Chloramine and Nitrification… Is There a Simple Solution?

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Workshop Objective

- Share your experiences and ideas
- Learn something new about controlling and monitoring your chloramination process
- Learn something new about detection, prevention and control of nitrification in your system

Workshop Outline

- Control of the Chloramination Process
- Nitrification, Prevention, Detection and Correction
- Analytical Methods
- Practice Problems

Potential Chloramination Problems

- 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

Free Chlorine (Cl_2):

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

Total Cl_2

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

Free Ammonia (NH_3)

- Can be in the form of NH_3 at higher pH (pH >9.3) or 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)
- Lots of ways to measure free NH_3...more on this later (!)

Combined NH_3

- Represents the ammonia bound with Cl_2 to form chloramine
- Combined NH_3 is not food for bacteria
- Combined ammonia is about 24% of the total chlorine residual

Total NH_3

- Represents the sum of combined ammonia tied up in chloramines and free ammonia (NH_3 and NH_4^+)

Chloramine

- Chemical compound formed from the combination of Cl_2 and 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 (NH_2Cl)

- The combination of chlorine and NH_3 that under normal pH conditions (7-8.5) predominates at an applied Cl_2:NH_3 ratio up to 4.2:1
- Higher pH favors formation of monochloramine...lower pH favors formation of di- and trichloramine

Dichloramine ($NHCl_2$)

- Symptom of a Cl_2-rich chloramination process
- Begins to show up under normal pH conditions (7-8.5) when Cl_2:NH_3 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 (NCl_3)

- Symptom of a Cl_2-rich chloramination process
- Occurs at normal pH (7-8.5) when $Cl_2:NH_3$ ratio increases beyond ~8:1
- At pH less than 3 is the only chloramine specie present

Organic Chloramines

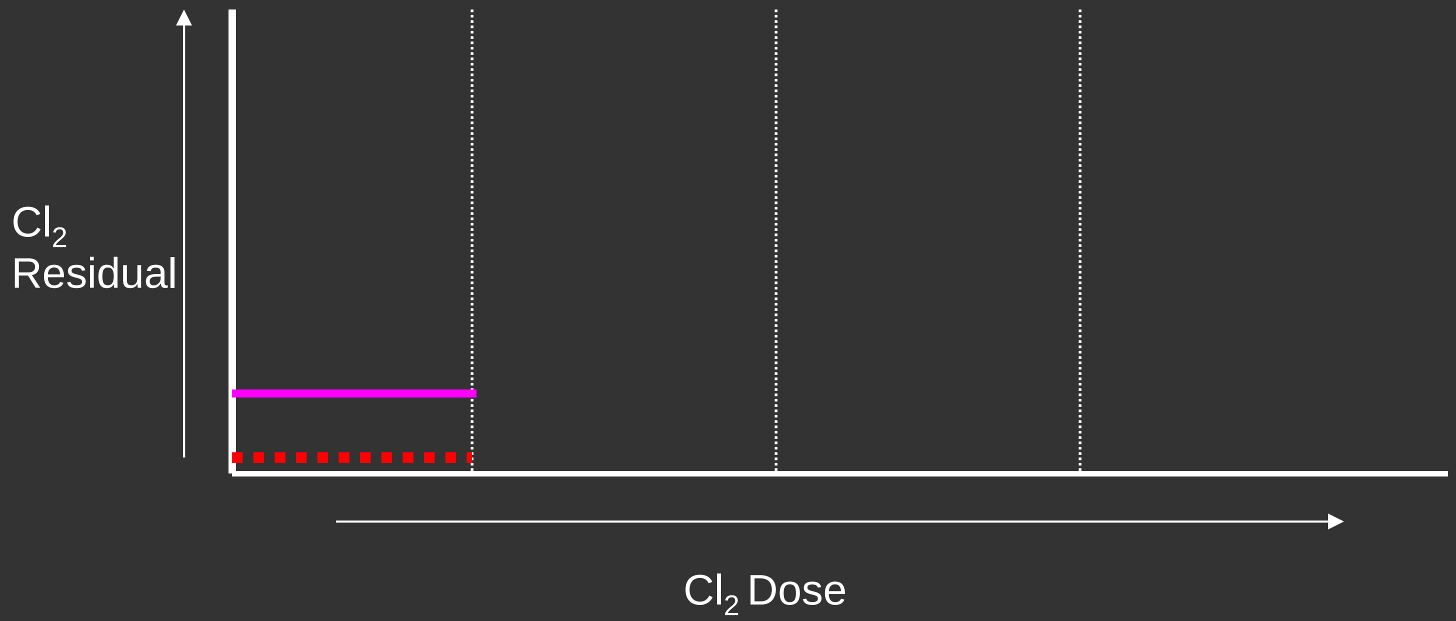
- The product of reactions of organic amines and amino acids with chlorine
- May be reflected in the total chlorine measurement
- Constitutes a portion of oxidant demand
- Also constitute demand on monochloramine

