

# Detection, Prevention, and Correction of Nitrification In Potable Water Distribution Systems

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Dave Baker

Enprotec/Hibbs & Todd

402 Cedar; Abilene TX 79601

325.698.5560 eht.com

# Material Outline

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- Nitrification, what is it?
- Control of the Chloramination Process
- Nitrification
  - Prevention
  - Detection and
  - Correction
- Nitrification Monitoring Plan

# Potential Problems In a Chloraminated System

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- Potential problems related to chloramination
  - Overfeeding chlorine
    - Short term to immediate problems of bad taste/odor and loss of disinfectant residual
  - Overfeeding ammonia
    - Potential long term problems promoting nitrification
  - Nitrification
    - Loss of disinfectant residual
    - Growth of bacteria in the system

# Nitrification

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- Ammonia oxidizing bacteria in the biofilm of the distribution system use free ammonia as a food source.
- Byproducts from nitrification cause a decrease in the disinfectant residual.
- Sign of nitrification problems are of dropping total chlorine residual in the distribution system.
- Common in older and more distant parts of the system.

# Terms

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- Before getting into nitrification, a quick review of the terms we're using...

# Free Chlorine ( $\text{Cl}_2$ ):

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- Unbound chlorine in water
- Present only after reduction demand has been satisfied and reducing agents are oxidized
- Present in water as hypochlorous acid ( $\text{HOCl}$ ) and hypochlorite ion ( $\text{OCl}^-$ )
- Potent disinfectant
- Is eventually reduced to chloride

# Free Chlorine

- Be aware that monochloramine interferes with DPD Free Chlorine Colorimetric measurement to give false high reading

NH <sub>2</sub> Cl (as Cl <sub>2</sub> )	Sample Temp Deg F			
	40	50	68	83
1.2 mg/L	+0.15	+0.19	+0.30	+0.29
2.5 mg/L	+0.35	+0.38	+0.55	+0.61
3.5 mg/L	+0.38	+0.56	+0.69	+0.73

From Hach *Water Analysis Handbook; 4<sup>th</sup> Edition*

# Total Cl<sub>2</sub>

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- Combined or free chlorine in water
- May be measuring free chlorine or chloramine

# Free Ammonia ( $\text{NH}_3$ )

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- Can be in the form of  $\text{NH}_3$  at higher pH (pH >9.3) or  $\text{NH}_4^+$  (ammonium) at normal pH (pH 7-8.5)
- Each part of free ammonia will combine with 4.2 parts of chlorine to form monochloramine
- Represents food for ammonia oxidizing bacteria (AOB)

# Unreactive Measured Free $\text{NH}_3$

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- Refers to the measured free ammonia that shows up in the distribution system that resists efforts to eliminate via chlorination.
- Causes problems when the effort is made to neutralize in the distribution system using chlorination.
- Commonly results in loss of all chlorine residual through overchlorination.

# Combined $\text{NH}_3$

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- Represents the ammonia bound with  $\text{Cl}_2$  to form chloramine
- Combined  $\text{NH}_3$  is not food for bacteria
- Combined ammonia is about 24% of the total chlorine residual

# Total $\text{NH}_3$

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- Represents the sum of combined ammonia tied up in chloramines and free ammonia ( $\text{NH}_3$  and  $\text{NH}_4^+$ )

# Chloramine

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- Chemical compound formed from the combination of  $\text{Cl}_2$  and  $\text{NH}_3$  (inorganic and organic)
- Much less potent disinfectant than free chlorine
- Types present are highly dependent on pH, temperature, and chlorine to ammonia ratio
- Four types commonly encountered
  - Monochloramine- no taste or odor
  - Dichloramine- bad taste and odor
  - Trichloramine
  - Organic chloramines

# Monochloramine ( $\text{NH}_2\text{Cl}$ )

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- The combination of chlorine and  $\text{NH}_3$  that under normal pH conditions (7-8.5) predominates at an applied  $\text{Cl}_2:\text{NH}_3$  ratio up to 4.2:1
- Higher pH favors formation of monochloramine...lower pH favors formation of di- and trichloramine

# Dichloramine (NHCl<sub>2</sub>)

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- Symptom of a Cl<sub>2</sub>-rich chloramination process
- Begins to show up under normal pH conditions (7-8.5) when Cl<sub>2</sub>:NH<sub>3</sub> ratio increases above 4.2:1 up to ~8:1.
- Results in lowered total chlorine residual and taste and odor problems
- Unstable in solution
- Lower pH favors formation of dichloramine

# Trichloramine / Nitrogen Trichloride ( $\text{NCl}_3$ )

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- Symptom of a  $\text{Cl}_2$ -rich chloramination process
- Occurs at normal pH (7-8.5) when  $\text{Cl}_2:\text{NH}_3$  ratio increases beyond ~8:1
- At pH less than 3 is the only chloramine specie present

# Organic Chloramines

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- The product of reactions of organic amines and amino acids with chlorine
- May be reflected in the total chlorine measurement
- Constitutes a portion of oxidant demand
- Also constitute demand on monochloramine

# Breakpoint Chlorination

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- Before getting into nitrification, a quick review of breakpoint chlorination...

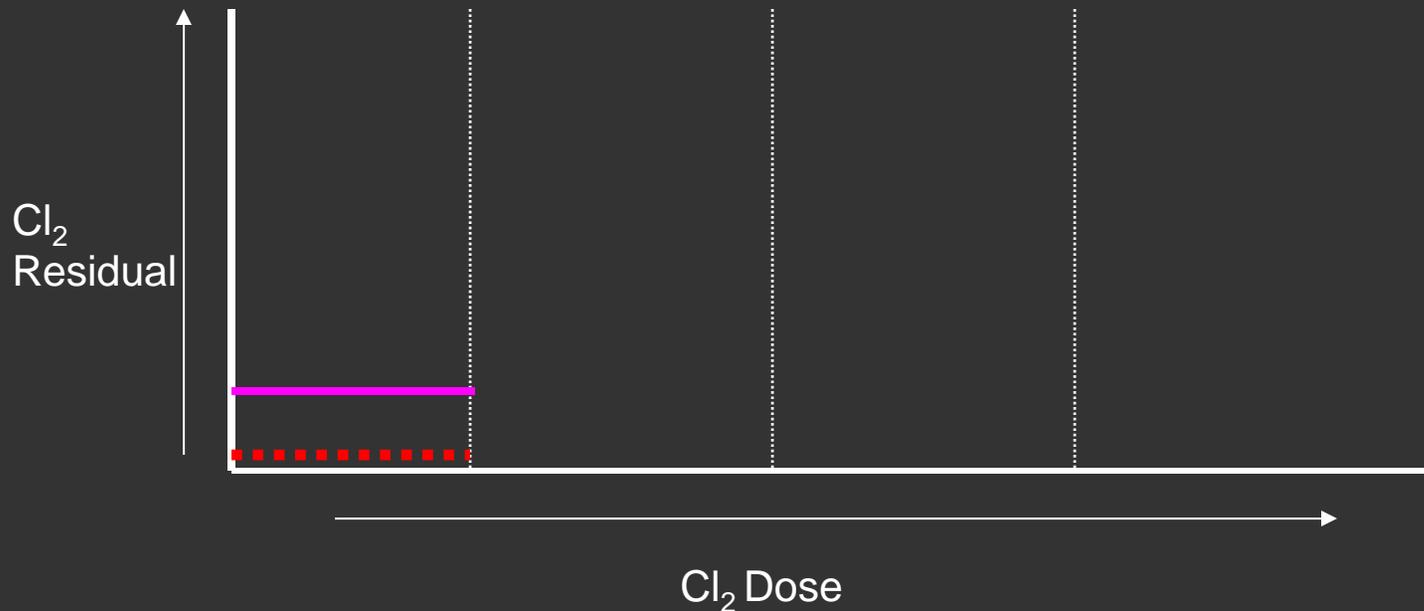
# Breakpoint Chlorination

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- At normal pH (7-8.5) occurs at a  $\text{Cl}_2:\text{NH}_3$  ratio of about ~8:1
- Ratio at which breakpoint occurs is pH dependent
  - Lower pH = Lower Breakpoint Ratio
- At breakpoint there is little chlorine or ammonia left in the water
- Beyond breakpoint chlorination adding more  $\text{Cl}_2$  results in rising free  $\text{Cl}_2$  residual

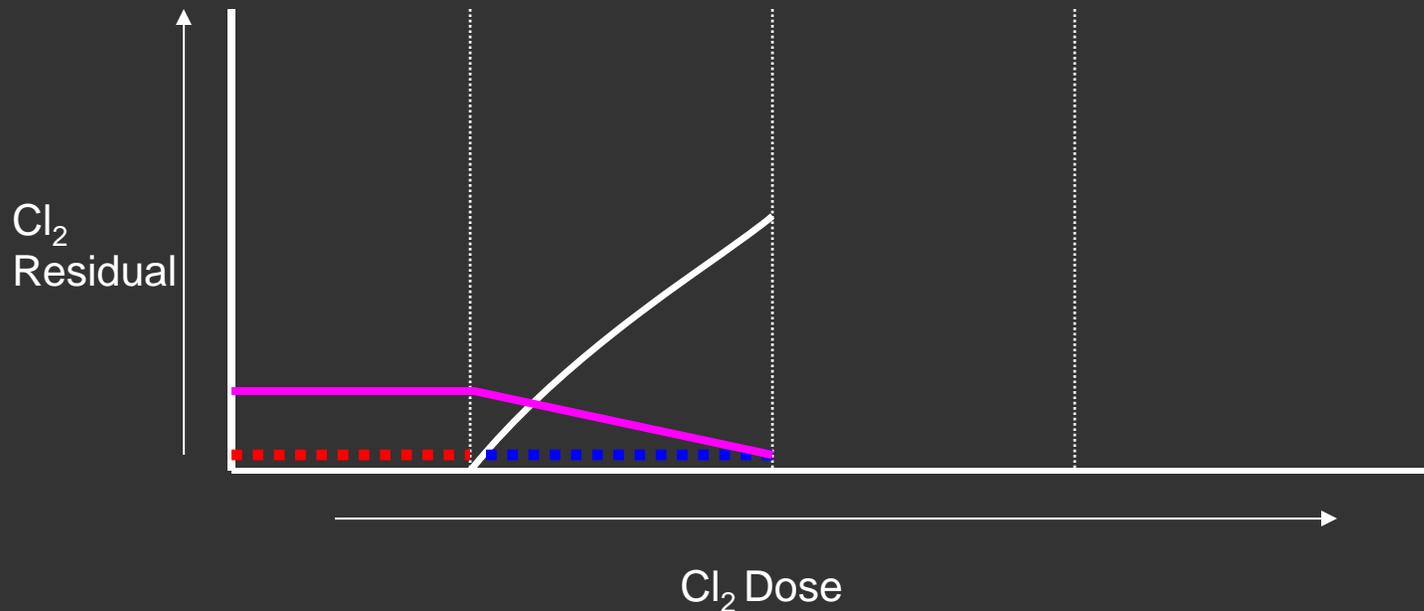
# Breakpoint Curve

- The graph depicting what happens when chlorine is added to water.
- First (red), the added chlorine reacts with reducing compounds in the water to use up the chlorine, producing no chlorine residual. Free ammonia (pink) is not affected by chlorine addition.



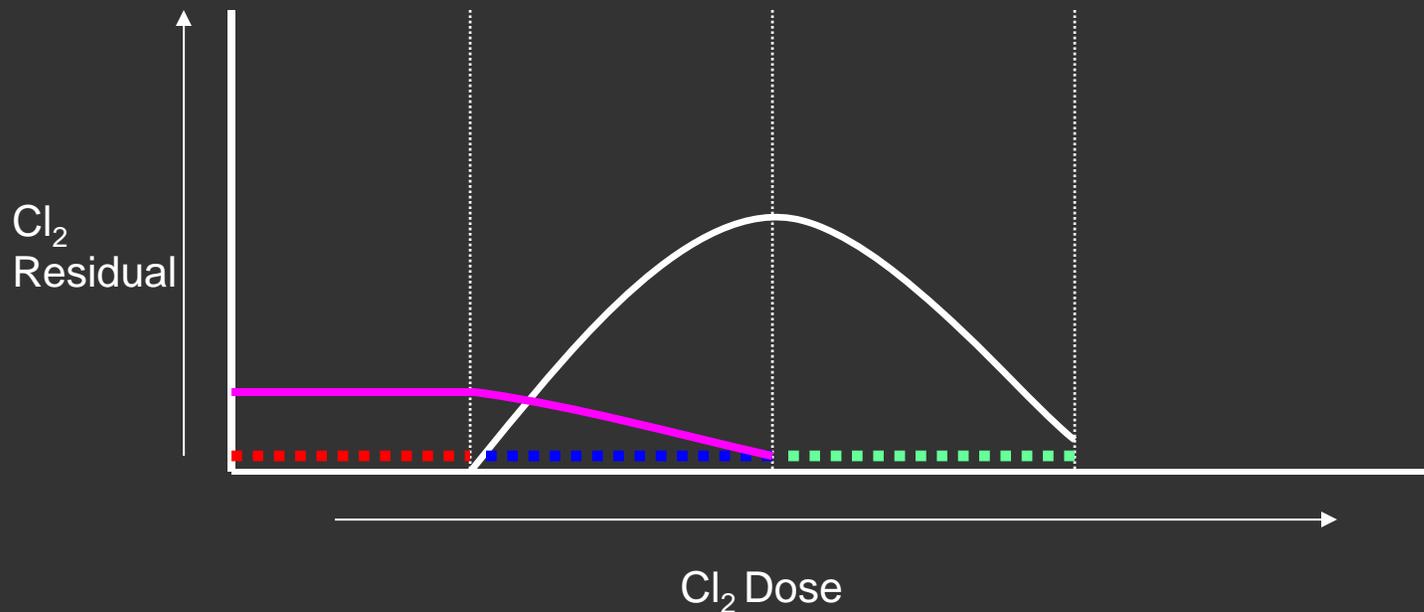
# Breakpoint Curve

- Next, (blue) when additional chlorine is added the chlorine reacts with organics and ammonia to form chloramines. Free ammonia residual (pink) begins to decrease.



