

# Chloramine Treatment & Management

**NHWWA Operator Training Session**

*Presented by:*

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# Acknowledgements

- NEWWA Disinfection Committee
- Professor Jim Malley, UNH
- Cynthia Klevens, NHDES
- Manchester Water Works Operators & Laboratory Staff

# References

- *Alternative Disinfectants and Oxidants Guidance Manual*, USEPA, 1999
- *A Guide for the Implementation and Use of Chloramines*, AwwaRF, 2004
- *Water Chlorination/Chloramination Practices and Principles (M20)*, AWWA, Latest Edition

# Presentation Outline

- Why Use Chloramines?
  - Pathogen Inactivation & Disinfection
  - DBP Formation Control
  - Chlorine & Chloramine Chemistry
  - Chlorine & Ammonia Feed Methods
  - Safety Considerations
  - Managing the Chloramination Process
  - Impact on other Treatment Processes
- 
- The background of the slide features several concentric, light blue circular ripples that resemble water droplets or ripples on a pond, positioned in the lower right and bottom center areas.

# Why Use Chloramines?

- Secondary (residual) Disinfection
  - Reduce DBP risks to public health
  - Less reactive with organics than free chlorine therefore forms less THMs
  - Monochloramine residual more stable and lasts longer than free chlorine residual
  - Monochloramine superior to free chlorine at penetrating biofilm
  - Less likely to have taste & odor complaints
  - Normal dosage: 1.0 to 4.0 mg/L
  - Minimum residual: 0.5 mg/L

# Pathogen Inactivation & Disinfection

## ➤ Mechanism

- Inhibits organism cell protein production & respiration

## ➤ pH Effect

- Controls chloramine species distribution

## ➤ Temperature Effect

- Bacteria & virus inactivation increases with temperature

## ➤ Bacteria, Virus, and Protozoa Inactivation

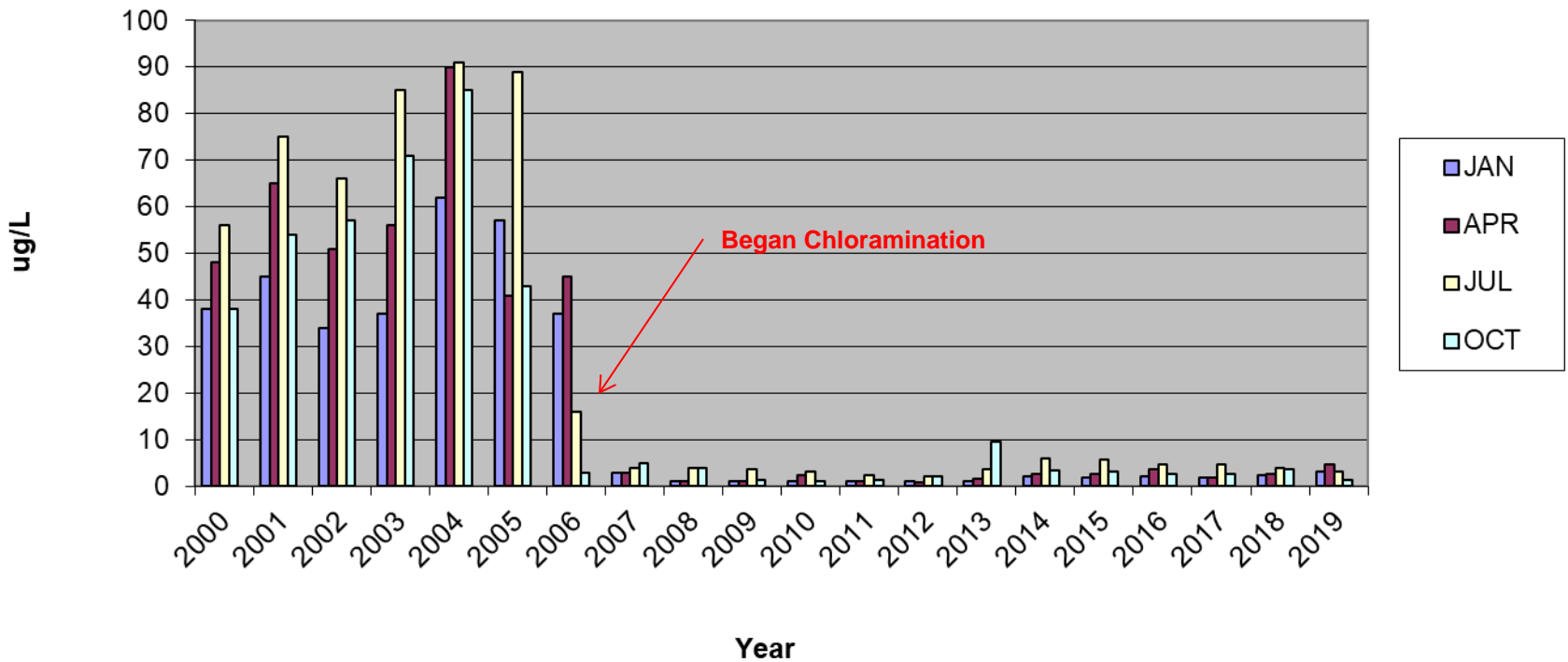
- Far less effective than chlorine
- Experiment (Wattie & Butterfield, 1944):
  - 0.3 mg/L monochloramine required 240 minutes (4 hrs) for 3-log inactivation of *E. coli* whereas 0.14 mg/L of free chlorine required only 5 minutes.