Breakpoint Chlorination

- At normal pH (7-8.5) occurs at a Cl_2: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 Cl_2 results in rising free Cl_2 residual

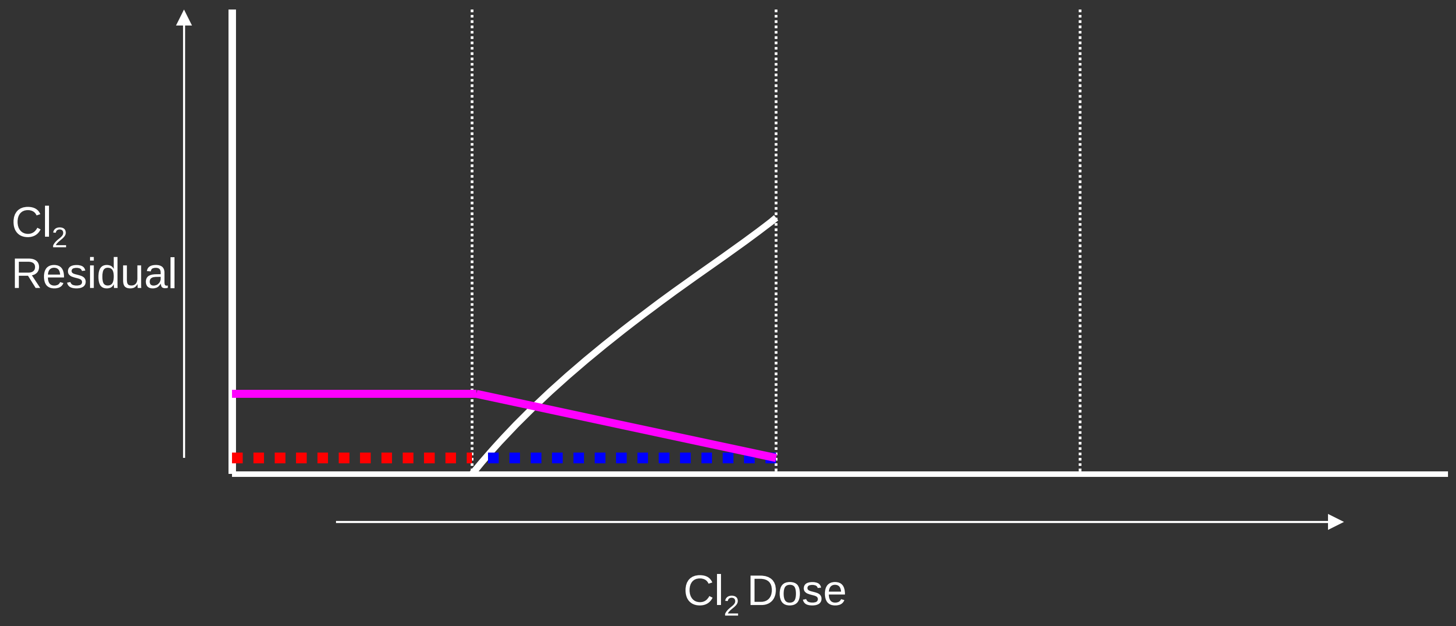
Breakpoint Curve

- 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.