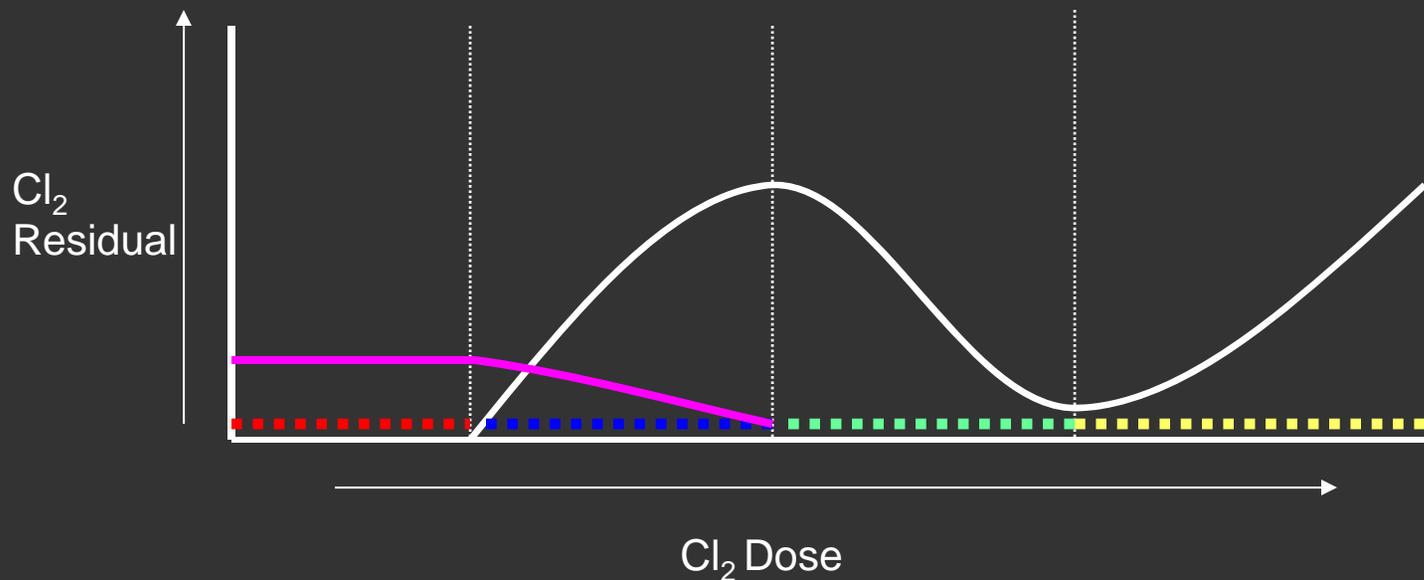
# Breakpoint Curve

- Next (green) when additional chlorine is added the chlorine breaks down most of the chloramines in the water to dichloramines, nitrous oxide, nitrogen trichloride, and nitrogen gas causing the total chlorine and total ammonia concentrations to fall.



# Breakpoint Curve

- Adding more chlorine causes the water to reach the breakpoint, (green to yellow) and any further chlorine addition results in free chlorine residual in direct proportion to chlorine addition. The breakpoint is the point at which the chlorine demand has been satisfied.



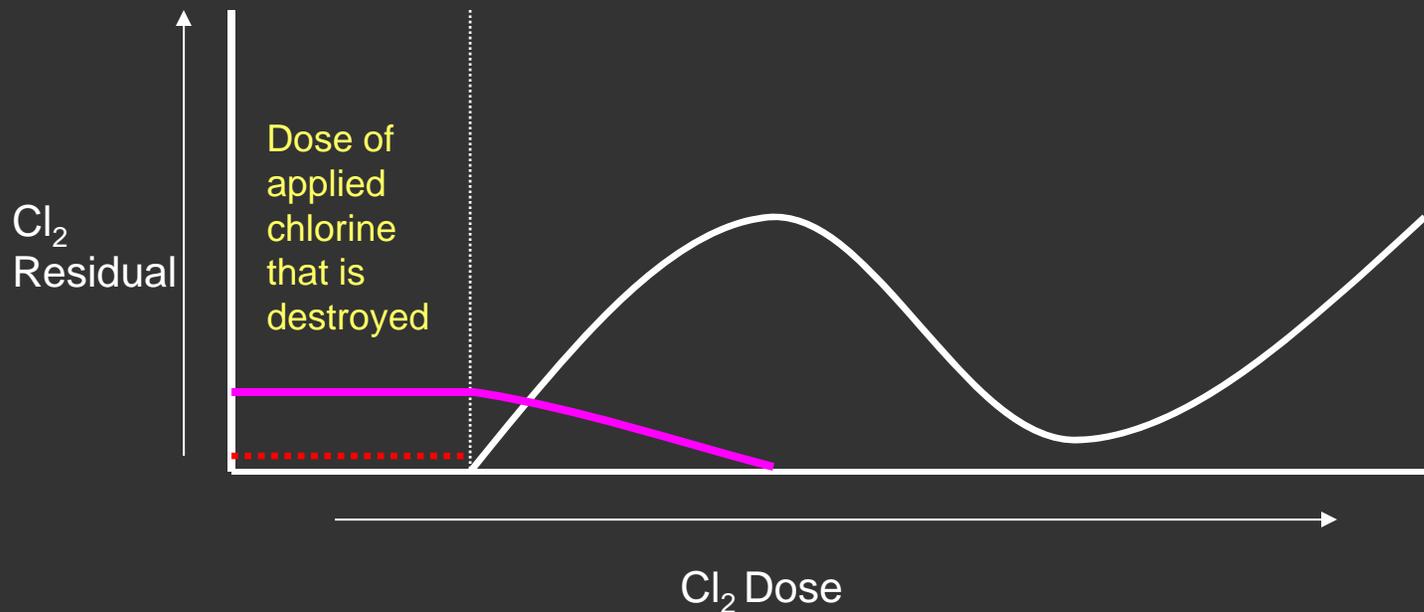
# Cl<sub>2</sub> Demand

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- When chlorine enters impure water, it immediately begins to oxidize reducing compounds present in the water.
- Common reducing compounds found in raw water include organic compounds, sulfur compounds, ferrous ions, manganous ions, nitrite ions, ammonium ions and ammonia.
- Preferential reactivity with certain reducing compounds results in destruction of some amount of chlorine as it is added to water before total chlorine residual appears.

# Cl<sub>2</sub> Demand (\*)

- The chlorine that is reduced or destroyed is not factored into the chlorine to ammonia ratio because the chlorine that was destroyed was not able to react with ammonia to form chloramine.



# Cl<sub>2</sub> Demand

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- Chlorine demand is naturally variable and changes due to a variety of fluctuating conditions including weather, season, lake turnover, lake level changes, algae blooms, etc.
- As with demand, the amount of chlorine destroyed by initial reduction demand is variable
- If chlorine and ammonia feed rates remain constant and chlorine demand changes, so too does chlorine to ammonia ratio

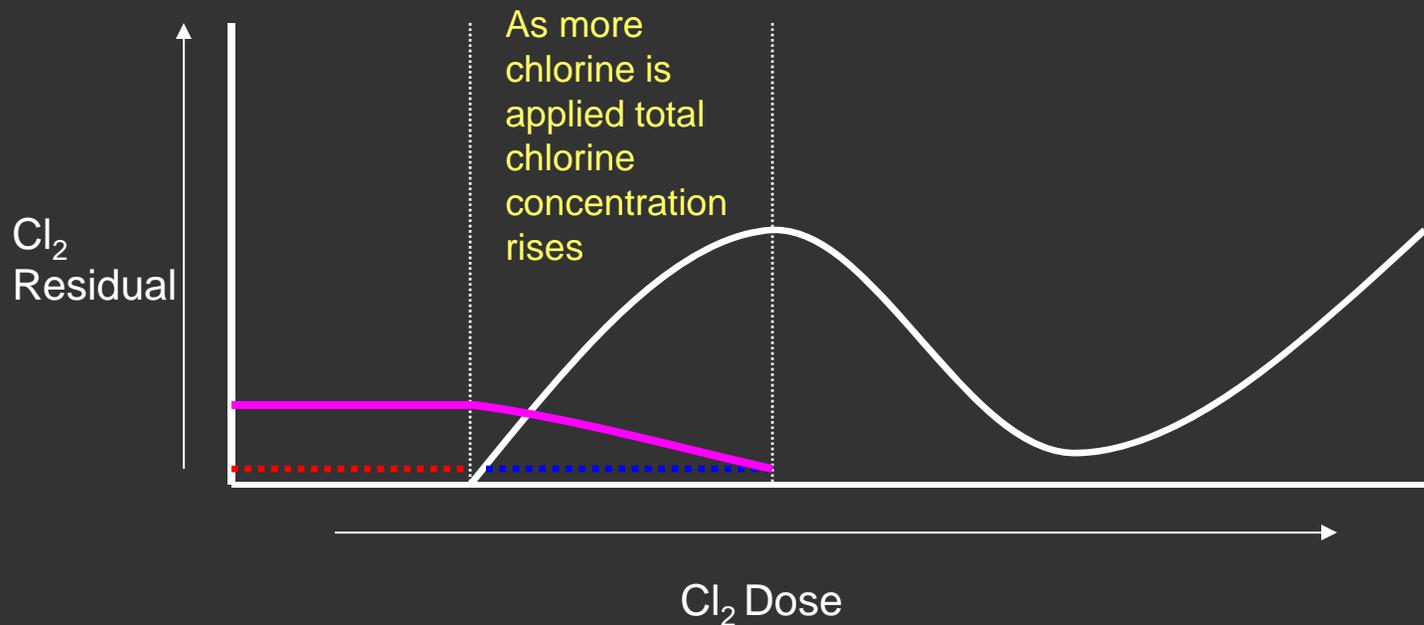
# Cl<sub>2</sub> Demand

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- Point to consider is this...the chlorine to ammonia ratio is subject to change based on variable raw water chlorine demand.
- Even though chemical feed rates and raw water flows may remain constant, the chlorine to ammonia ratio might not.
- Important if primary oxidant is not used ahead of the chloramination process.

# Formation of Chloramine

- Once destructive chlorine demand is overcome applied chlorine reacts with available ammonia to form chloramine. Total chlorine residual increases as more chlorine is applied.



# Formation of Chloramine

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- In water at normal pH (7-8) chlorine reacts almost instantaneously with ammonia
  - At a pH of 4 it takes 147 seconds to bind 99% of free ammonia with chlorine
  - At a pH of 7 it takes 0.2 seconds...
  - At a pH of 8.3 it takes 0.07 seconds...
- When 1.0 mg/L free chlorine combines with ammonia it forms 1.0 mg/L chloramine (\*)

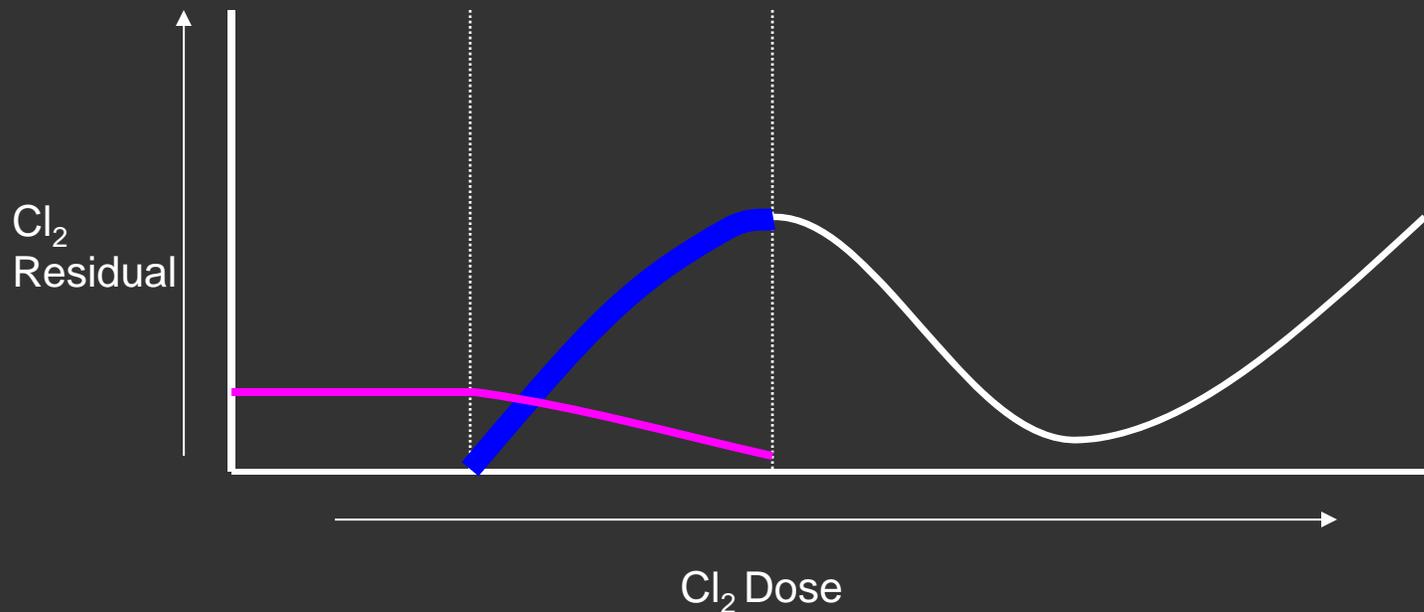
# Cl<sub>2</sub>:NH<sub>3</sub> Ratio

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- In water 1 part of free Cl<sub>2</sub> combines with 1 part of NH<sub>3</sub> to form chloramine but 1 part of Cl<sub>2</sub> weighs 5 times more than 1 part of NH<sub>3</sub>
- The unit weight of Cl<sub>2</sub> is 71 and of NH<sub>3</sub> is 17  
 $71 \div 17 = 4.2$  or 4.2:1
- At normal pH, 4.2 mg/L of available free Cl<sub>2</sub> will combine with 1 mg/L NH<sub>3</sub> to produce monochloramine as will 0.42 mg/L chlorine with 0.1 mg/L ammonia

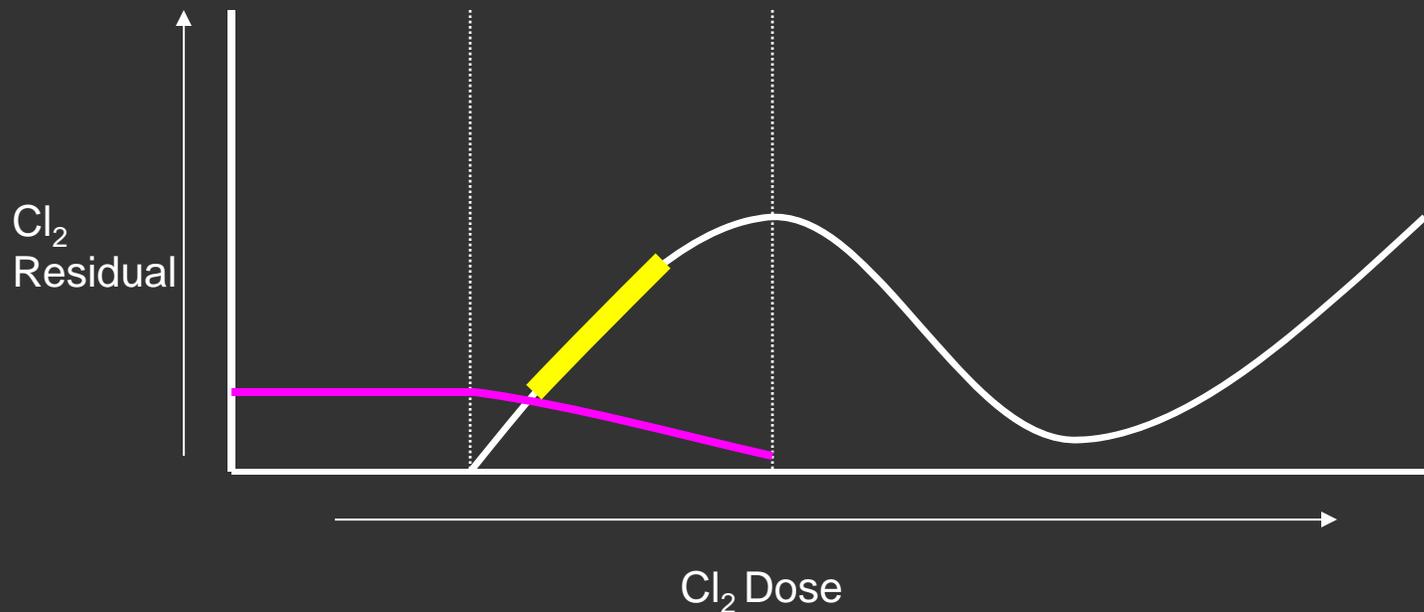
# Formation of Chloramine

- At normal pH of 7-8.5, the predominant form of chloramine formed on this portion of the curve (blue) is monochloramine.