# DBP Formation Control

- Chloramines reduce levels of chlorinated & halogenated by-products in treated water
- Impacted by:
  - $\text{Cl}_2$ :N ratio
  - Point of ammonia addition relative to chlorine
  - MIXING
  - pH
- Chloramines can produce (currently unregulated) by-products!
  - Cyanogen chloride – gas, pungent/pepper odor, highly toxic
  - NDMA – Highly toxic, suspected carcinogen. Forms when nitrogen reacts with chlorine/chloramines

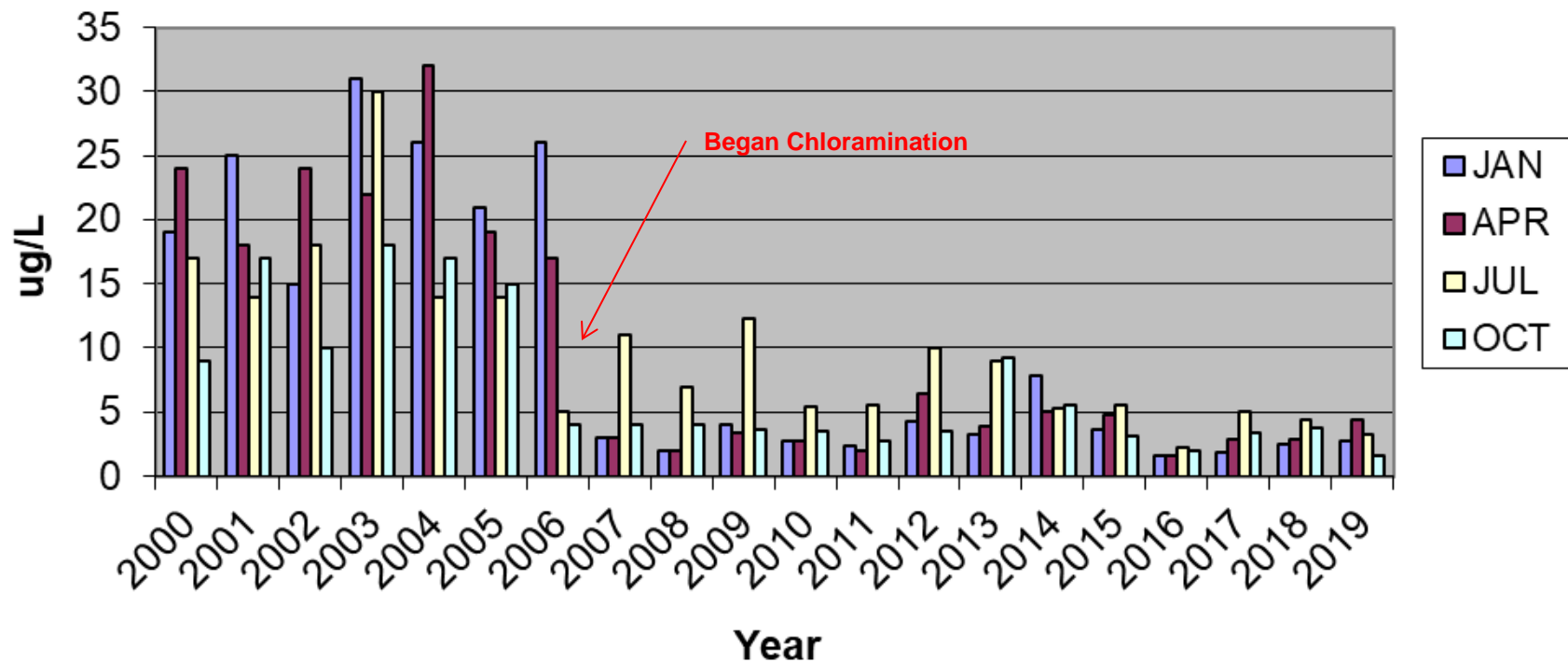
# MWW TTHM's Since 2000

Total Trihalomethanes  
(Average of all Locations)