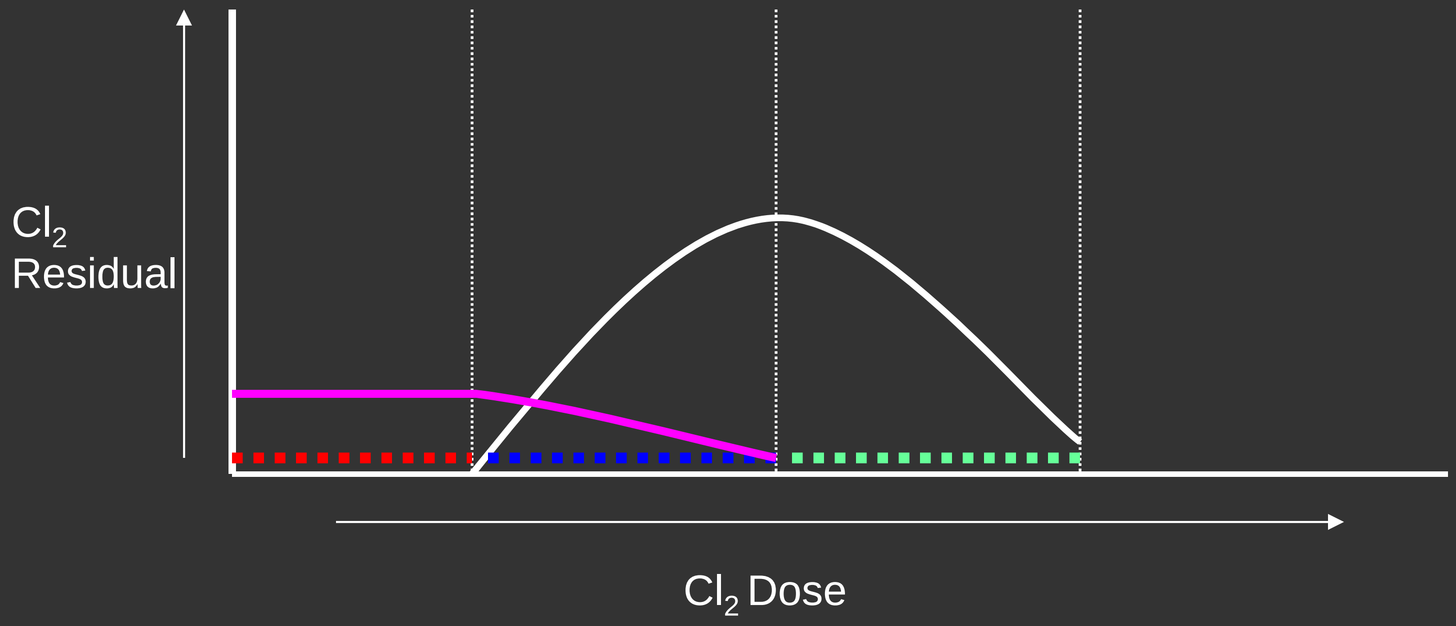
Breakpoint Curve

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



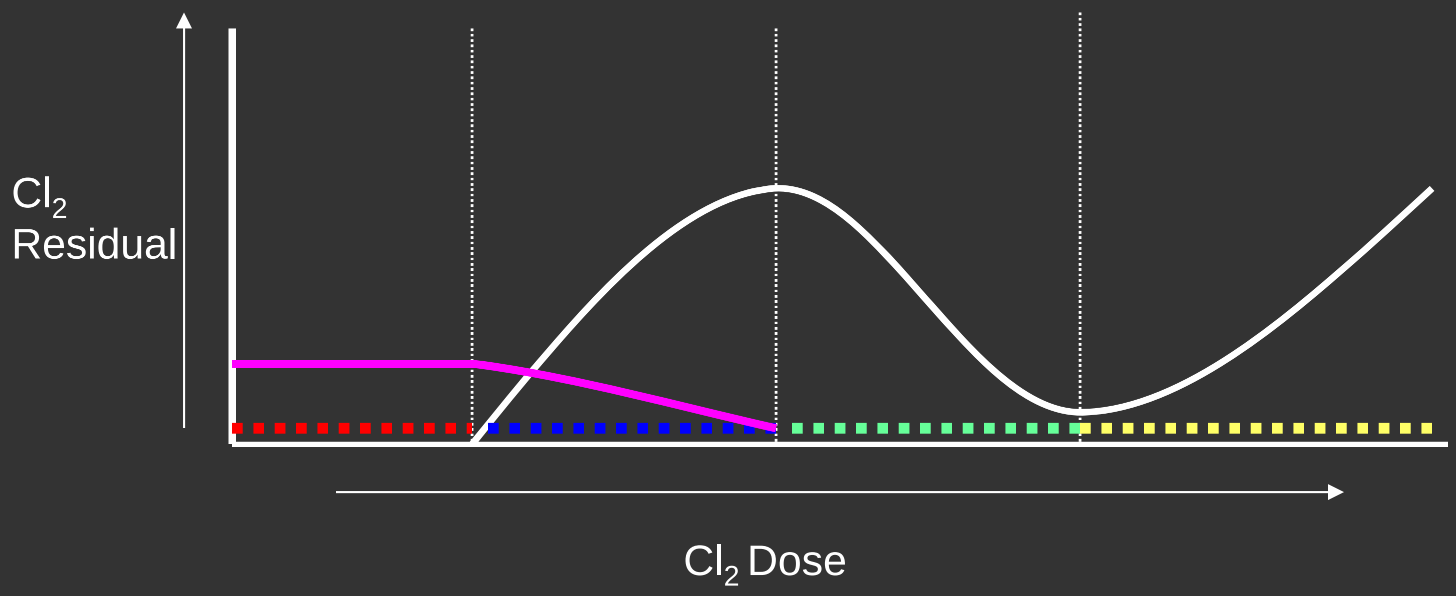
Breakpoint Curve

- 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.