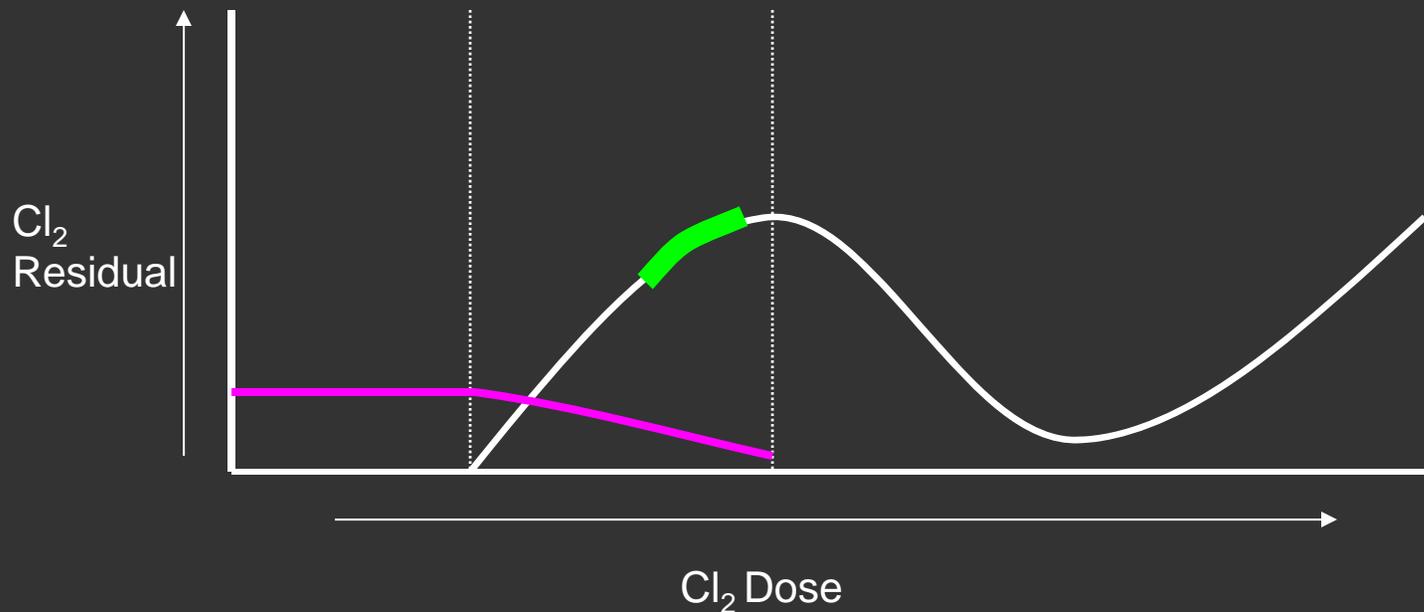
# Formation of Chloramine

- Operating at low chlorine to ammonia ratios (3:1 and below) leaves undesirably high levels of free ammonia in the system.



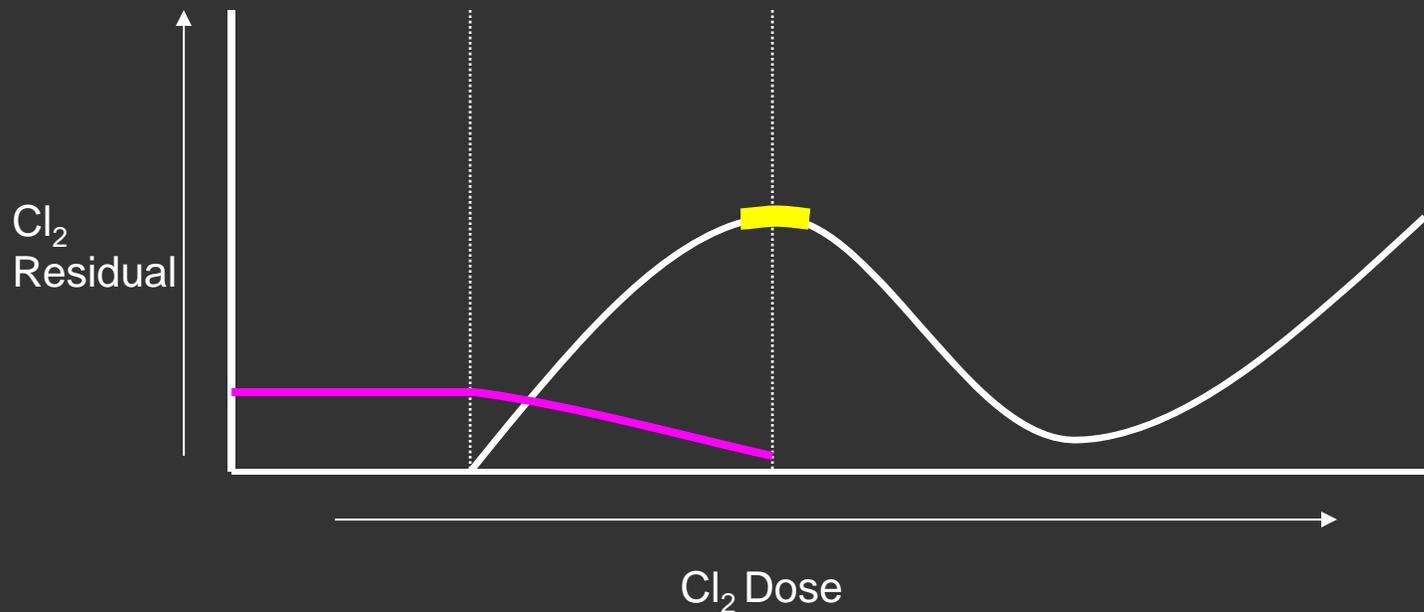
# Formation of Chloramine

- Operating at chlorine to ammonia ratios of about 4:1 results in a small amount of free ammonia in the system (0.05-0.1 mg/L) and a stable total chlorine residual.



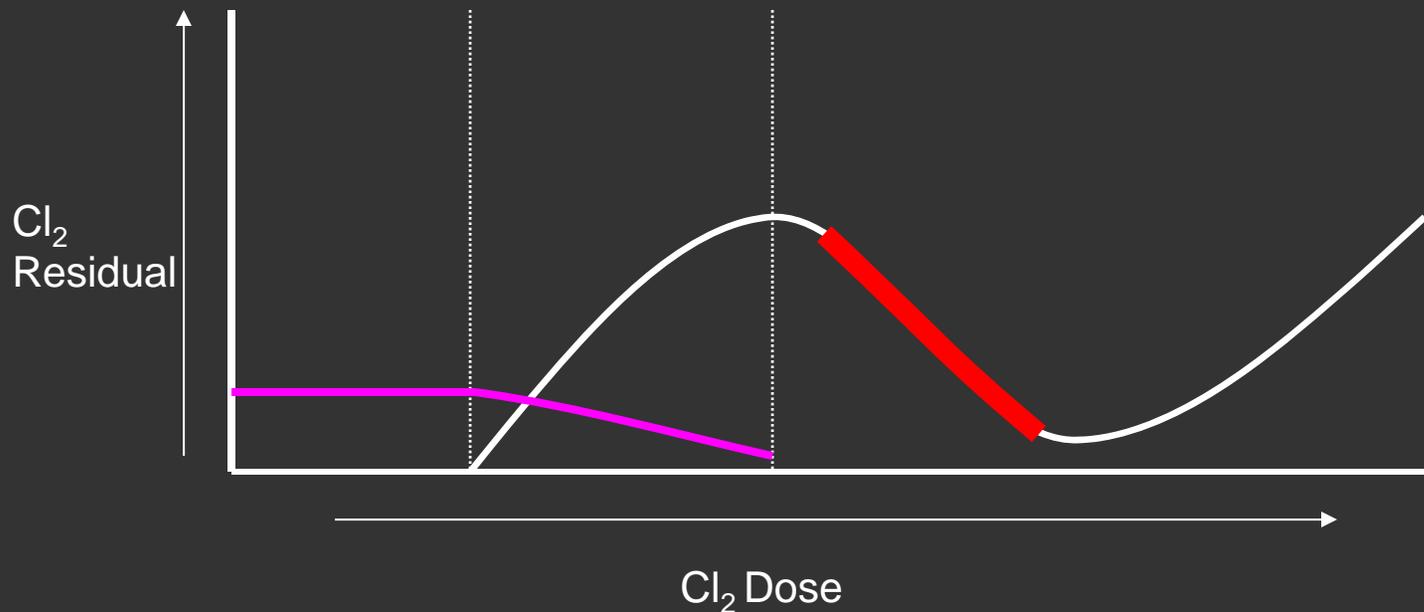
# Formation of Chloramine

- Operating here results in no free ammonia left to react with chlorine that is present.



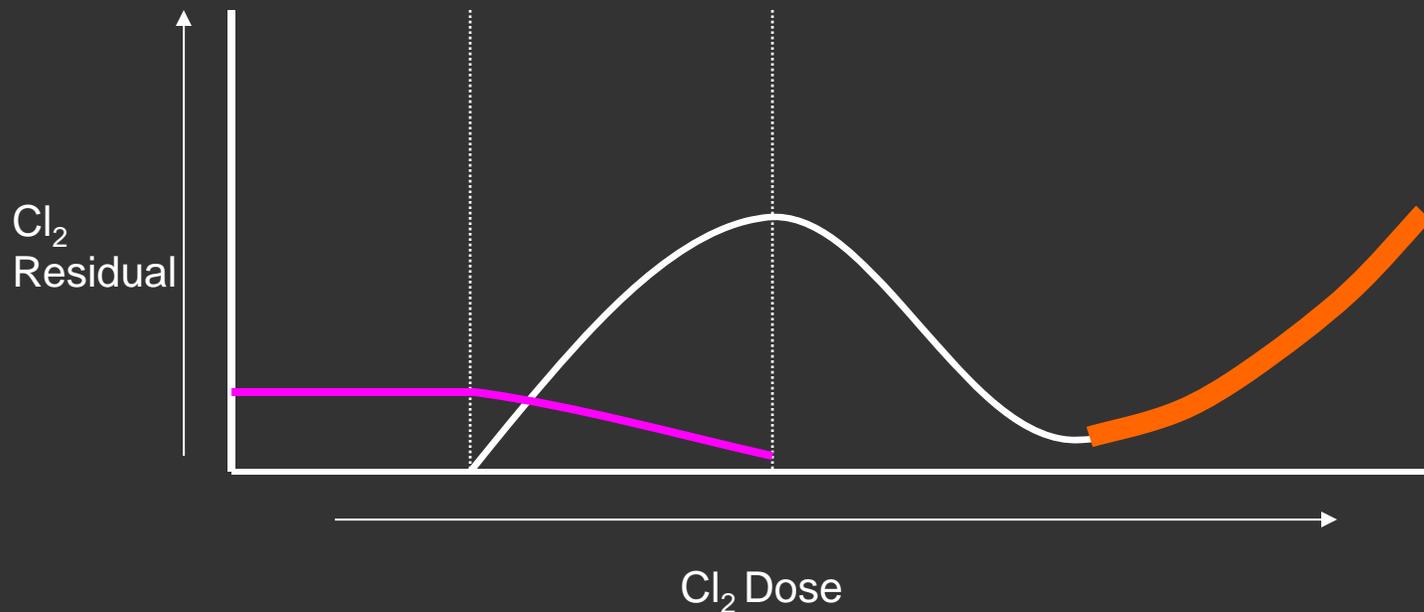
# Destruction of Chloramine

- Adding additional chlorine beyond a 4.2:1 ratio forces the total chlorine residual to fall into this area of the curve where monochloramine is being oxidized to dichloramine and total chlorine residual falls.