# MWW HAA's Since 2000

## Haloacetic Acids (Average all Locations)



# Chlorine/Chloramine Chemistry

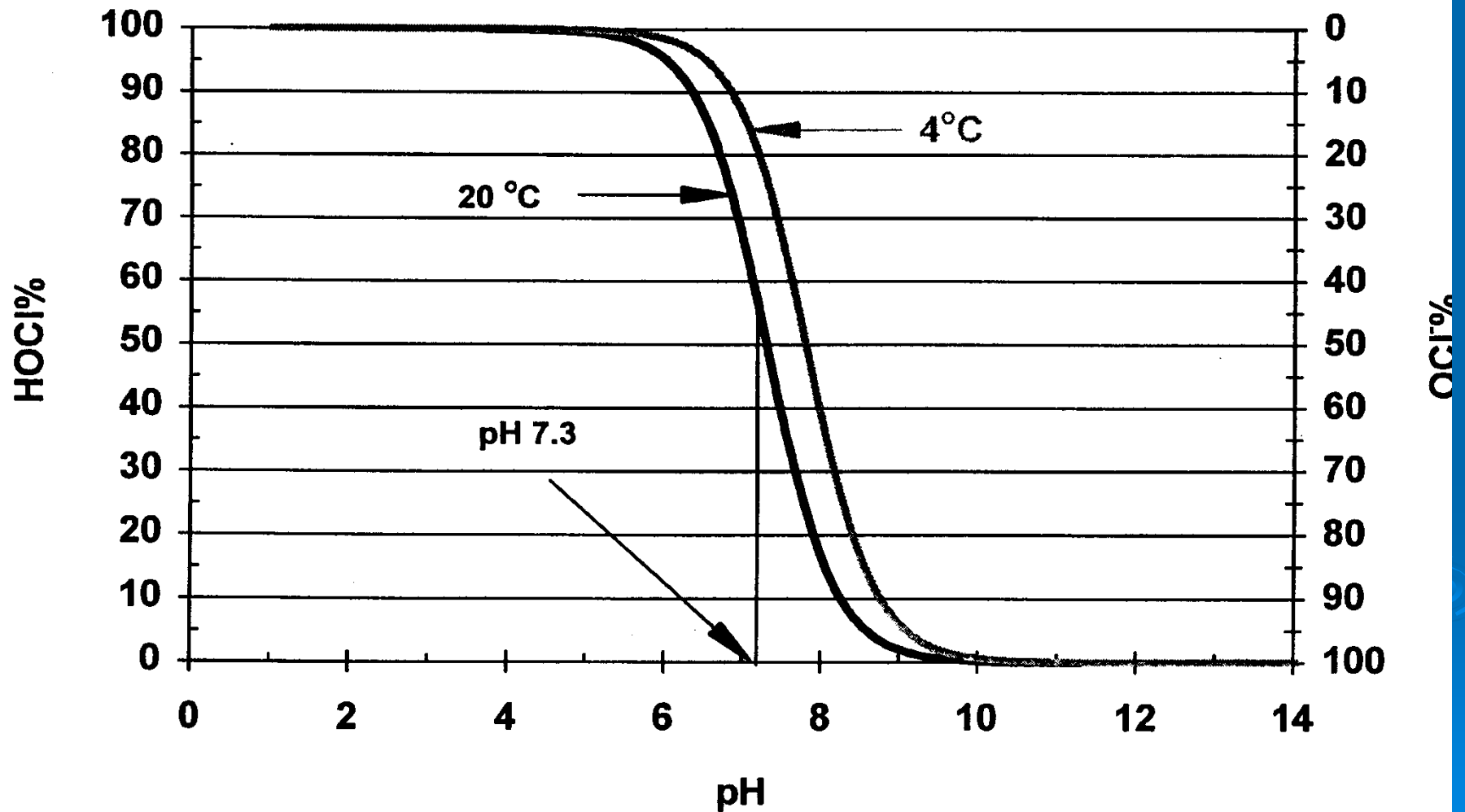
*When chlorine is added to water:*