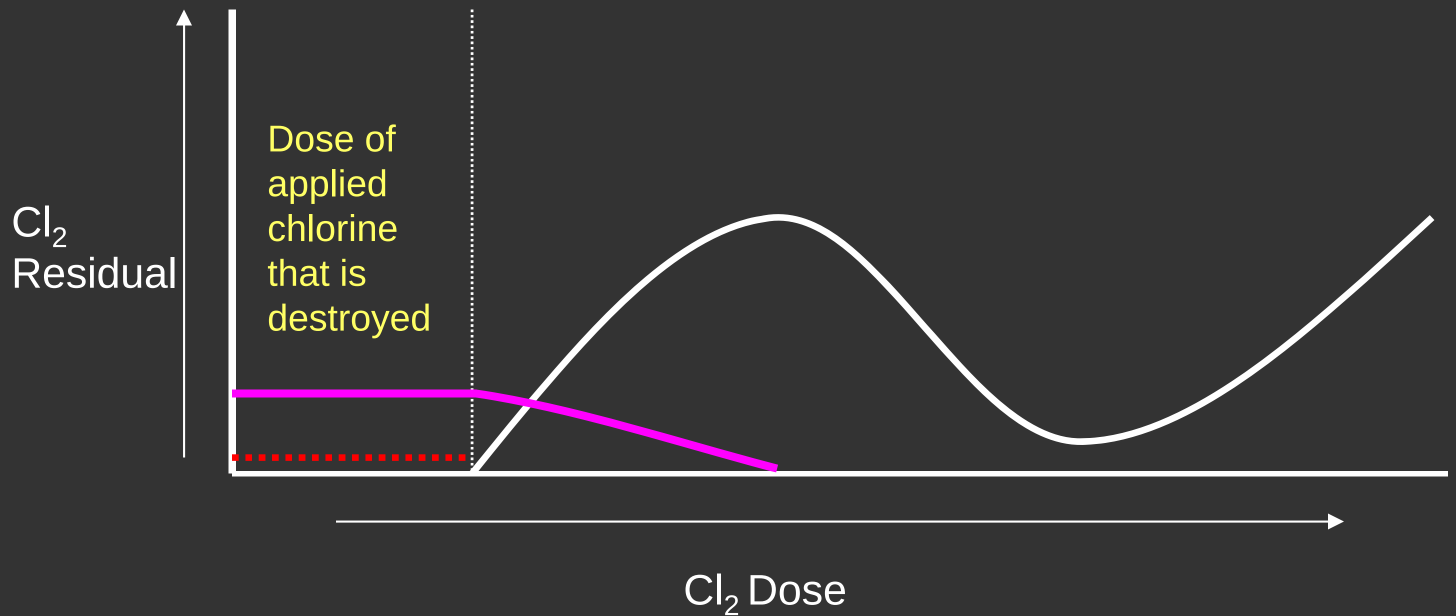


Cl_2 Demand

- 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_2 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_2 Demand

