEP related to free chlorine burn thereafter
  - Free chlorine burn initiated Sept 2, 2019

Nitrification Case Study

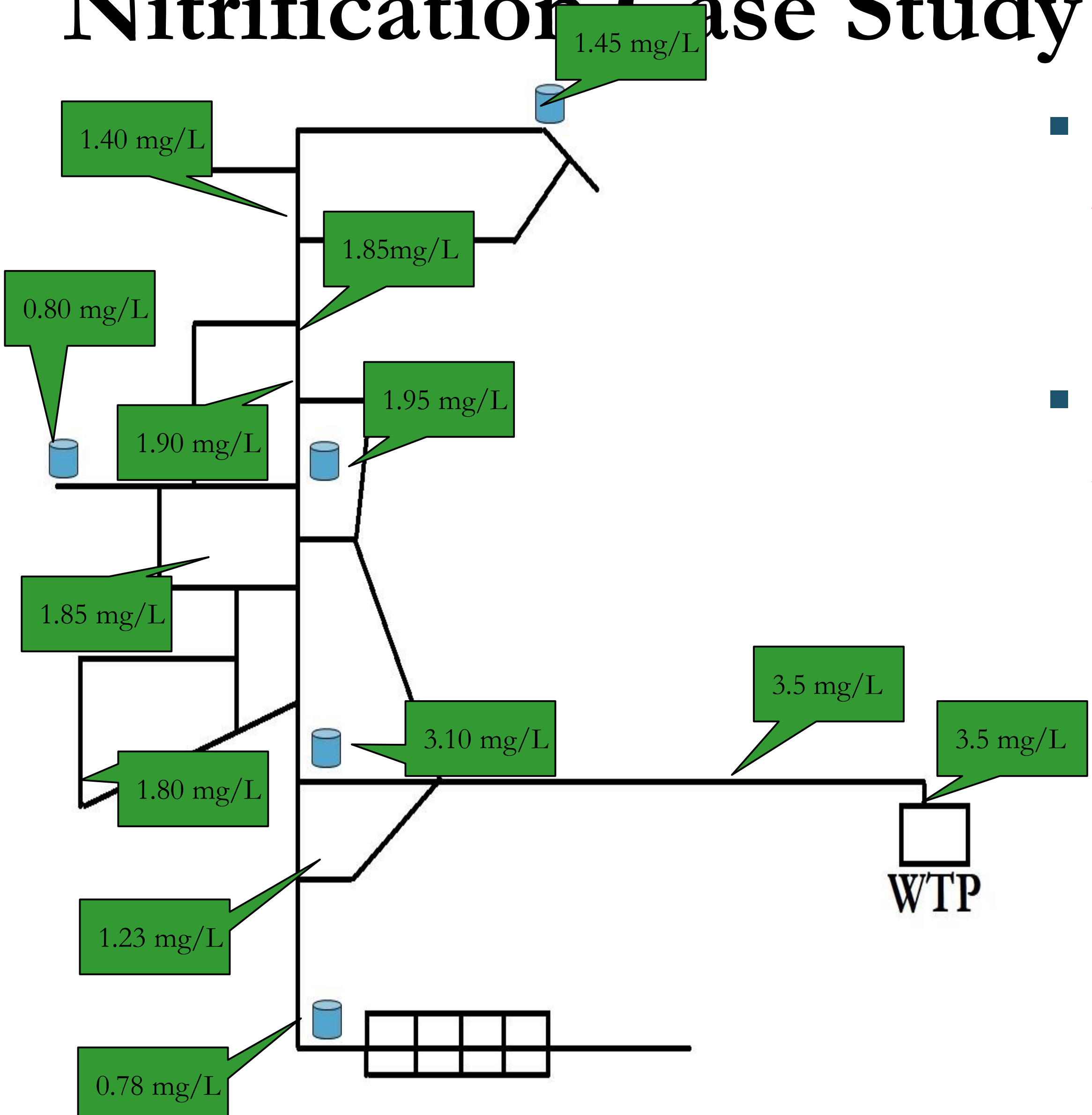


- Most significant residual decline in northern end, south end, and western end near industrial park
  - Reduced pH and increased nitrite observed into August waiting for public notice
    - pH reductions observed from 0.5 units to 1.1 units
  - Maximum nitrite 0.44 mg/L
    - Variations showed nitrification primarily at system extremities with highest water age in storage tanks