Hypochlorous  
acid

Hypochlorite  
ion

# pH and Temperature effects



# Chlorine/Chloramine Chemistry

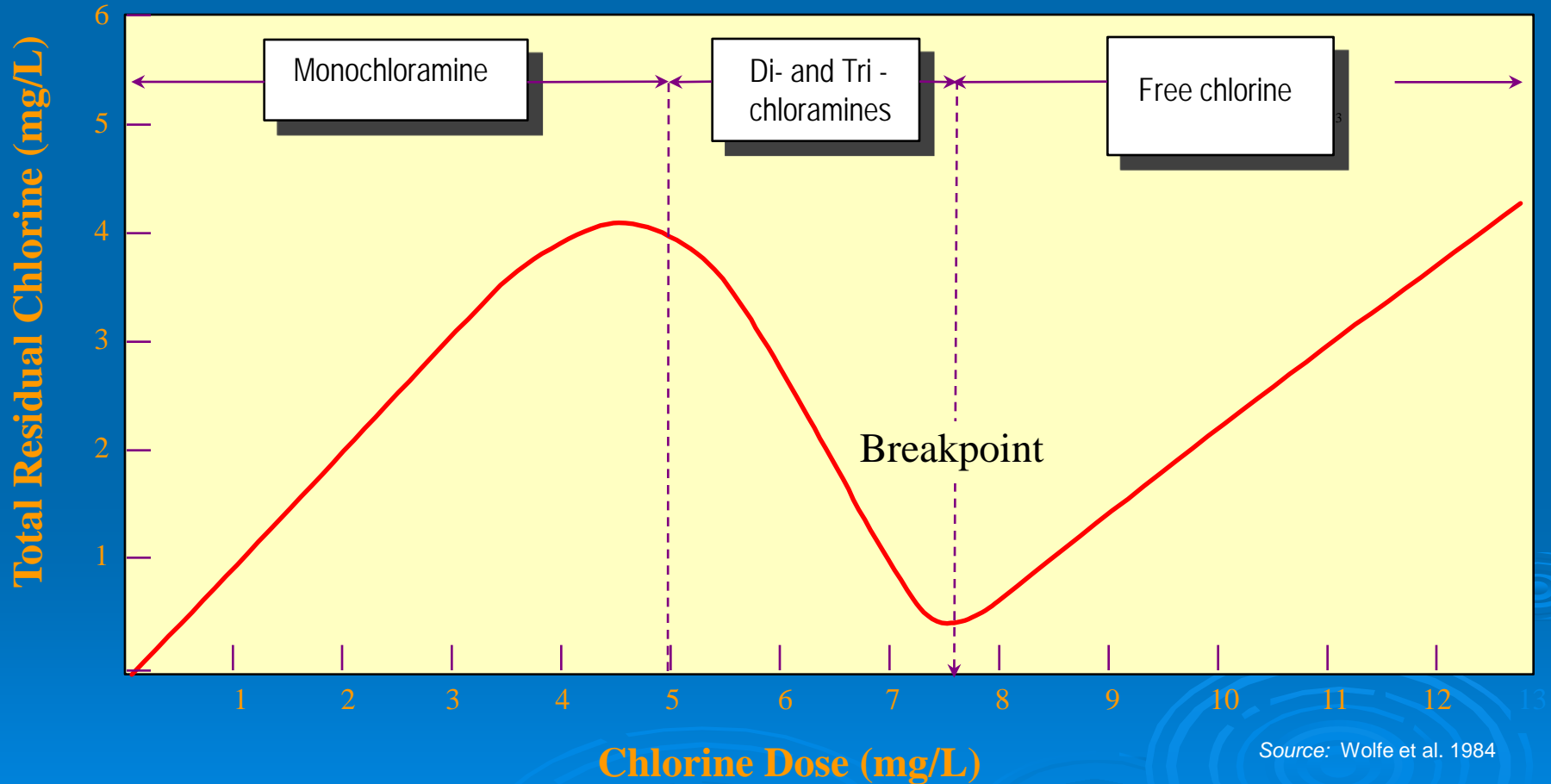
*When ammonia is added after chlorine:*