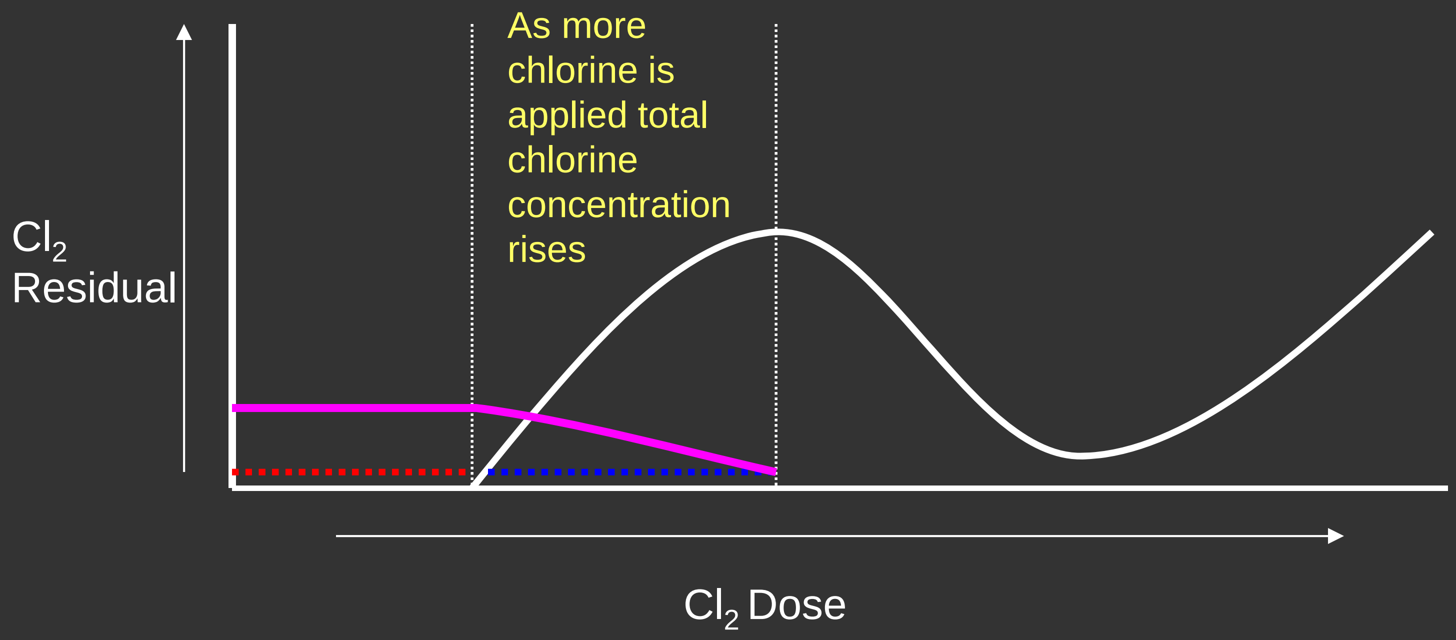
- Chlorine demand is naturally variable and changes due to a variety of fluctuating conditions including weather, season, lake turnover, lake level changes, algae blooms, etc.
- As with demand, the amount of chlorine destroyed by initial reduction demand is variable
- If chlorine and ammonia feed rates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

Cl_2 Demand

- 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

- 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 (*)

$Cl_2:NH_3$ Ratio

- In water 1 part of free Cl_2 combines with 1 part of NH_3 to form chloramine but 1 part of Cl2 weighs 5 times more than 1 part of NH3

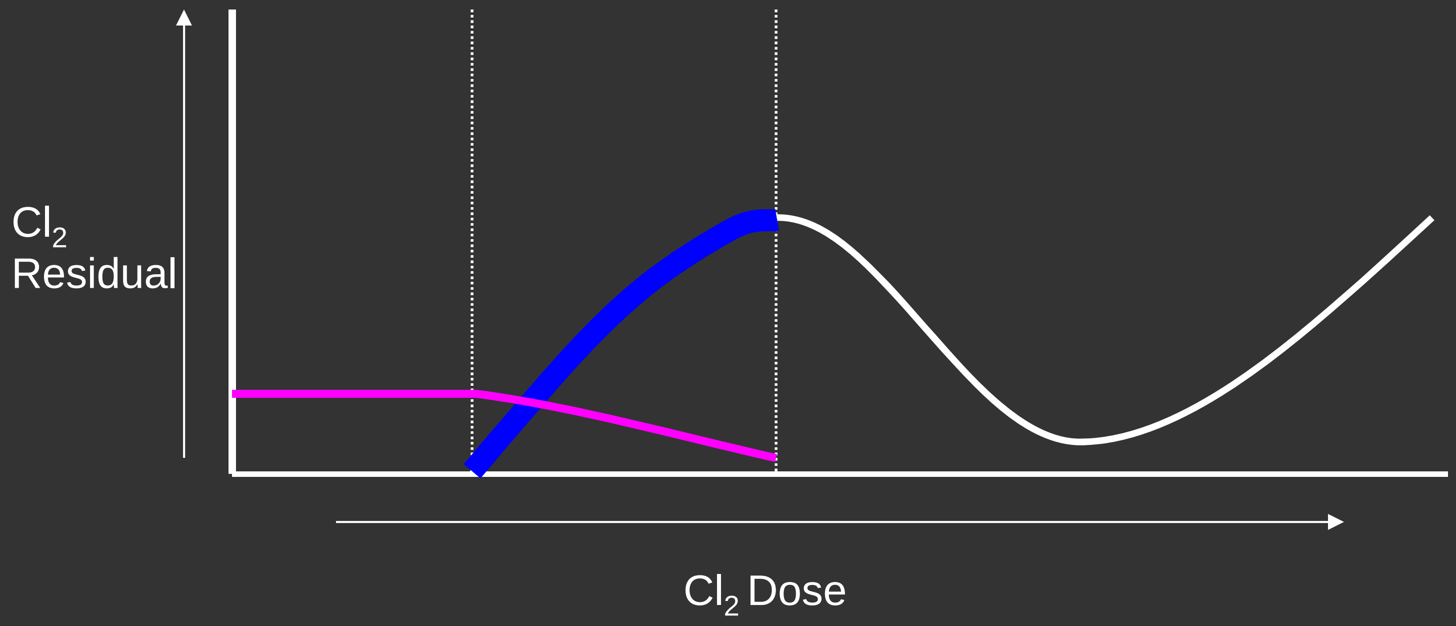
- The unit weight of Cl_2 is 71 and of NH_3 is 17