Nitrification Case Study

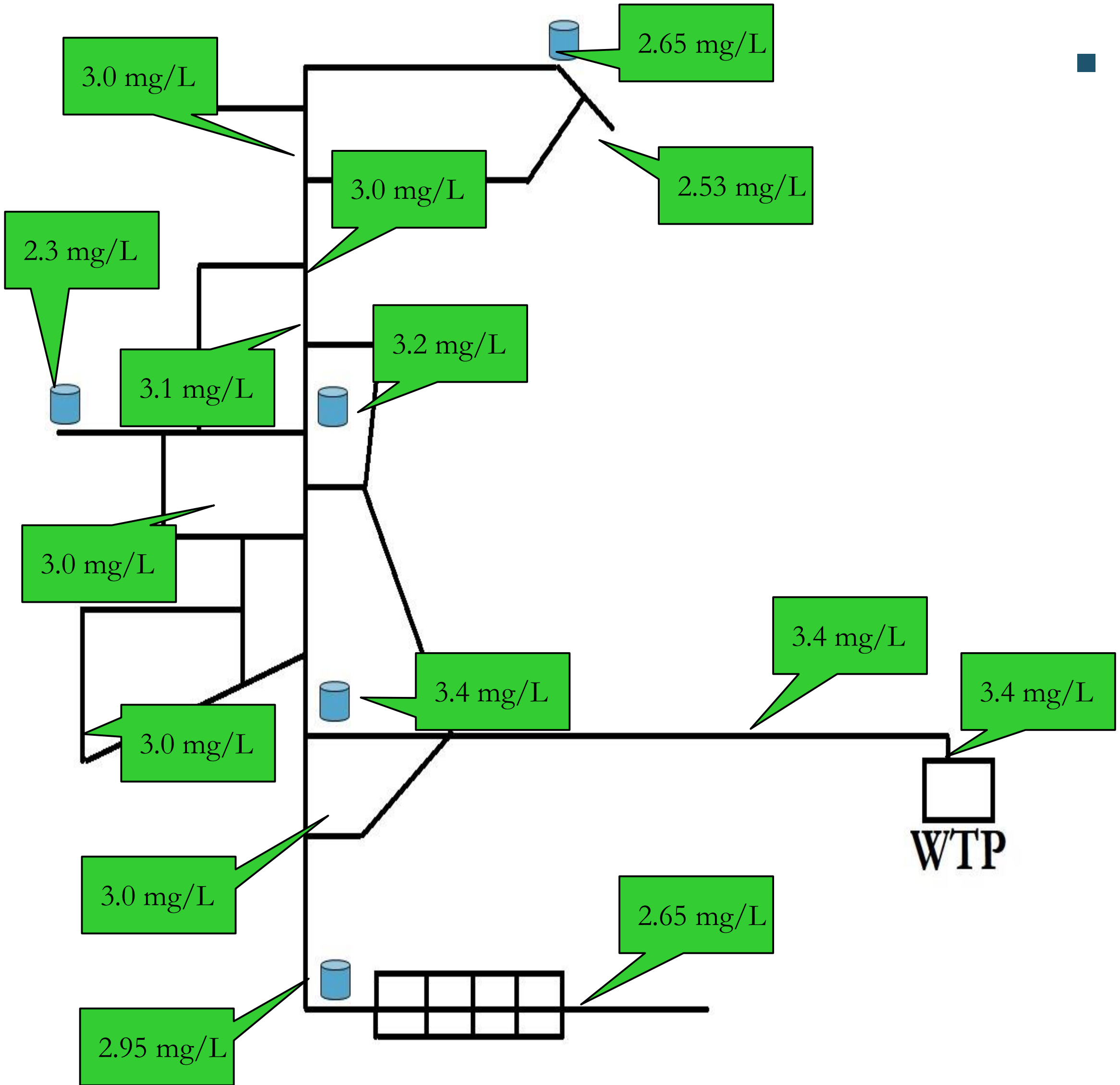
- Public notice request and chlorine burn procedures approval by state regulators late August
  - 10-day public notice followed by termination of ammonia feed
    - One phone call received simply to verify what we were doing (Water District official)
    - Flushed clearwells at the plant to remove chloraminated water quickly
    - Adjusted water pH levels from 8.35 to 8.6
    - Adjusted free chlorine in finished water to 3.5 mg/L (hot weather and likely chlorine decay reactions)
    - Continued monitoring system residuals, nitrite levels, pH, alkalinity

Nitrification Case Study



- Free chlorine reduced nitrite levels within three days to background levels (≤0.02 mg/L)
- Chlorine residuals responded well close to the treatment plant
  - Residuals increased in extremities within 10 days well above 1.3 mg/L
  - Maintained free chlorine for three weeks to ensure nitrification stopped
  - Began ammonia application Sept 25, 2019
    - Chloramines re-established within 5 days to normal levels

Nitrification Case Study



- Chloramine residuals after 5 days ammonia feed shown
  - Decay modeling predictions very close to actual residual levels after burn period
  - No nitrite above background since burn period

Nitrification Case Study

- Nitrification monitoring plan and response plan functioned well
  - No previous written plans, developed onsite for the event and implemented procedures
  - SOPs now being developed for the next event
- First-ever event likely caused by several issues
  - High rainfall in June and July increased finished TOC at 2.4 mg/L (21 mg/L raw)
  - Extremely hot weather August and September averaging over 94°F
    - Observed tank temperatures were 42°C (108°F)
  - Cl_2:N ratios lower than optimum (4.0 average, 3.6 in some cases)
  - Excess free ammonia entering distribution (0.16 mg/L to 0.22 mg/L)
    - NH_3 and AOC nutrients plentiful for AOB and NOB growth
  - Increased water age due to conservation and low demands (June and July rains)
    - Data confirmed nitrification began in extremities and worked inward
  - Lack of nitrification planning and response activities (SOPs)

Part 2

Questions

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