These reactions are  $\text{Cl}_2:\text{N}$  ratio and pH dependent

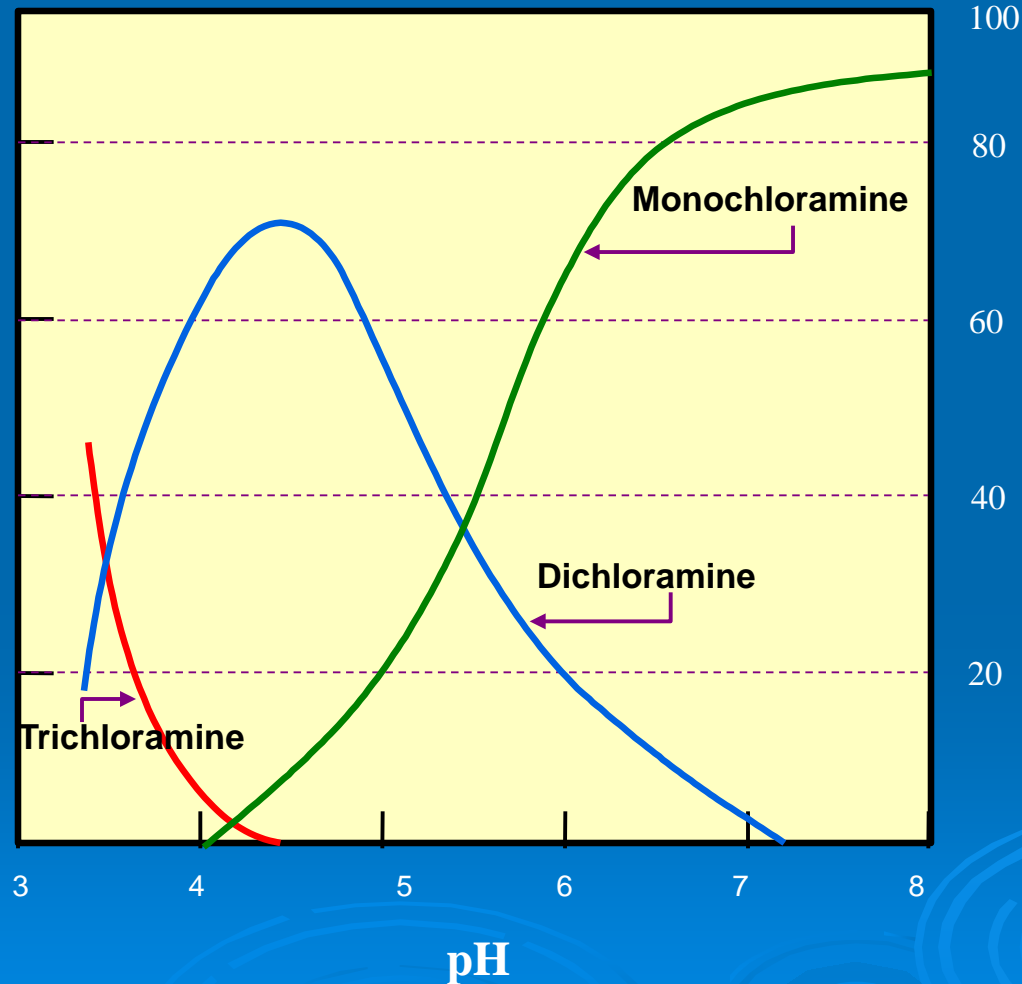
# Theoretical Breakpoint Curve

(1.0 mg/L ammonia-nitrogen; pH 7; temperature 25°C)