  71 ÷ 17 = 4.2 or 4.2:1

- At normal pH, 4.2 mg/L of available free Cl_2 will combine with 1 mg/L NH_3 to produce monochloramine as will 0.42 mg/L chlorine with 0.1 mg/L ammonia

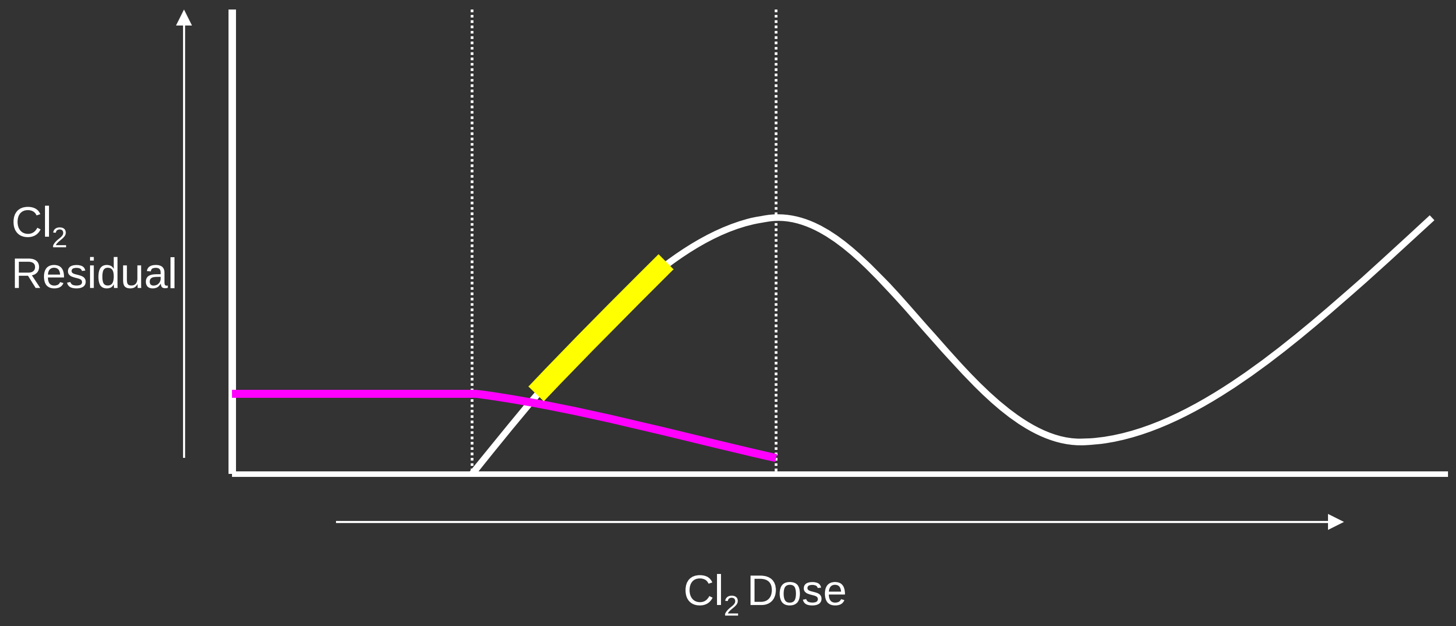
