Chloramine Update Training – Outline
EBMUD, April 13 and 15, 1999

1. Introduction and Objectives
   - What are chloramines? Why use them?
   - Advantages/disadvantages of chloramines
   - Chemicals used to form chloramine
   - Distribution system disinfectant residual goal

2. Chloramine Chemistry
   - Chloramine formation reactions. Breakpoint.
   - Chloramine decomposition reactions
   - Total/free chlorine and ammonia analysis
   - Verification of HACH instruments

3. Chloramine Dose Calculations
   - Review of chloramine math
   - Estimating ammonia chemical inventory

4. Review of Plant Chloramine Formation
   - Plant by plant review
   - Process diagnostics

5. Distribution System Update
   - Long-term water quality trends
   - Nitrification update
   - Where do we go from here?

The "Life Cycle" of Chloramine I – WTPs

Monochloramine Formation (5:1 Cl_2:N ratio)

NH_3	+	Cl_2	→	NH_2Cl	+	HCl
14g N	to	71g Cl_2	equals	5.1 ratio		

at pH = 7.0 – 9.0 reaction with 0.2 seconds or less – at 25°C
temperature slows down reaction to 5 minutes at 0°C

Breakpoint Reaction (7.6:1 Cl_2:N ratio)

NH_3	+	1.5 Cl_2	→	0.5 N_2	+	3 HCl
14g N	to	106g Cl_2	equals	7.6 ratio		

at pH = 9.0 reaction takes hours; faster at pH = 8.0
pH and water source affects the breakpoint ratio (could be, e.g., 11:1)
temperature slows down reaction

Dichloramine Formation (10:1 Cl_2:N ratio)

$$NH_3 + 2\,Cl_2 \rightarrow NHCl_2 + 2\,HCl$$

Only trace levels following breakpoint at pH = 7.0 – 9.0,
reaction takes hours

Trichloramine Formation (15:1 Cl_2:N ratio)

$$NH_3 + 3\,Cl_2 \rightarrow NCl_3 + 3\,HCl$$

Only trace levels following breakpoint
rarely in routine WTP operations

WTP – Chloramine Formation & Stability

Below 5:1 Cl_2:N ratio

- Instantaneous formation of chloramine
- Free ammonia is present
- Free chlorine is not present (false-positive)

Above 5:1 Cl_2:N ratio

- Gradual loss of total chlorine and ammonia
- Breakpoint reaction is slow at pH > 8.0
- Free ammonia is not present
- Initially free chlorine may be present

Chloramine stability is reduced by:

- Breakpoint and loss of total chlorine
- pH < 8.3
- Lack of free chlorine contact in clearwell at USL and Sobrante
- High ozone doses and peroxide (preliminary results to be verified)

Chloramine stability is not affected much by:

- Chloramine dose
- Cl_2:N ratio (as long as it is below 5:1)
- Lack of free chlorine contact in clearwell at Aqueduct plants

The "Life Cycle" of Chloramine II – System

Monochloramine Reaction with Organics

$$TOC + NH_2Cl \rightarrow NH_3 + HCl + \text{Products}$$

Conceptual reaction simplified after (Harrington et al., 1999)
1 mg/L combined ammonia releases 1 mg/L free ammonia

Monochloramine Auto-Decomposition

$$3\ NH_2Cl \rightarrow NH_3 + N_2 + HCl$$

nitrogen gas pathway after (Valentine, 1998)
1 mg/L combined ammonia releases 1/3 mg/L free ammonia

Nitrification Microbiological Reactions

$$NH_3 + 1.5\ O_2 \rightarrow NO_2^- + H_2O + H^+$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2\ H^+$$

Nitrite is formed, oxygen is needed, pH is lowered eventually, reaction goes to nitrate

Nitrite Reaction with Monochloramine

$$NO_2^- + NH_2Cl + H_2O \rightarrow NO_3^- + NH_3 + HCl$$

Simplified complex reaction after (Valentine, 1998; p. 56)
Chloramine does not react with nitrite (White, 1992; p 227)
Chloramine and nitrite can be measured in the same sample

Distribution System – Chloramine Stability

Chloramine stability is reduce by:

- Presence of natural organics (TOC)
  TOC reaction releases more free ammonia and occurs soon after chloramine formation
- Auto-decomposition reaction
  chloramine will decay at some base rate not much effect of alkalinity observed
- Release of nitrite during nitrification
  nitrification rate increases above 15°C although can occur even at 4°C if water age is long

The "Life Cycle" of Chloramine III – System

<u>Nitrite</u> Reaction with Free Chlorine (5:1 Cl_2:N ratio)

$NO_2^- + Cl_2 + H_2O \rightarrow NO_3^- + 2\,HCl$
14g N to 71g Cl_2 equals 5:1 ratio

free chlorination of nitrified water in the distribution system
nitrite represents significant chlorine demand (White, 1992; p. 226)

<u>Dechloramination</u> with GAC

$NH_2Cl + H_2O + C^* \rightarrow NH_3 + HCl + CO^*$

Monochloramine reacts slower with GAC than free chlorine
carbon surface gets oxidized but not destroyed as with free chlorine

<u>Dechloramination</u> with Bisulfite

$NH_2Cl + Na_2SO_3 + H_2O \rightarrow NH_3 + HCl + H_2SO_4$

Process Diagnostics

<u>Plant Effluent Chloramine Goals</u>

- Total Cl_2 = 2.0 $\pm$ 0.1 mg/L Cl_2 – Mokelumne
  Total Cl_2 = 2.5 $\pm$ 0.1 mg/L Cl_2 – USL/Sobrante
- Cl_2:N ratio = 4.5 – 4.7 to 1
- Free ammonia = 0.02 – 0.06 mg/L N