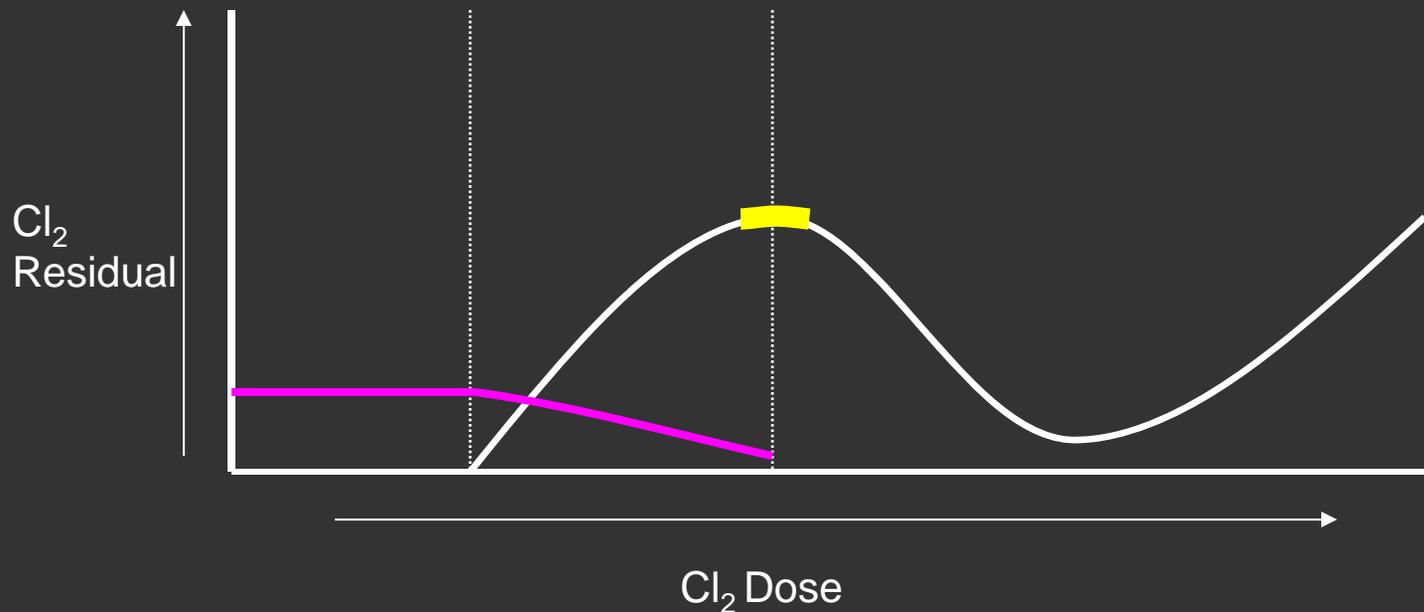
# Increasing Free Chlorine

- Adding additional chlorine beyond breakpoint results in increasing free chlorine residual.



# Formation of Chloramine

- Operating here minimizes the free ammonia but not much room for fluctuation in operating conditions. A little bit of free ammonia is more desirable than a chlorine-rich blend.



# Process Control Summary

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- To keep a stable total chlorine residual the  $\text{Cl}_2:\text{NH}_3$  ratio should be maintained at about 4:1 up to 4.5:1
- A small amount of ammonia in the finished water leaving the chloramination point is desirable in that it enables the operator to know where the chloramination process is operating
- Maintaining the total chlorine above 1.5 mg/L reduces the likelihood of nitrification episodes
- As distance from the chloramination point increases the level of total chlorine naturally drops and free ammonia levels naturally rise

# Process Control Summary (cont)

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- When  $\text{NH}_3$  is not a limiting factor and some excess free  $\text{NH}_3$  is available:
  - The total chlorine residual represents monochloramine.
  - Combined  $\text{NH}_3 = \sim 1/5^{\text{th}}$  of the total chlorine residual
  - Total  $\text{NH}_3 = \text{combined } \text{NH}_3 + \text{free } \text{NH}_3$
- When some free  $\text{NH}_3$  is present we can divide the measured total chlorine by the total  $\text{NH}_3$  to determine the  $\text{Cl}_2:\text{NH}_3$  ratio.
- When free  $\text{NH}_3$  is not present the only reliable means to determine the  $\text{Cl}_2:\text{NH}_3$  Ratio is applying  $\text{NH}_3$  to water with a free  $\text{Cl}_2$  residual

# Process Control Summary (cont)

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- Performance of the total chlorine residual after making a feed rate change is the best indicator of where on the curve the chloramination process is running. (\*)
- If chlorine feed is increased and total chlorine residual increases then there was excess  $\text{NH}_3$  in the system.
- If chlorine feed is increased and the total chlorine residual drops then there was insufficient  $\text{NH}_3$  in the system.

# Nitrification

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- What is it?
- Detection
- Prevention
- Correction

# Nitrification

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- In most cases conversion to chloramine has resolved the problem of elevated DBPs
- Problems of elevated DBPs have been replaced by problems related to nitrification
  - Localized low total chlorine residual
  - Bacteriological growth in the distribution system
  - Loss of alkalinity resulting in corrosive water problems (Lead and Copper concerns)

# Nitrification

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- Occurs as a result of ammonia oxidizing bacteria which utilize free ammonia as a food source
- Ammonia oxidizing bacteria produce nitrite which creates a chlorine demand and depletes chlorine
- Problem may become serious enough to jeopardize compliance with minimum disinfectant residual requirements and Total Coliform Rule

# Nitrification

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- Risks of nitrification increase with
  - Decreasing total chlorine residual (<1.5 mg/L)
  - Increasing free ammonia concentration
  - Distance from chloramine formation point
  - Increasing temperature
  - Decreasing pH (6.0-8.0 is optimum for growth of ammonia-oxidizing bacteria)
  - Age and tuberculation of pipe or tank

# Nitrification

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- Risks of nitrification decrease with
  - Increasing total chlorine residual (>2.0 mg/L)
  - Decreasing free ammonia concentration (less is better)
  - Proximity to chloramine formation point
  - Decreasing temperature
  - Increasing pH (over 8.8)
  - Increasing chlorite concentration (as low as 0.05 mg/L prevents growth of ammonia-oxidizing bacteria)

# Nitrification Detection

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- Nitrification problems are commonly detected when localized portions of the distribution system see falling total chlorine residuals where previously the residual was OK
- Other areas in the system may continue to see strong and lasting total chlorine residuals

# Nitrification Detection

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- If nitrification problems are suspected as a result of low chlorine readings follow-up sampling can be used to confirm suspicions
  - Free  $\text{NH}_3$ -Abnormally low ammonia readings in the distribution system serve to indicate utilization by AOB
  - pH-Alkalinity is consumed in nitrification reaction so depressed pH levels in areas where chlorine residuals are low help indicate nitrification
  - Nitrite-Is the partial endpoint of ammonia oxidation stage of nitrification; look for nitrite levels in excess of the AWWA proposed critical threshold level of 0.05 mg/L  $\text{NO}_2\text{-N}$  to confirm

# Nitrification Prevention

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- As chlorine degrades over time chloramines dissociate releasing ammonia
- Concentrations of free ammonia increase with increasing detention time in the distribution system
- Increasing temperature speeds up the decay process
- Excess free ammonia can promote nitrification in the distribution system if the total chlorine residual is not high enough to prevent growth of AOB
- Operating at higher pH (>8.8) reduces degree of chloramine decomposition and makes for less than optimum growth conditions for ammonia oxidizing bacteria

# Nitrification Prevention

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- Several ways to prevent nitrification while operating in chloramination mode
  - Maintain total chlorine residual above 1.5 mg/L in all parts of the system
  - Maintain  $\text{Cl}_2:\text{NH}_3$  ratio in the range of 4:1 to 4.5:1 to minimize free  $\text{NH}_3$  levels in the finished water
  - Maintaining pH in finished water at 8.8+

# Nitrification Prevention

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- Effect of chlorine dioxide use
  - Chlorite which is a byproduct of chlorine dioxide use inhibits growth of ammonia oxidizing bacteria at concentrations as low as 0.05 mg/L
  - MCL for chlorite is 1.0 mg/L
  - Common to see chlorite levels of 0.2-0.9 mg/L in distribution systems using chlorine dioxide

# Nitrification Correction

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- If nitrification is suspected the “fix” involves temporarily returning to free chlorine in affected parts of the distribution system to eliminate the nitrifying bacteria
- Maintaining monochloramine residuals in excess of 1.5 mg/L serves as effective means of preventing nitrification but once nitrification is established monochloramine is not effective at correcting the problem
- If feasible may try to treat only the problem area rather than the entire system

# Nitrification Correction

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- If the entire distribution system is to be converted to free chlorine then the free chlorine maintenance period must last long enough to ensure the free chlorine residual makes it throughout the system
- Commonly lasts from 2-4 weeks but should be system specific
- Unidirectional flushing helps to draw the free chlorine residual through the system

# Nitrification Correction

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- Prior to making the switch the producer should notify the system users of the upcoming change
- Presently not required but will be at some point in the future when the draft 30 TAC 290 is accepted
- It is not required that notification be made to TCEQ but is a good idea to let the Regional office know
- May need to reschedule quarterly DBP samples to avoid sampling during free chlorine use

# Nitrification Correction

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- From the proposed 30 TAC 290.122...

“A public water system that wholesales chloraminated water to other public water systems must notify the commission and each of its wholesale customers at least 14 days before converting back to free chlorine. This notice must be issued in writing and include the date that the wholesaler will begin distributing water that contains free chlorine and the date the wholesaler will revert back to free chlorine.”

# Suggested Language

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"On *(date)* *(System Name)* will be temporarily changing back to free chlorine as the disinfectant in the *(system name)*'s treated drinking water. This temporary return to free chlorine is being made according to standard water treatment practices to help with water delivery system maintenance. The *(system name)* plans to begin distributing water with free chlorine residual on *(date)*. The planned free chlorine maintenance period will last for *(insert #)* days. On *(date)* the *(system name)* will revert back to the chloramine disinfection which is the normal method used by the *(system name)* for water system disinfection. If you have questions about this planned water system maintenance event please call *(insert name)* with the *(system name)* at *(telephone number)*."

# Nitrification Correction

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- System may need to restart chlorine booster stations
- Will begin monitoring again for free chlorine residual
- Possible taste, odor, and color problems may arise

## Practice Problem 2 (cont)

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- You would like to boost the total  $\text{Cl}_2$  residual from to 2.3 mg/L to 3.0 mg/L which represents a 0.7 mg/L boost.
  - Can you do that without adding more  $\text{NH}_3$ ?
    - No... $0.05 \text{ mg/L free ammonia} \times 5 = 0.25 \text{ mg/L Cl}_2$
    - You can increase the  $\text{Cl}_2$  dosage by only 0.25 mg/L which only gives you about 2.5 mg/L total  $\text{Cl}_2$  and you will no longer have any free  $\text{NH}_3$  to cushion your process
  - What do you do?

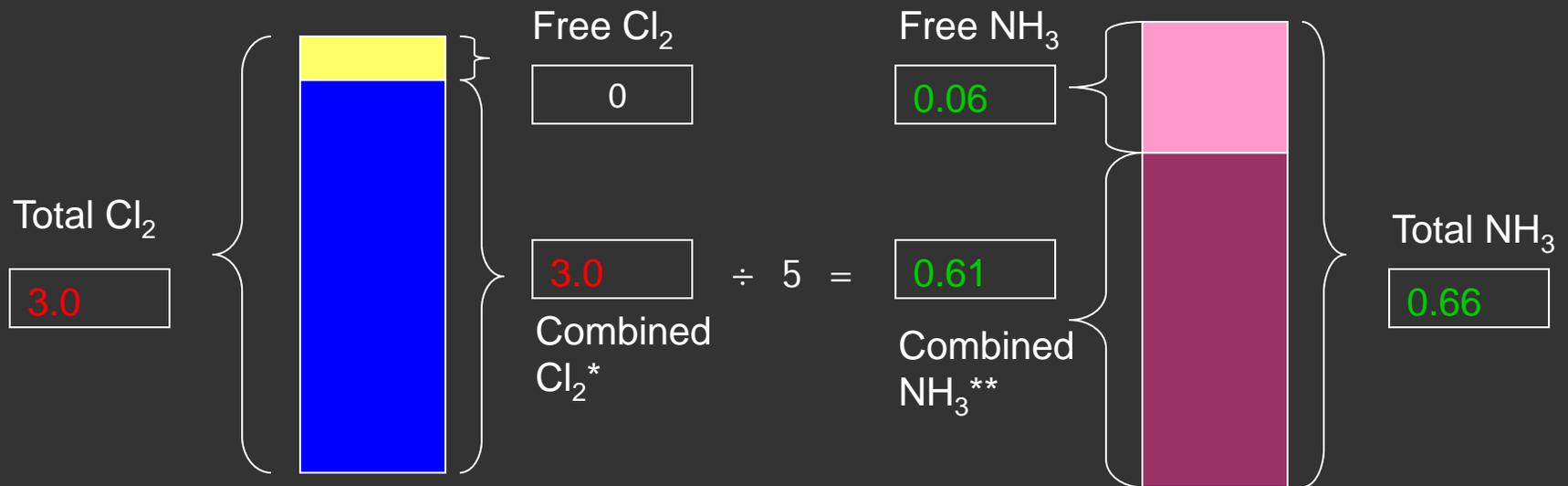
## Practice Problem 2 (cont)

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- You must first raise the  $\text{NH}_3$  dose by 0.15 mg/L. After raising the  $\text{NH}_3$  dose the  $\text{Cl}_2$  dose is then raised by 0.7 mg/L.
  - What will you expect the finished water total  $\text{Cl}_2$  residual to do?
    - Would expect to see it increase to 3.0 mg/L
  - What will you expect the finished water  $\text{NH}_3$  to do?
    - New total  $\text{Cl}_2$  of 3.0 mg/L  $\div$  5 = 0.60 mg/L combined  $\text{NH}_3$
    - Had 0.51 mg/L total  $\text{NH}_3$  so if we increase  $\text{NH}_3$  feed by 0.15 mg/L would expect a new total  $\text{NH}_3$  of 0.66 mg/L
    - Total  $\text{NH}_3$  of 0.66 mg/L - combined of 0.60 mg/L = 0.06 mg/L free  $\text{NH}_3$

# Determining Cl<sub>2</sub>: NH<sub>3</sub> Ratio

$$\text{Cl}_2: \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{3.0}{0.66} = 4.5$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