Source: Wolfe et al. 1984

# Chloramine Speciation with pH



(2.5 mg/L chlorine; 0.5 mg/L ammonia-nitrogen; temperature 25°C; contact time 2 hours)

# Generation of Chloramines

- Monochloramine is the preferred species
  - Provides a persistent residual
  - Dichloramine & trichloramine produce objectionable tastes & odors
- 3:1 to 5:1 ratio of  $\text{Cl}_2$ :N produces monochloramine

# Chlorine Feed Methods

- Gaseous Chlorine
  - 150lb or 1-ton cylinders
  - “Chlorinator”
  - Safety concerns
- Sodium Hypochlorite
  - Typically bulk purchased
  - Fed directly into process stream
- **MIXING IS CRITICAL**

# Ammonia Feed Methods

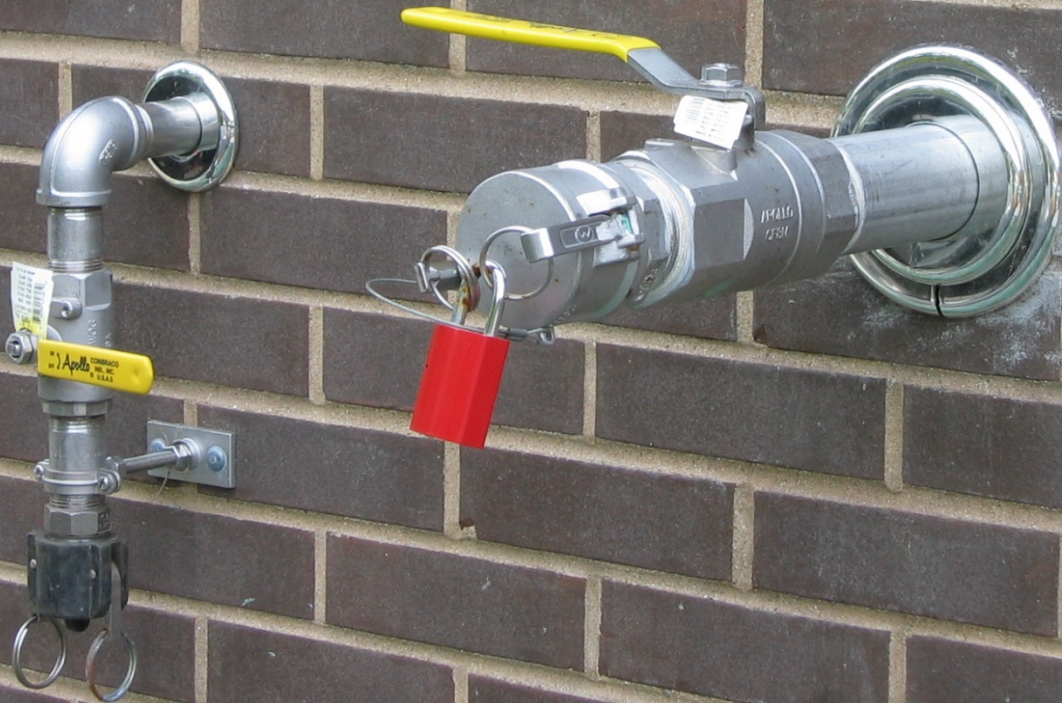
## ➤ Anhydrous Ammonia (gas)

- Portable cylinders or 1,000 gallon tanks
- Minimum working pressure of 250 psi
- “Ammoniator”
  - self-contained modular unit w/PRV, flow meter & rate control valve
  - Typically auto-paced
- Direct Feed Method: low process stream pressure
- Solution Feed Method: larger applications, high process stream pressure

# Ammonia Feed Methods

- Aqueous Ammonia (liquid)
  - Delivered by tank truck
  - Stored on-site in steel or fiberglass tank
    - Tank vented through “scrubber” to atmosphere
  - Tank connected to typical chemical feed pump arrangement (relief valve, pulsation dampener, back pressure valve, flow meter)
- **MIXING IS CRITICAL**