<u>Process Diagnostics</u>

Free ammonia must be present (within goal)
- If outside goal → verify flows, repeat analysis
  - If zero → increase NH_3-N or lower Cl_2 dose
  - If high → lower NH_3-N or increase Cl_2 dose

Free chlorine cannot be present
- If present & free NH_3-N > 0 → False-positive
  - Verify immediate color against white paper
  - Do not shake, do not place in HACH
  - Use short vial for free Cl_2
  - Use dedicated vials for free and total Cl_2
- If present & free NH_3-N = 0 → Breakpoint
  - Verify flows
  - Increase NH_3-N or lower Cl_2 dose

Total $Cl_2 \geq$ Free Cl_2 (before ammoniation)

- If not & Free NH_3-N = 0 → Breakpoint
    - Verify flows
    - Confirm low total Cl_2 on 15-min sample
    - Increase NH_3-N or lower Cl_2 dose

Strategies to Maintain Chloramine

Implemented – Not long-term solutions

- Breakpoint Chlorinating Reservoirs: short-term, high THMs, customer complaints
- Flushing Pipelines: improved conditions but does not impact reservoirs
- Cleaning Reservoirs: improved hygiene but does not impact reservoirs
- Increased pH to 9.0: helped in Sobrante, may cause precipitation – reduce to 8.7
- Blend Orinda Water: need 50% + ratio, nitrification will return in the summer

Not Implemented – Risky or Unfeasible

- Increase Chloramine Dose: would also increase ammonia
- Reduce Water Age: impractical due to system design, fire flows

Potential Future Implementation

- Further Minimize Free Ammonia: improve control at WTPs; on-line ammonia
- Apply Chlorine Dioxide & Chlorite: experimental – may try next year
- Remove TOC: very expensive – either GAC or membranes

Calculation Examples

A. <u>Calculate aqua ammonia feed rate in (mL/min)</u>

Ammonia weight percent = 19% NH_3
Plant rate = 25.3 MGD
Ammonia dose desired = 0.52 mg/L N

1. NH_3-N concentration in stock:
   19% aqua ammonia weighs 7.74 lbs NH_3/gal
   $$\frac{(7.74 \text{ lbs } NH_3/\text{gal}) \times 19\% \times (14 \text{ g N})}{(17 \text{ g } NH_3)} = 1.21 \text{ lbs } NH_3\text{-N/gal}$$

2. Ammonia nitrogen NH_3-N feed rate:
   (25.3 MGD) x [(8.34 lb/M) (1 L/mg)] x (0.52 mg/L N) = <u>109.7 lbs NH_3-N/day</u>

3. Aqua ammonia feed rate in (mL/min):

$$\frac{(109.7 \text{ lbs } NH_3\text{-N/day}) \times (3785 \text{ mL/gal})}{(1.21 \text{ lbs } NH_3\text{-N/gal}) \times (1440 \text{ min/day})} = 238.3 \text{ mL/min}$$

B. Calculate expected free ammonia as N

Total chlorine = 2.0 mg/L Cl_2
Chlorine to ammonia-N ratio = 4.5:1

1. Total NH_3-N dose:
(2.0 mg/L Cl_2) / 4.5 = <u>0.44 mg/L NH_3-N</u>

2. Combined NH_3-N in chloramine:
(71 g Cl_2) / (14 g N) = 5 Cl_2 : NH_3-N ratio in chloramine
(2.0 mg/L Cl_2) / 5 = <u>0.40 mg/L NH_3-N</u>

3. Free NH_3-N expected leaving the plant:
0.44 – 0.40 = <u>0.04 mg/L NH_3-N</u>

C. Calculate required change in ammonia dose

Total chlorine = 2.0 mg/L Cl_2
Total ammonia dose is 0.67 mg/L NH_3-N
Required Cl_2 : NH_3-N ratio is 4.5:1

1. Where are you on breakpoint curve?

(2.0 mg/L Cl_2) / (0.67 mg/L NH_3-N) = <u>3:1</u> Cl_2 : <u>NH_3-N ratio</u>
increasing portion of breakpoint curve – OK
Ammonia dose needs to be reduced

2. Required NH_3-N dose:

(2.0 mg/L Cl_2) / 4.5 = <u>0.44 mg/L NH_3-N</u>

3. Required reduction in total NH_3-N dose:

0.67 – 0.44 = <u>0.23 mg/L NH_3-N</u>

D. Calculate required change in ammonia dose

Total chlorine = 2.0 mg/L Cl_2
Total ammonia dose is 0.30 mg/L NH_3-N
Required Cl_2 : NH_3-N ratio is 4.5:1

1. Where are you on breakpoint curve?

   (2.0 mg/L Cl_2) / 0.30 mg/L NH_3-N = 6.6:1 Cl_2 : NH_3-N ratio
   decreasing portion of breakpoint curve – NOT GOOD
   Ammonia dose needs to be increased

2. Required NH_3-N dose:

   (2.0 mg/L Cl_2) / 4.5 = 0.44 mg/L NH_3-N

3. Required increase in total NH_3-N dose:

   0.44 – 0.30 = 0.14 mg/L NH_3-N

Source: Kirmeyer, et. al., © 1993