Formation of Chloramine

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



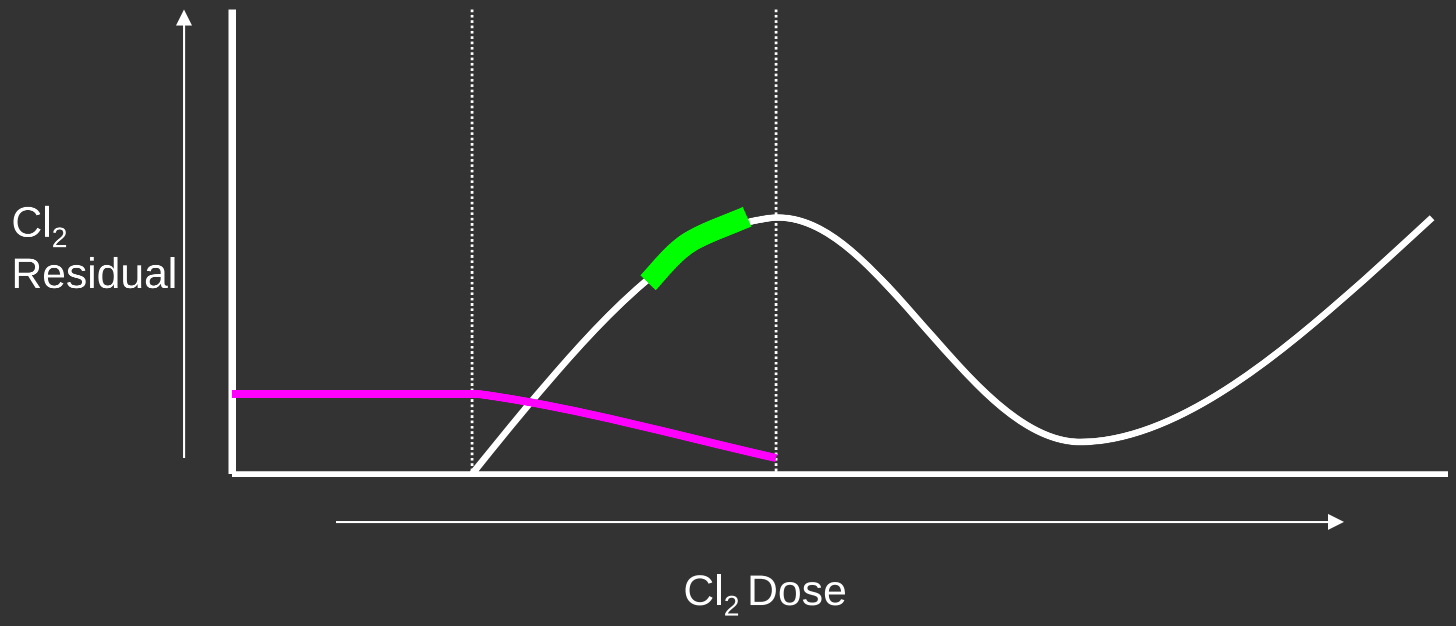
Formation of Chloramine

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



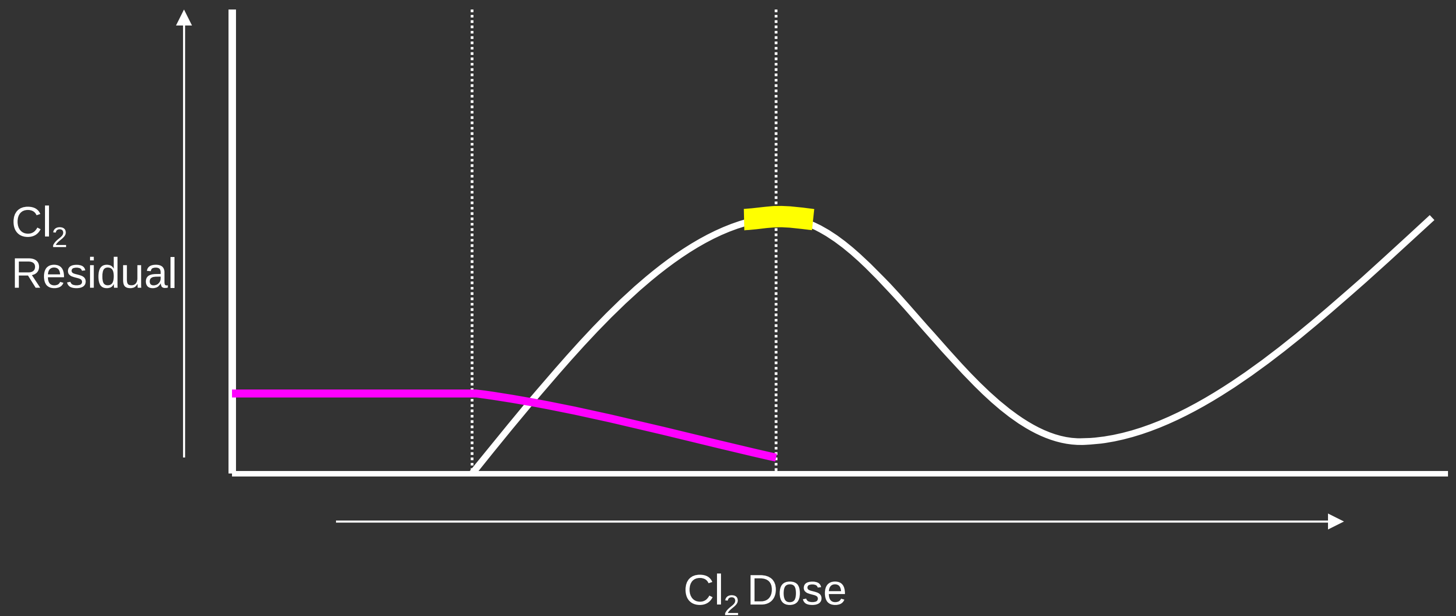