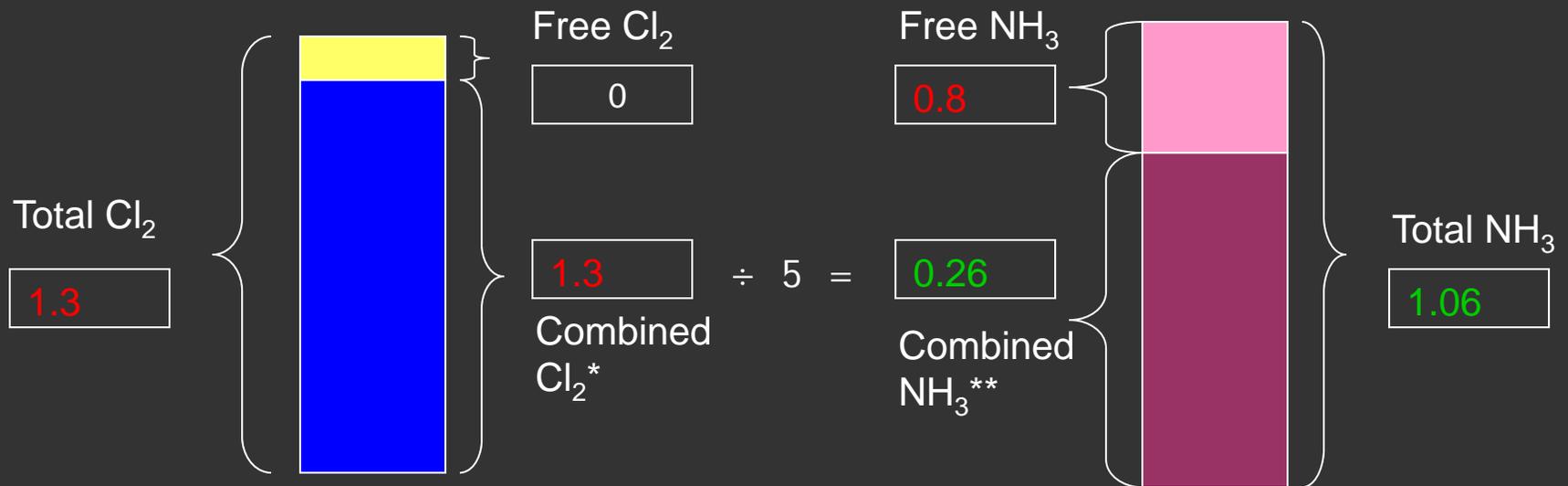
# Practice Problem 3

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- Purchased water entering your system arrives with 1.30 mg/L total  $\text{Cl}_2$  and 0.80 mg/L free  $\text{NH}_3$ . You'd like to raise your total chlorine residual and lower your free  $\text{NH}_3$ 
  - What is the  $\text{Cl}_2:\text{NH}_3$  ratio in the water reaching your system?
    - $1.30 \text{ mg/L } \text{Cl}_2 \div 5 = 0.26 \text{ mg/L combined } \text{NH}_3$
    - $0.26 \text{ mg/L combined } \text{NH}_3 + 0.80 \text{ mg/L free } \text{NH}_3 = 1.06 \text{ mg/L total } \text{NH}_3$
    - $1.30 \text{ mg/L } \text{Cl}_2 \div 1.06 \text{ mg/L total } \text{NH}_3 = 1.2:1$

# Determining Cl<sub>2</sub>: NH<sub>3</sub> Ratio

$$\text{Cl}_2: \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{1.3}{1.06} = 1.2$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

## Practice Problem 3 (cont)

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- You would like to increase the total chlorine residual to 4.0 mg/L at your chlorination point
  - Can you do that without adding more  $\text{NH}_3$ ?
    - Yes... $0.8 \text{ mg/L free } \text{NH}_3 \times 5 = 4.0 \text{ mg/L } \text{Cl}_2$
    - You can add up to 4.0 mg/L chlorine before you reach a 5:1 ratio...we only want to raise the residual by 2.7 mg/L  $\text{Cl}_2$

## Practice Problem 3 (cont)

- You adjust the chlorine dosage to feed 2.7 mg/L  $\text{Cl}_2$  to the water at your chlorination point where the water already has a 1.3 mg/L total  $\text{Cl}_2$  residual and a free  $\text{NH}_3$  residual of 0.8 mg/L (before your applied  $\text{Cl}_2$ )
  - What would you expect the total  $\text{Cl}_2$  residual to do?
    - Would expect the total  $\text{Cl}_2$  residual to increase 2.7 mg/L to 4.0 mg/L
  - What would you expect the free  $\text{NH}_3$  residual to do?
    - Would expect the free  $\text{NH}_3$  residual to drop from 0.8 mg/L to 0.26 mg/L  
(2.7 mg/L  $\text{Cl}_2$  increase  $\div 5 = 0.54$  mg/L free  $\text{NH}_3$  to combined  $\text{NH}_3$ )

## Practice Problem 3 (cont)

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- If residuals respond as expected what will the new  $\text{Cl}_2:\text{NH}_3$  ratio be in water downstream from your chlorination point?
  - $4.0 \text{ mg/l Cl}_2 \div 5 = 0.8 \text{ mg/L combined NH}_3$
  - $0.8 \text{ mg/L combined NH}_3 + 0.26 \text{ mg/L free NH}_3 = 1.06 \text{ mg/L total NH}_3$  (Note that this did not change)
  - $4.0 \text{ mg/L total Cl}_2 \div 1.06 \text{ mg/L total NH}_3 = 3.8:1$

# Practice Problem 4

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- Purchased water entering your system arrives at a GST with 1.30 mg/L total  $\text{Cl}_2$  and 0.80 mg/L free  $\text{NH}_3$  at a rate of 2.0 mgd.
- Chlorinated groundwater with a free chlorine residual of 1.0 mg/L is blended at the GST at a rate of 0.5 mgd.
  - Is there sufficient  $\text{NH}_3$  present in the purchased water to chloramine the groundwater flow as well?
    - Will have to determine overall pounds of available chlorine to overall pounds of available ammonia

## Practice Problem 4 (cont)

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- Let's start with total pounds of available chlorine...
  - lbs Cl<sub>2</sub> in PW = 1.30 mg/l Cl<sub>2</sub> x 2.0 mgd x 8.34 = 21.7 lbs Cl<sub>2</sub>
  - lbs Cl<sub>2</sub> in GW = 1.00 mg/l Cl<sub>2</sub> x 0.5 mgd x 8.34 = 4.2 lbs Cl<sub>2</sub>
  - Total lbs Cl<sub>2</sub> in Blended Water = 21.7 lbs + 4.2 lbs = 25.9 lbs Cl<sub>2</sub>
- There are 25.9 lbs Cl<sub>2</sub> available for chloramination of the blended water

# Practice Problem 4 (cont)

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- Now let's look at lbs of  $\text{NH}_3$ ...
  - Combined  $\text{NH}_3$  in PW =  $1.3 \text{ mg/l Cl}_2 \div 5 = 0.26 \text{ mg/L Combined NH}_3$
  - Total  $\text{NH}_3$  in PW =  $0.26 \text{ mg/L combined NH}_3 + 0.8 \text{ mg/L free NH}_3 = 1.06 \text{ Total NH}_3$
  - lbs  $\text{NH}_3$  in PW =  $1.06 \text{ mg/l Cl}_2 \times 2.0 \text{ mgd} \times 8.34 = 17.7 \text{ lbs NH}_3$
- There are 17.7 lbs of total  $\text{NH}_3$  available for chloramination of the blended water

# Practice Problem 4 (cont)

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- Now let's compare...
  - $25.9 \text{ lbs available Cl}_2 \div 17.7 \text{ lbs of available NH}_3 = 1.46 \text{ Cl}_2:\text{NH}_3 \text{ ratio}$
  - Yes there is enough  $\text{NH}_3$  present but what can we expect for blended water residuals?

## Practice Problem 4 (cont)

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- Blended water flow in mgd =  $2.0 \text{ mgd} + 0.5 \text{ mgd} = 2.5 \text{ mgd}$
- Blended water  $\text{Cl}_2$  in mg/L =  $25.9 \text{ lbs available } \text{Cl}_2 \div (2.5 \text{ mgd} \times 8.34) = 1.2 \text{ mg/L}$
- Blended water total  $\text{NH}_3$  in mg/L =  $17.7 \text{ lbs available } \text{NH}_3 \div (2.5 \text{ mgd} \times 8.34) = 0.8 \text{ mg/L}$
- Blended water combined  $\text{NH}_3$  in mg/L =  $1.2 \text{ mg/L} \div 5 \text{ mgd} = 0.2 \text{ mg/L}$
- Blended water free  $\text{NH}_3$  in mg/L =  $0.8 \text{ mg/L total } \text{NH}_3 - 0.2 \text{ mg/L free } \text{NH}_3 = 0.6 \text{ mg/L free } \text{NH}_3$

## Practice Problem 4 (cont)

---

- Given that we project blended water total  $\text{Cl}_2$  residual to be 1.2 mg/L and blended water free  $\text{NH}_3$  to be 0.6 mg/L free  $\text{NH}_3$  can we safely boost our existing chlorine residual to a target of 3.0 mg/L without adding more  $\text{NH}_3$ ?
  - $0.6 \text{ mg/L free } \text{NH}_3 \times 5 = 3.0 \text{ mg/L total } \text{Cl}_2 \text{ boost}$
  - It is anticipated that there will be sufficient free  $\text{NH}_3$  available to raise the total chlorine residual by 3.0 mg/L so raising the total chlorine by 1.8 mg/L without adding more  $\text{NH}_3$  is possible
  - But...

## Practice Problem 4 (cont)

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- In order to make this work the purchased water source has to remain in service and active. If it is anticipated that the purchased water source will only be used intermittently then without providing an alternate ammonia source the system will shift between a chloramine and free chlorine system which is not desirable.

# Practice Problem 5

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- Raw water flow rate to the plant is 2.5 mgd
- The chlorinator is set to feed 185 lbs/day
- Measured free chlorine residual at the  $\text{NH}_3$  application point is 4.3 mg/L
  - How much chlorine is being destroyed initially by reducing compounds in the water being treated?

## Practice Problem 5 (cont)

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- Let's first look at chlorine dose...
  - $185 \text{ lbs/day Cl}_2 \text{ feed} \div (2.5 \text{ mgd} \times 8.34) = 8.9 \text{ mg/L Cl}_2 \text{ dosed}$
- Now look at measured  $\text{Cl}_2$  residual in comparison to  $\text{Cl}_2$  dose...
  - $8.9 \text{ mg/L Cl}_2 \text{ dosed} - 4.3 \text{ mg/L Cl}_2 \text{ measured} = 4.6 \text{ mg/L Cl}_2 \text{ destroyed}$

## Practice Problem 5 (cont)

---

- With a target  $\text{Cl}_2:\text{NH}_3$  ratio of 4.2:1 how much  $\text{NH}_3$  should be dosed?
  - $4.3 \text{ mg/L measured Cl}_2 \div 4.2 \text{ Cl}_2:\text{NH}_3 \text{ ratio} = 1.0 \text{ mg/L NH}_3 \text{ dose}$
- How much free  $\text{NH}_3$  can we expect to see in the finished water?

## Practice Problem 5 (cont)

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- To answer that we'll first determine combined  $\text{NH}_3$ ...
  - $4.3 \text{ mg/L measured Cl}_2 \div 5 = 0.86 \text{ mg/L combined NH}_3$
  - $1.0 \text{ mg/L NH}_3 \text{ dose} - 0.86 \text{ mg/L combined NH}_3 = 0.14 \text{ mg/L free NH}_3$

## Practice Problem 5 (cont)

---

- Assuming we are still dosing  $\text{Cl}_2$  at 8.9 mg/L what would you expect to see happen if demand in the raw water changed from 4.6 mg/L of the  $\text{Cl}_2$  dose being destroyed to 5.6 mg/L of the  $\text{Cl}_2$  dose destroyed?
  - $8.9 \text{ mg/L } \text{Cl}_2 \text{ dosed} - 5.6 \text{ mg/L } \text{Cl}_2 \text{ destroyed} = 3.3 \text{ mg/L } \text{Cl}_2 \text{ destroyed}$

## Practice Problem 5 (cont)

---

- Assuming we are still dosing  $\text{NH}_3$  at 1.0 mg/L what would you expect to see happen to the finished water free  $\text{NH}_3$  residual?
  - $3.3 \text{ mg/L Cl}_2 \div 5 = 0.67 \text{ mg/L combined NH}_3$
  - $1.0 \text{ mg/L NH}_3 \text{ dose} - 0.67 \text{ mg/L combined NH}_3 = 0.33 \text{ mg/L free NH}_3$

# Free Cl<sub>2</sub> Exposure

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- Limited use of free Cl<sub>2</sub> to disinfect surface water during the water treatment process may be possible depending on the DBP formation tendencies of the water (slower forming DBPs). If use of free Cl<sub>2</sub> is possible then the Cl<sub>2</sub>:NH<sub>3</sub> ratio can be determined by comparing the measured free Cl<sub>2</sub> residual to the NH<sub>3</sub> dose.
- Due to the presence of naturally occurring bromide in Texas it is common to see DBPs exceed MCLs when exposed to any free Cl<sub>2</sub>. In such a case NH<sub>3</sub> must be added upstream from Cl<sub>2</sub> and setting NH<sub>3</sub> dosage based on free Cl<sub>2</sub> is not possible.