Aqua  
Ammonia







**AQUA  
AMMONIA**

PROTECTED WATER



# Safety Considerations

- Never store chlorine gas & ammonia gas in same room
- Room ventilation at high point ( $\geq 6$  air exchanges per minute)
- Vapor detection device/alarm
- Protect ammonia gas storage tanks from direct sunlight and heat sources
- Review MSDS regularly and have available appropriate personal protective gear

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# Sequence of Application

## ➤ Ammonia then Chlorine

- Less likely to form objectionable taste and odors

## ➤ Chlorine then Ammonia

- Most common in drinking water industry
- Enables achievement of required CT for inactivation of viruses and *Giardia*

*(germacidal effectiveness of chloramines 200 times less than chlorine)*

# Managing the Chloramination Process

## ➤ Manchester Water Works Disinfection Process:

Primary Disinfectant

Source > Pretreatment > **OZONE** > Filtration >



# Managing the Chloramination Process

- How do we get this right?
  - Establish a POE Total Chlorine Target
    - Higher in warm water, lower in cold water
    - Residuals farthest from WTP tell the story!
  - Add chlorine MIX WELL!
  - Measure free chlorine then add ammonia at ratio approximately 4.5 : 1
  - MIX WELL again!
- Monitor the process several ways

# Managing the Chloramination Process

- Process Analyzer: HACH 5500sc Ammonia Monochloramine Analyzer
  - Directly measures Monochloramine and Total Ammonia
  - Calculates **Free Ammonia**, Total Chlorine, Chlorine to Ammonia Ratio
  - If OOS, operators use HACH SL1000 to check parameters



# Managing the Chloramination Process

## ➤ SCADA calculation

- Uses free chlorine residual and ammonia dose to keep a running tally of chlorine to ammonia ratio based on:
  - 2-hour running average
  - 8-hour running average

## ➤ Daily Laboratory Confirmation

- Using lab bench readings of total chlorine, monochloramine, free chlorine, & free ammonia

# Managing the Chloramination Process

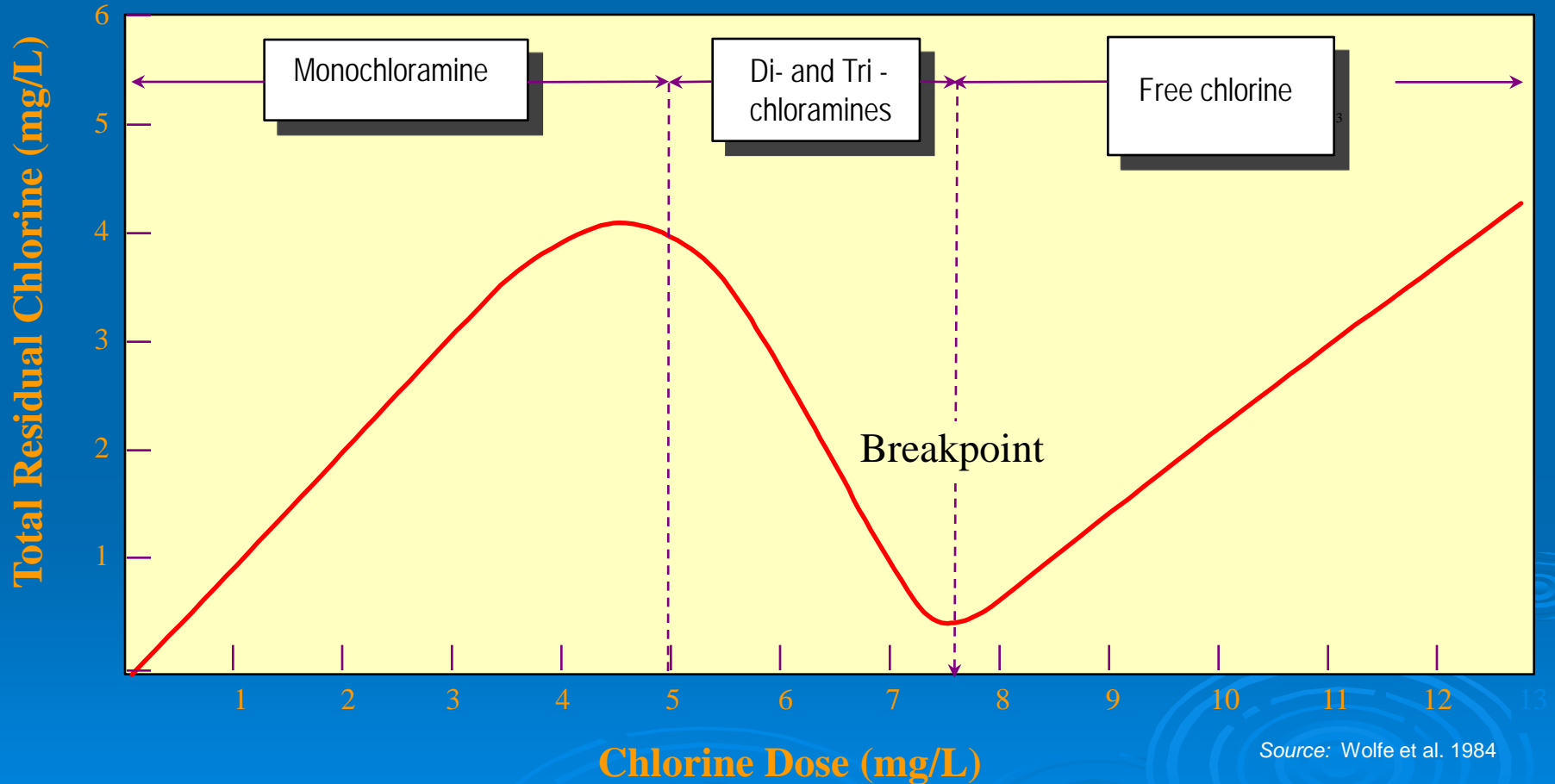
➤ Free Ammonia is the key!