# Cl<sub>2</sub>:NH<sub>3</sub> Ratio

---

- Two ways to determine Cl<sub>2</sub>:NH<sub>3</sub>
- Method used is dependent on the NH<sub>3</sub> application point in reference to the Cl<sub>2</sub> application point
- It is possible to use both methods in systems that apply Cl<sub>2</sub> upstream from NH<sub>3</sub> and sustain a free chlorine zone
- Only one method available to systems applying NH<sub>3</sub> upstream from the Cl<sub>2</sub> application point

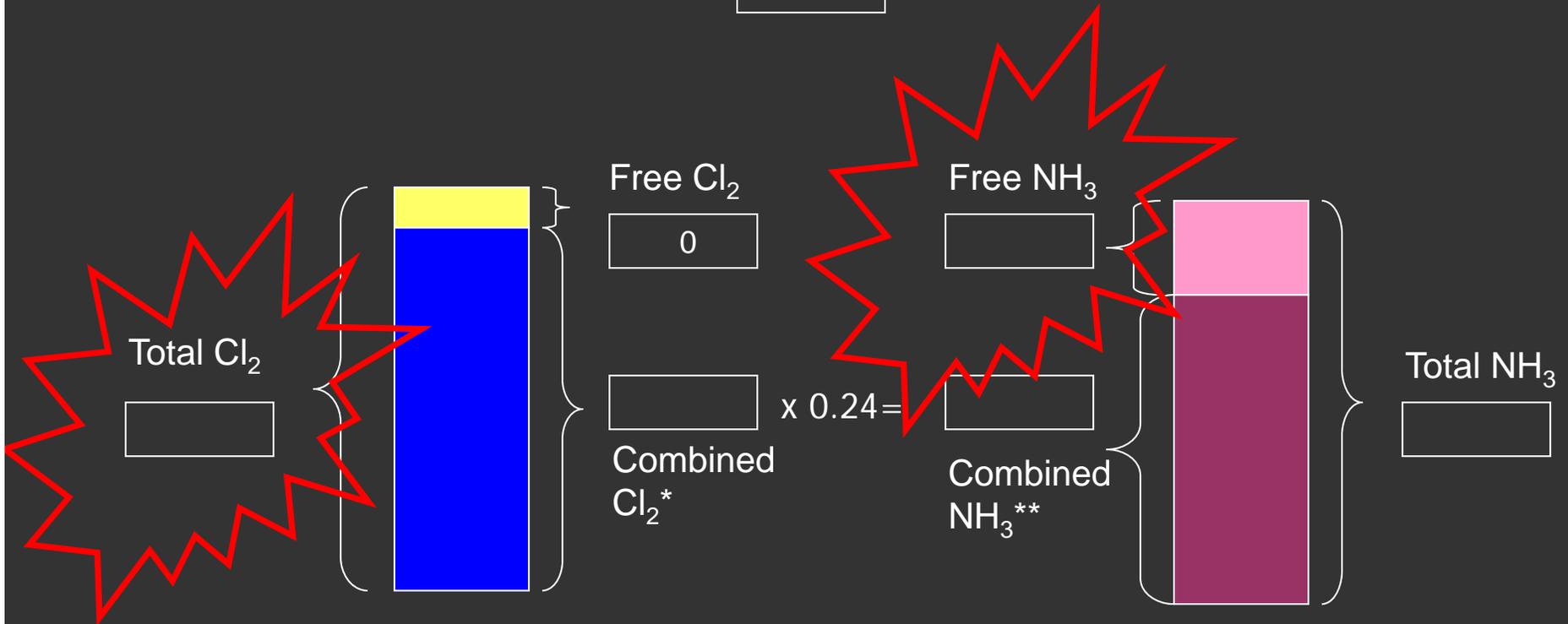
# Determining Ratios

---

- For systems that apply  $\text{NH}_3$  upstream from the  $\text{Cl}_2$  application point measurable total  $\text{Cl}_2$  and measurable free  $\text{NH}_3$  must be present to accurately determine the  $\text{Cl}_2:\text{NH}_3$  ratio

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{\boxed{\phantom{0000}}}{\boxed{\phantom{0000}}} = \boxed{\phantom{0000}}$$



*\*Note: With Free NH<sub>3</sub> greater than 0  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

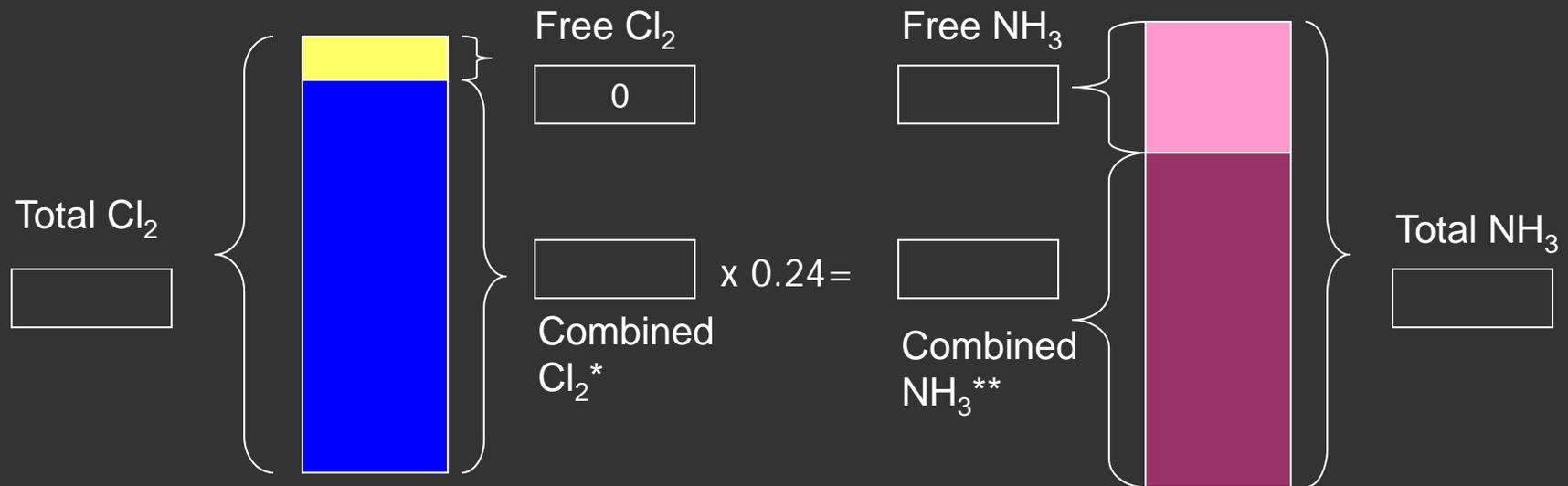
# Determining $\text{Cl}_2:\text{NH}_3$ Ratio

---

- In all cases when some excess free ammonia is present in chloraminated water...
  - Total chlorine residual represents combined chlorine
  - Combined ammonia equals 24% of the total chlorine residual
  - Total chlorine divided by total ammonia equals the  $\text{Cl}_2:\text{NH}_3$  ratio for this water

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{\boxed{\phantom{0000}}}{\boxed{\phantom{0000}}} = \boxed{\phantom{0000}}$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

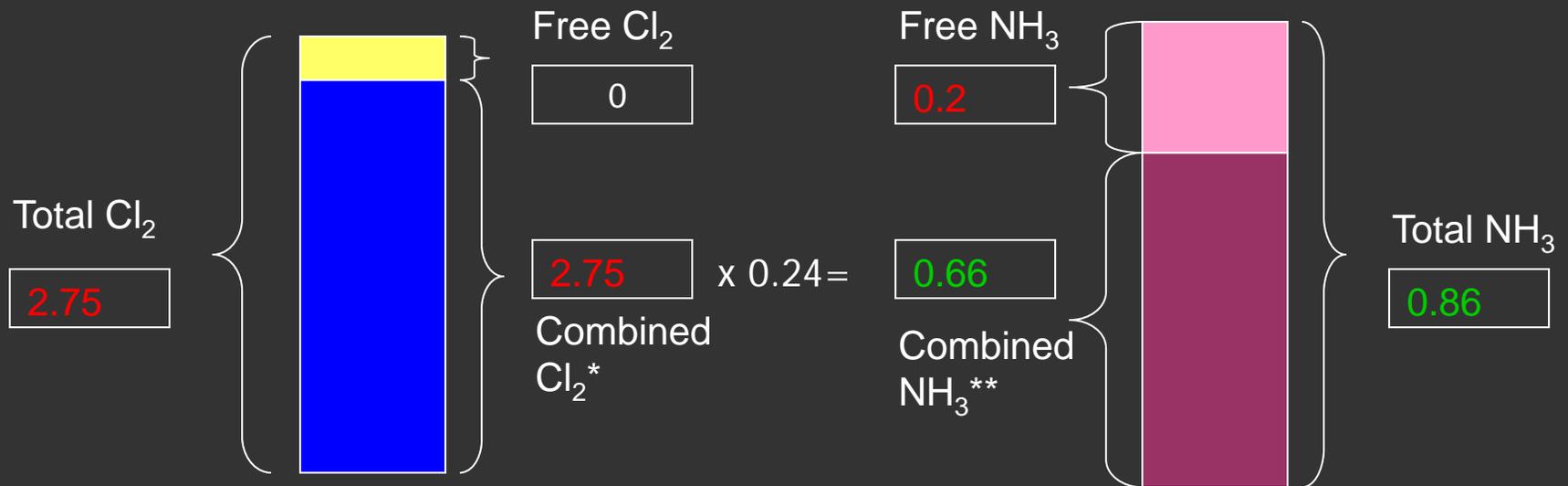
# Example 1

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- The finished water sample shows a total chlorine residual of 2.75 mg/L and a free ammonia concentration of 0.2 mg/L
  - With free ammonia present we know total chlorine represents monochloramine and that combined ammonia equals 1/5<sup>th</sup> of the total chlorine residual so...
    - $2.75 \text{ mg/L Cl}_2 \times 0.24 = 0.66 \text{ mg/L combined NH}_3$
    - $0.2 \text{ mg/L free NH}_3 + 0.66 \text{ combined NH}_3 = 0.86 \text{ total NH}_3$
    - $2.75 \text{ mg/L Cl}_2 \div 0.86 \text{ total NH}_3 = 3.2:1 \text{ Cl}_2:\text{NH}_3 \text{ Ratio}$

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{2.75}{0.86} = 3.2$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

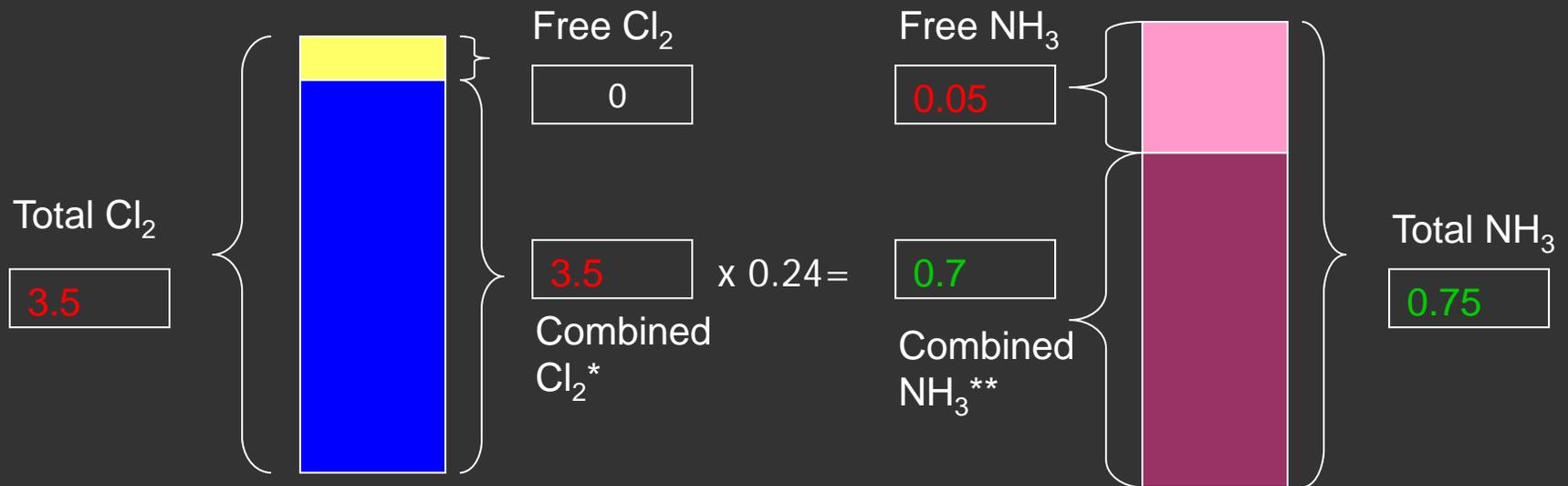
## Example 2

---

- The finished water sample shows a total chlorine residual of 3.50 mg/L and a free ammonia concentration of 0.05 mg/L
  - With free ammonia present we know total chlorine represents monochloramine and that combined ammonia equals 24% of the total chlorine residual so...
    - $3.50 \text{ mg/L Cl}_2 \times 0.24 = 0.84 \text{ mg/L combined NH}_3$
    - $0.05 \text{ mg/L free NH}_3 + 0.84 \text{ combined NH}_3 = 0.89 \text{ total NH}_3$
    - $3.50 \text{ mg/L Cl}_2 \div 0.89 \text{ total NH}_3 = 3.9:1 \text{ Cl}_2:\text{NH}_3 \text{ Ratio}$

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{3.5}{0.75} = 4.7$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

# Excess Chlorine

---

- When excess  $\text{Cl}_2$  is applied in the chloramination process (above a 4.2:1 ratio) excess chlorine destroys monochloramine at a 1:1 ratio
- Each part of  $\text{Cl}_2$  added above the 4.2:1 ratio will destroy a part of monochloramine (1 mg/L  $\text{Cl}_2$  will destroy 1 mg/L  $\text{NH}_2\text{Cl}$ )

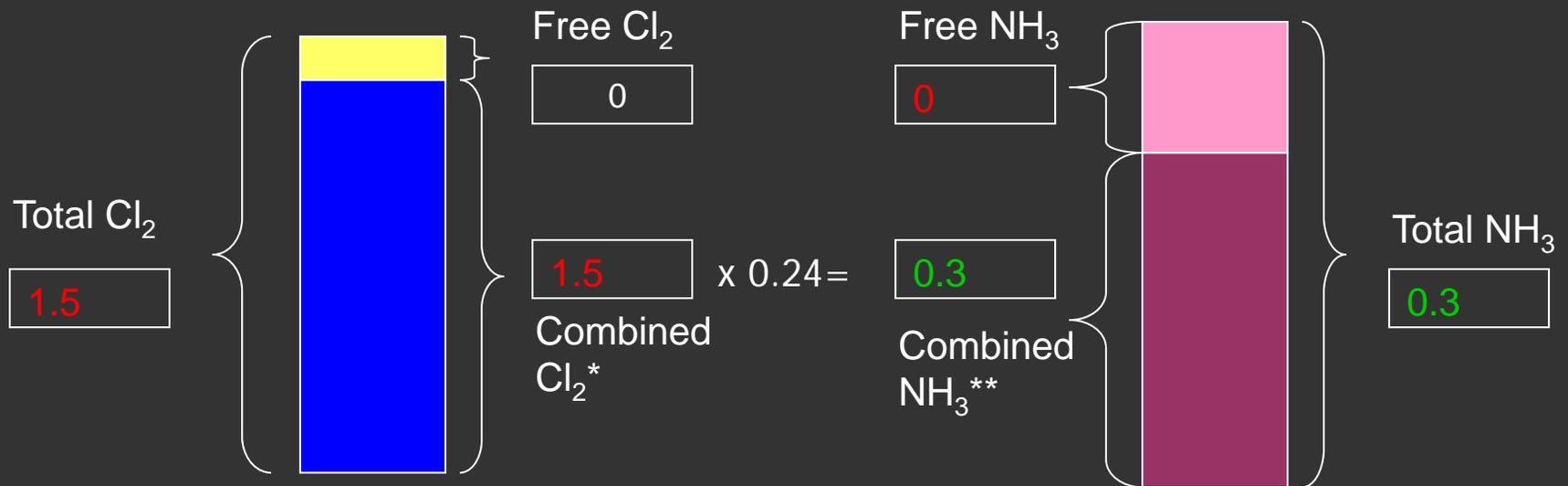
## Example 3

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- The finished water sample shows a total chlorine residual of 1.50 mg/L and a free ammonia concentration of 0 mg/L with ammonia feed rate set at 0.75 mg/L
  - With  $\text{NH}_3$  feed set at 0.75 mg/L we have sufficient  $\text{NH}_3$  present to give a total  $\text{Cl}_2$  residual of 3.75 mg/L ( $0.75 \times 5 = 3.75$ ).
  - We see only a 1.5 mg/L total  $\text{Cl}_2$  residual which amounts to 0.3 mg/L total  $\text{NH}_3$

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{\boxed{1.5}}{\boxed{?}} = \boxed{?}$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

## Example 3-continued

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- We subtract combined  $\text{NH}_3$  from applied  $\text{NH}_3$  to give an indication of the excess  $\text{Cl}_2$  feed ( $0.75 \text{ applied } \text{NH}_3 - 0.3 \text{ combined } \text{NH}_3 = 0.45 \text{ } \text{NH}_3 \text{ lost}$ ).
- We now know we're losing  $0.45 \text{ mg/L}$  of the applied  $\text{NH}_3$
- $0.45 \text{ mg/L}$  applied  $\text{NH}_3$  represented  $2.25 \text{ mg/L}$  of lost  $\text{NH}_2\text{Cl}$
- Since excess  $\text{Cl}_2$  destroys  $\text{NH}_2\text{Cl}$  at a 1:1 rate we know now that we're overfeeding about  $2.25 \text{ mg/L } \text{Cl}_2$

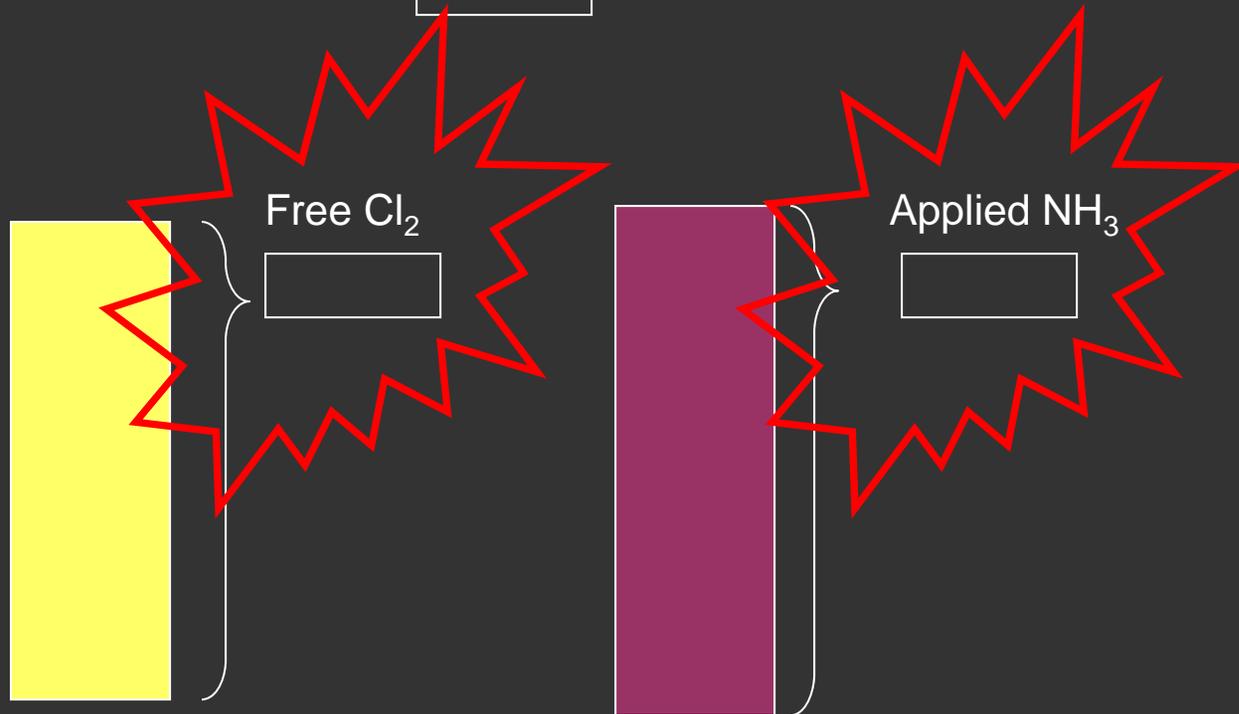
# Determining Ratios

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- If the treatment process sees a period of free chlorine exposure followed by ammonia application then it is possible to determine the chlorine to ammonia ratio without free  $\text{NH}_3$  present
- Requires knowing free chlorine residual at the ammonia application point and ammonia dose

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Free Cl}_2}{\text{Applied NH}_3} = \frac{\boxed{\phantom{0000}}}{\boxed{\phantom{0000}}} = \boxed{\phantom{0000}}$$



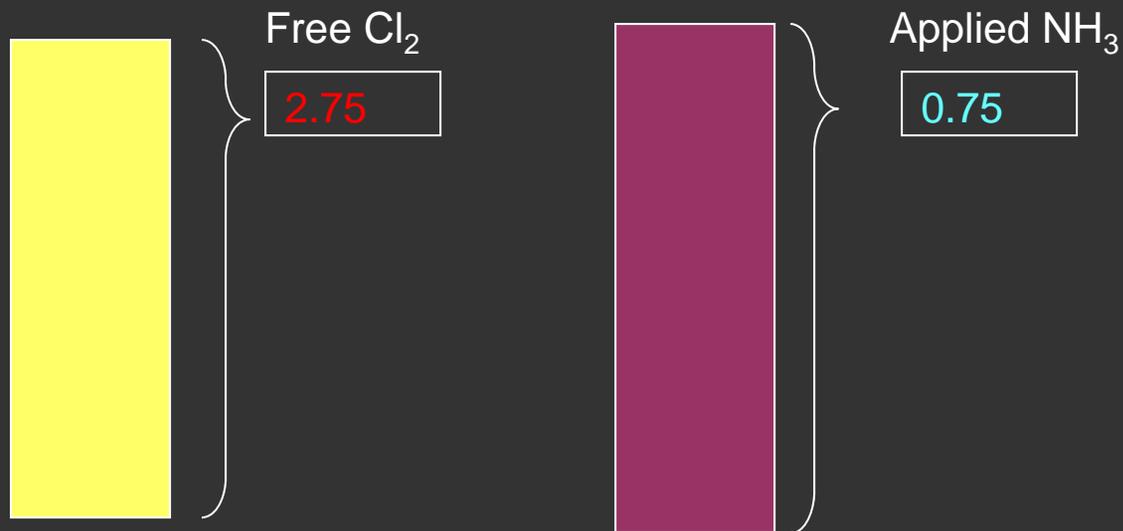
# Example 4

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- Water just upstream from the  $\text{NH}_3$  application point has a free  $\text{Cl}_2$  residual of 2.75 mg/L and 0.75 mg/L  $\text{NH}_3$  - nitrogen is added at the  $\text{NH}_3$  application point
  - To determine  $\text{Cl}_2:\text{NH}_3$  Ratio free  $\text{Cl}_2$  is divided by applied  $\text{NH}_3$ 
    - $2.75 \text{ mg/L } \text{Cl}_2 \div 0.75 \text{ applied } \text{NH}_3 = 3.7:1 \text{ } \text{Cl}_2:\text{NH}_3 \text{ Ratio}$
    - The 2.75 mg/L  $\text{Cl}_2$  will combine with 0.55 mg/L  $\text{NH}_3$  ( $2.75 \div 5$ )
    - $0.75 \text{ applied } \text{NH}_3 - 0.55 \text{ mg/L combined } \text{NH}_3 = 0.20 \text{ mg/L free } \text{NH}_3$

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2:\text{NH}_3 \text{ Ratio} = \frac{\text{Free Cl}_2}{\text{Applied NH}_3} = \frac{\boxed{2.75}}{\boxed{0.75}} = \boxed{3.7}$$



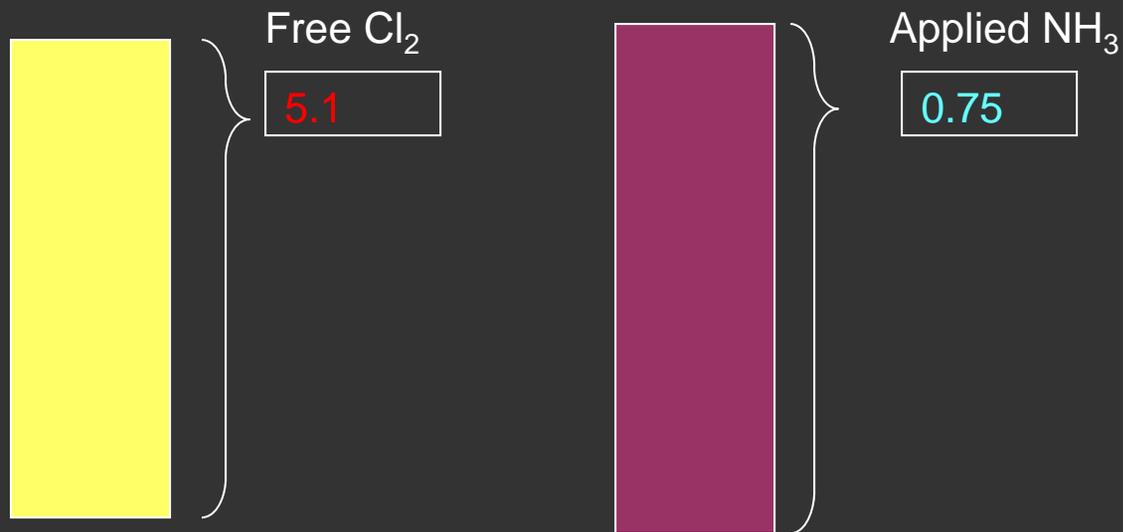
# Example 6

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- Water just upstream from the  $\text{NH}_3$  application point has a free  $\text{Cl}_2$  residual of 5.10 mg/L and 0.75 mg/L  $\text{NH}_3$  - nitrogen is added at the  $\text{NH}_3$  application point
  - To determine  $\text{Cl}_2:\text{NH}_3$  Ratio free  $\text{Cl}_2$  is divided by applied  $\text{NH}_3$ 
    - $5.10 \text{ mg/L } \text{Cl}_2 \div 0.75 \text{ applied } \text{NH}_3 = 6.7:1 \text{ } \text{Cl}_2:\text{NH}_3 \text{ Ratio}$
    - The 5.10 mg/L  $\text{Cl}_2$  will combine with 1.02 mg/L  $\text{NH}_3$  ( $5.10 \div 5$ ) but only 0.75 mg/L  $\text{NH}_3$  was applied
    - 0.75 mg/L applied  $\text{NH}_3$  is consumed by the  $\text{Cl}_2$  residual and the excess free chlorine residual then begins to oxidize monochloramine and the total chlorine residual drops...headed towards breakpoint

# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2:\text{NH}_3 \text{ Ratio} = \frac{\text{Free Cl}_2}{\text{Applied NH}_3} = \frac{5.1}{0.75} = 6.7$$



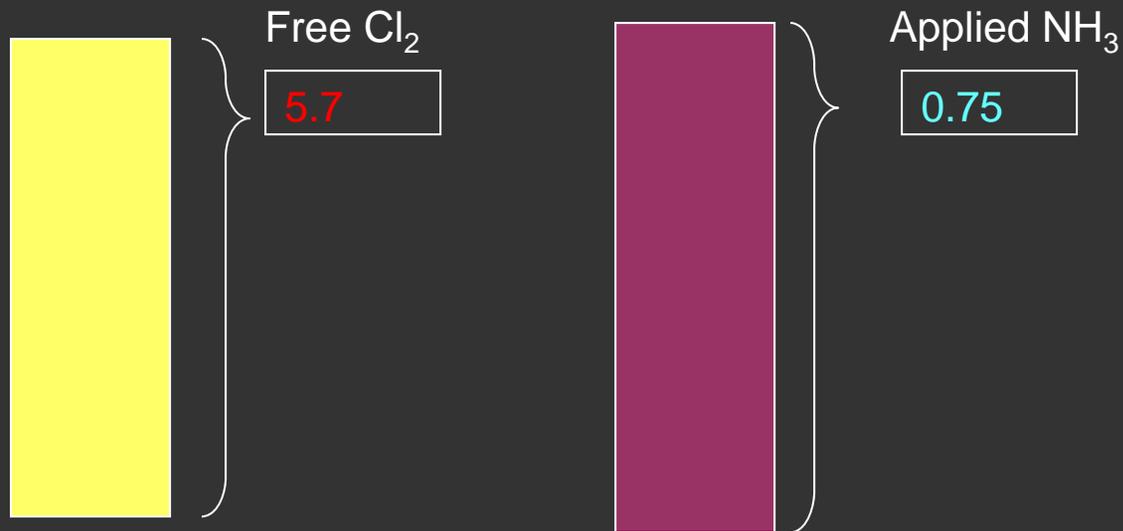
# Example 7

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- Water just upstream from the  $\text{NH}_3$  application point has a free  $\text{Cl}_2$  residual of 5.70 mg/L and 0.75 mg/L  $\text{NH}_3$  -nitrogen is added at the  $\text{NH}_3$  application point
  - To determine  $\text{Cl}_2:\text{NH}_3$  Ratio free  $\text{Cl}_2$  is divided by applied  $\text{NH}_3$ 
    - $5.70 \text{ mg/L } \text{Cl}_2 \div 0.75 \text{ applied } \text{NH}_3 = 7.6:1 \text{ } \text{Cl}_2:\text{NH}_3 \text{ Ratio}$
    - The 5.70 mg/L  $\text{Cl}_2$  will combine with 1.14 mg/L  $\text{NH}_3$  ( $5.70 \div 5$ ) but only 0.75 mg/L  $\text{NH}_3$  was applied
    - 0.75 applied  $\text{NH}_3$  is consumed by the  $\text{Cl}_2$  residual and the excess free chlorine residual then begins to oxidize monochloramine and the total chlorine residual drops to near 0...breakpoint