Target free ammonia between 0.05 and 0.1 mg/L



# Theoretical Breakpoint Curve

(1.0 mg/L ammonia-nitrogen; pH 7; temperature 25°C)



Source: Wolfe et al. 1984

# Impact on other Treatment Processes

- **Nitrification** - Excess ammonia can provide nutrients for nitrifying bacteria in distribution system
  - **Ammonia-Nitrogen** + *nitrosomonas* → Nitrite + *nitrobacter* → Nitrate
  - Can lead to loss of residual; decrease in pH, alkalinity, and DO; and increase in bacterial growth
  - Must closely monitor distribution system to detect signs of nitrification
  - Control: Convert to free chlorine, increase chloramine residual, increase ratio, adjust pH, system flushing, reduce water age.
- Monochloramine addition upstream of filters reduces biological growth on media
- Improper Cl<sub>2</sub>:N ratio control can lead to breakpoint reactions (loss of residual!)

# Impact on other Treatment Processes

- Switching to chloramines WILL change water quality conditions in the distribution system (especially ORP)
- Need to monitor system pH;  $\text{Cl}_2$  to  $\text{NH}_4\text{-N}$  Mass Ratio; **Lead** & Copper; Microbes; Ammonia; Nitrite & Nitrate
- Washington, D.C. Disaster
  - (In 2000 switched to chloramines without understanding potential corrosion control impacts and failed to monitor key parameters in distribution system)

# Some Take Home Messages

- Chloramines Reduce DBP Risks to Public Health
- Chloramines Reduce Microbial Regrowth and Risk in Distribution Systems and in Hospitals
- Chloramines alone DO NOT cause Corrosion Problems (failing to understand water chemistry impacts and monitor for signs of trouble certainly can)
- The Decision to Switch to Chloramines Requires:
  - An Experienced Team Effort
  - Careful Planning Including Public Education
  - Careful Implementation of Switching to Chloramines
  - System Monitoring of Key Water Quality Parameters {e.g., pH;  $\text{Cl}_2$  to  $\text{NH}_4\text{-N}$  Mass Ratio; Lead and Copper; Microbes, Ammonia, Nitrite and Nitrate} is Needed

# Questions?