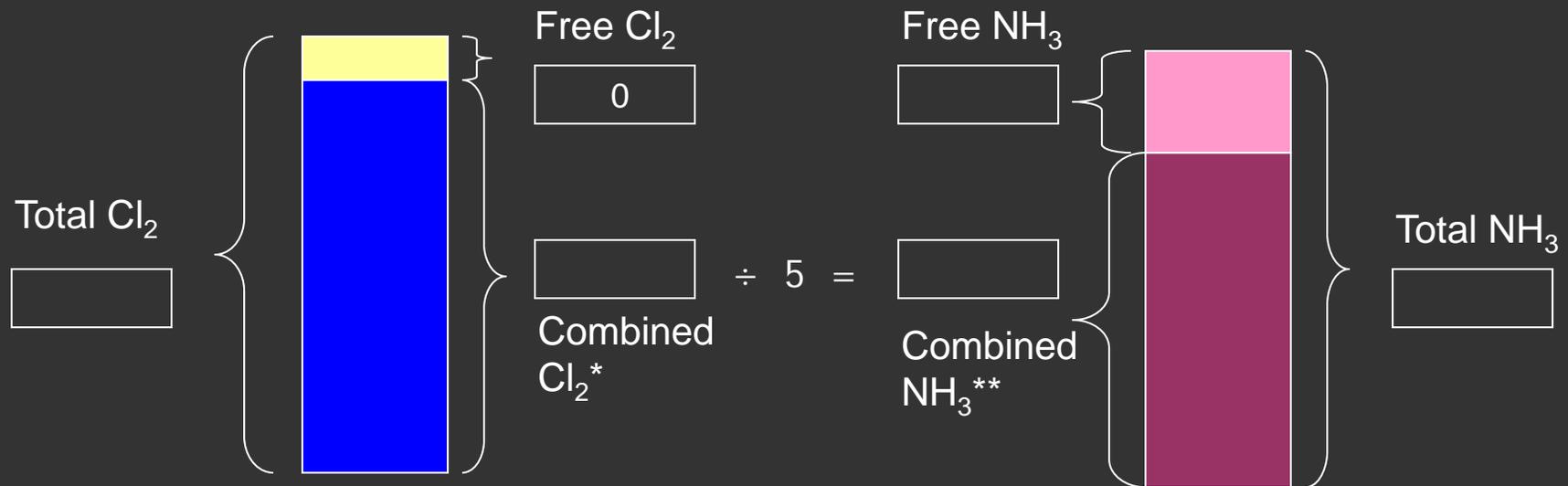
# Determining Cl<sub>2</sub>:NH<sub>3</sub> Ratio

$$\text{Cl}_2:\text{NH}_3 \text{ Ratio} = \frac{\text{Free Cl}_2}{\text{Applied NH}_3} = \frac{5.7}{0.75} = 7.6$$



# Cl<sub>2</sub>:NH<sub>3</sub> Ratio Calculation

$$\text{Cl}_2 : \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{\boxed{\phantom{0000}}}{\boxed{\phantom{0000}}} = \boxed{\phantom{0000}}$$



*\*Note: With Free NH<sub>3</sub> greater than 0  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

*\*\*Note: Combined NH<sub>3</sub> = Total Cl<sub>2</sub> ÷ 5*

# Practice Problems

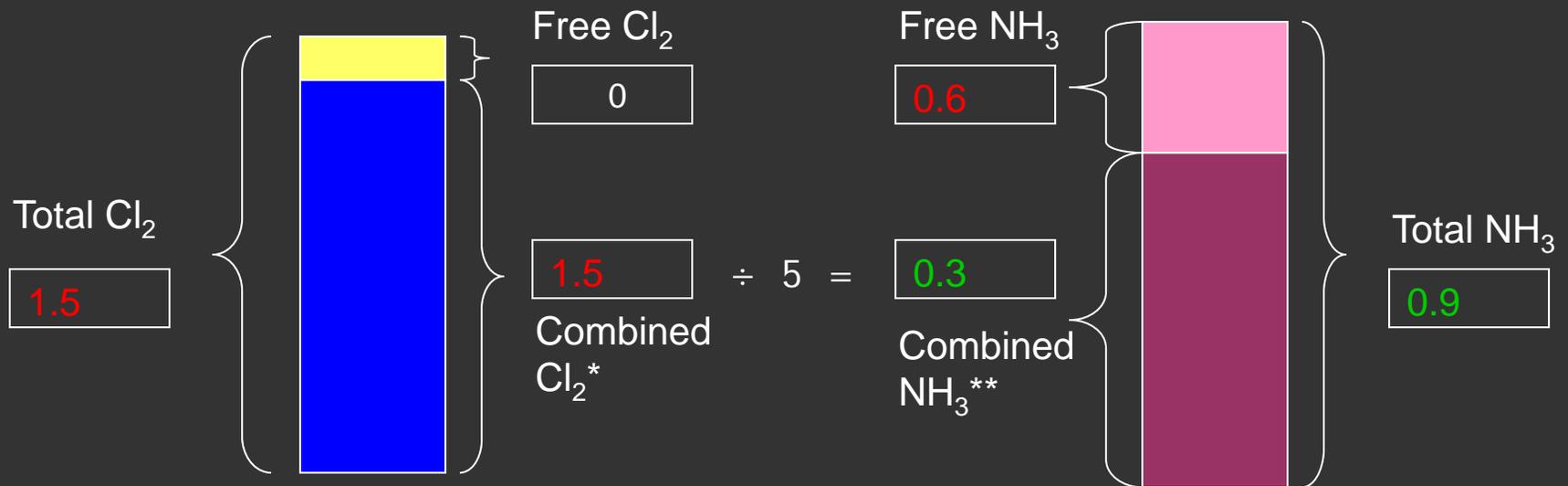
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# Practice Problem 1

- A ground storage tank in the distribution system receives water with a total  $\text{Cl}_2$  residual of 1.5 mg/L and a free  $\text{NH}_3$  residual of 0.6 mg/L
  - What is the  $\text{Cl}_2:\text{NH}_3$  ratio in the water reaching the tank?
    - $1.5 \text{ mg/L } \text{Cl}_2 \div 5 = 0.3 \text{ mg/L combined } \text{NH}_3$
    - $0.3 \text{ mg/L combined } \text{NH}_3 + 0.6 \text{ mg/L free } \text{NH}_3 = 0.9 \text{ mg/L total } \text{NH}_3$
    - $1.5 \text{ mg/L } \text{Cl}_2 \div 0.9 \text{ mg/L total } \text{NH}_3 = 1.7:1$

# Determining Cl<sub>2</sub>: NH<sub>3</sub> Ratio

$$\text{Cl}_2: \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{1.5}{0.9} = 1.7$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

## Practice Problem 1 (cont)

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- You would like to increase the total chlorine residual to 3.5 mg/L at the tank
  - Can you do that without adding more  $\text{NH}_3$ ?
    - Yes... $0.6 \text{ mg/L free } \text{NH}_3 \times 5 = 3.0 \text{ mg/L } \text{Cl}_2$
    - You can add up to 3.0 mg/L chlorine before you reach a 5:1 ratio...we only want to raise the residual by 2.0 mg/L  $\text{Cl}_2$

# Practice Problem 1 (cont)

---

- You adjust the chlorine dosage to feed 2.0 mg/L  $\text{Cl}_2$  to the water at the tank which already has a 1.5 mg/L total  $\text{Cl}_2$  residual and a free  $\text{NH}_3$  residual of 0.6 mg/L (before your applied  $\text{Cl}_2$ )
  - What would you expect the total  $\text{Cl}_2$  residual to do?
    - Would expect the total  $\text{Cl}_2$  residual to increase 2.0 mg/L to 3.5 mg/L
  - What would you expect the free  $\text{NH}_3$  residual to do?
    - Would expect the free  $\text{NH}_3$  residual to drop from 0.6 mg/L to 0.2 mg/L (2.0 mg/L  $\text{Cl}_2$  increase  $\div 5 = 0.4$  mg/L free  $\text{NH}_3$  to combined  $\text{NH}_3$ )

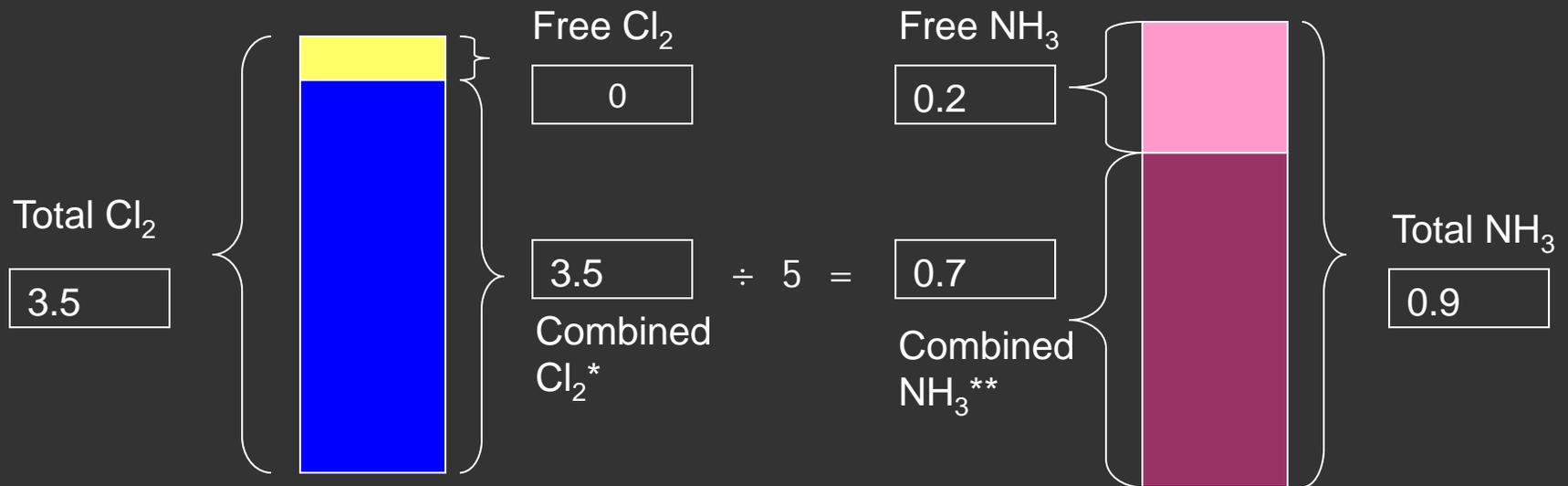
## Practice Problem 1 (cont)

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- If residuals respond as expected what will the new  $\text{Cl}_2:\text{NH}_3$  ratio be in water leaving the tank?
  - $3.5 \text{ mg/l Cl}_2 \div 5 = 0.7 \text{ mg/L combined NH}_3$
  - $0.7 \text{ mg/L combined NH}_3 + 0.2 \text{ mg/L free NH}_3 = 0.9 \text{ mg/L total NH}_3$  (Note that this did not change)
  - $3.5 \text{ mg/L total Cl}_2 \div 0.9 \text{ mg/L total NH}_3 = 3.9:1$

# Determining Cl<sub>2</sub>: NH<sub>3</sub> Ratio

$$\text{Cl}_2: \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{3.5}{0.9} = 3.9$$



*\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>*

*\*\*Note: Combined NH<sub>3</sub> = Total Cl<sub>2</sub> ÷ 5*

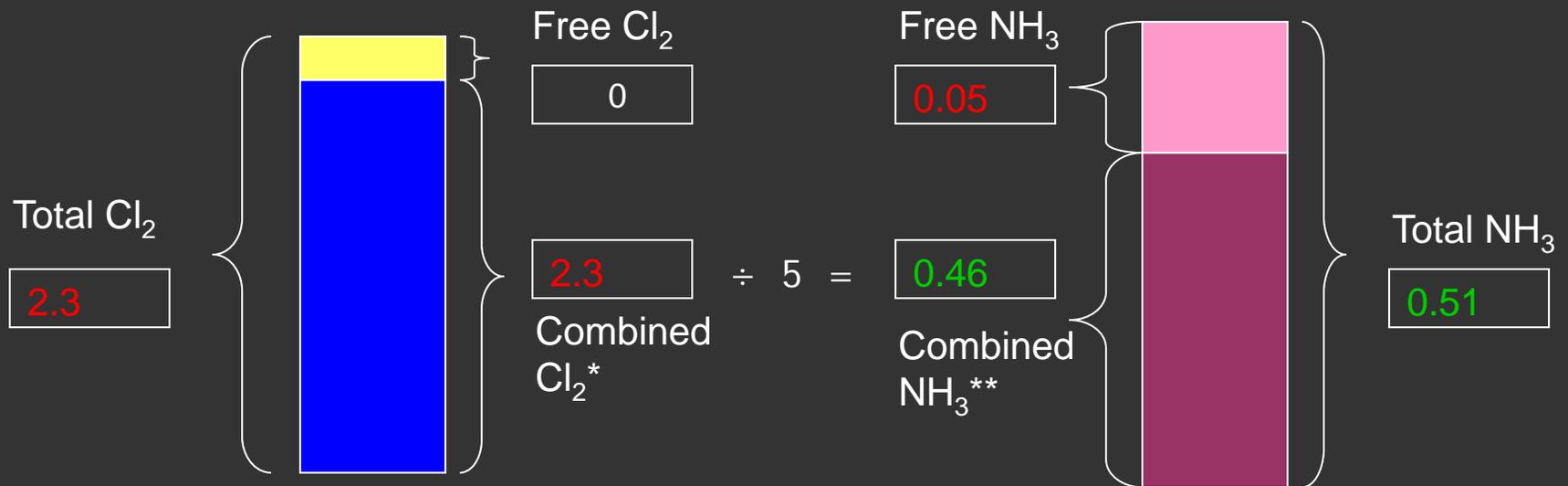
# Practice Problem 2

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- The finished water leaving your plant shows a total  $\text{Cl}_2$  residual of 2.3 mg/L and free  $\text{NH}_3$  of 0.05 mg/L.
  - What is the present  $\text{Cl}_2:\text{NH}_3$  ratio?
    - $2.3 \text{ mg/L } \text{Cl}_2 \div 5 = 0.46 \text{ mg/L combined } \text{NH}_3$
    - $0.46 \text{ mg/L combined } \text{NH}_3 + 0.05 \text{ mg/L free } \text{NH}_3 = 0.51 \text{ mg/L total } \text{NH}_3$
    - $2.3 \text{ mg/L total } \text{Cl}_2 \div 0.51 \text{ mg/L total } \text{NH}_3 = 4.5:1$

# Determining Cl<sub>2</sub>: NH<sub>3</sub> Ratio

$$\text{Cl}_2: \text{NH}_3 \text{ Ratio} = \frac{\text{Total Cl}_2}{\text{Total NH}_3} = \frac{2.3}{0.5} = 4.5$$



\*Note: With Measured Free NH<sub>3</sub> present  
Combined Cl<sub>2</sub> = Total Cl<sub>2</sub>

\*\*Note: Combined NH<sub>3</sub> = Total Cl<sub>2</sub> ÷ 5