Formation of Chloramine

- 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.



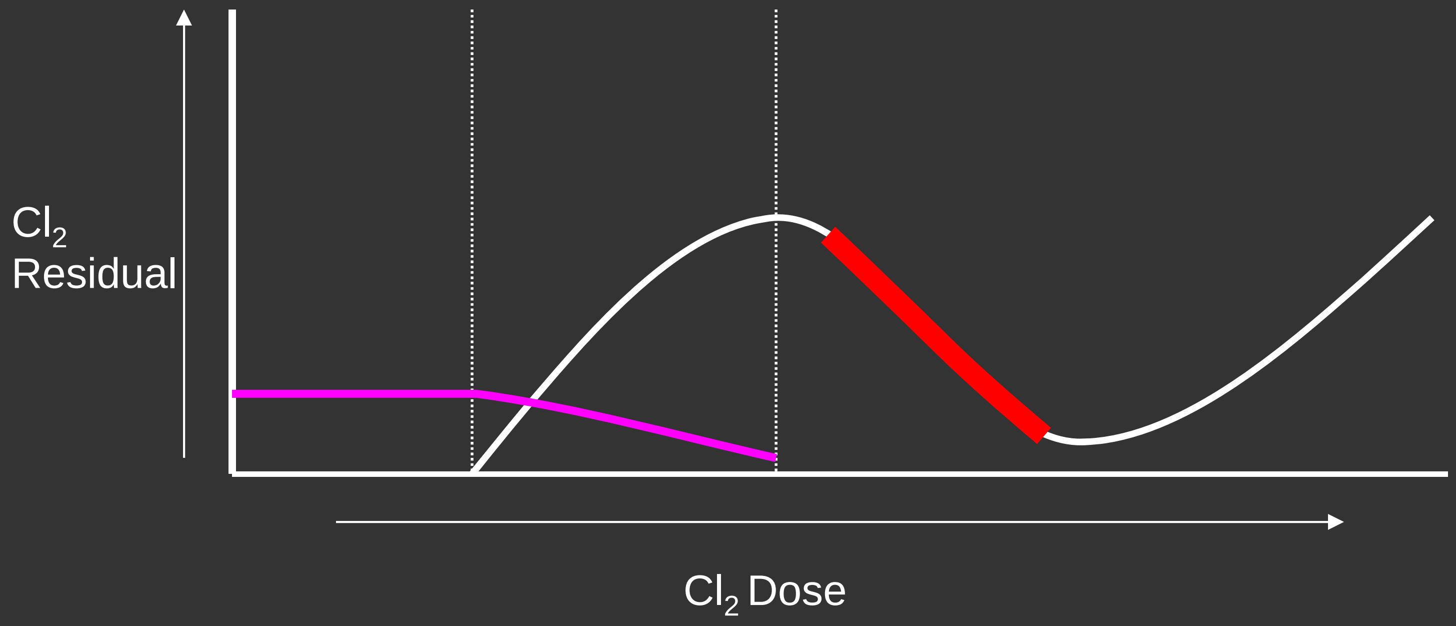
Formation of Chloramine

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



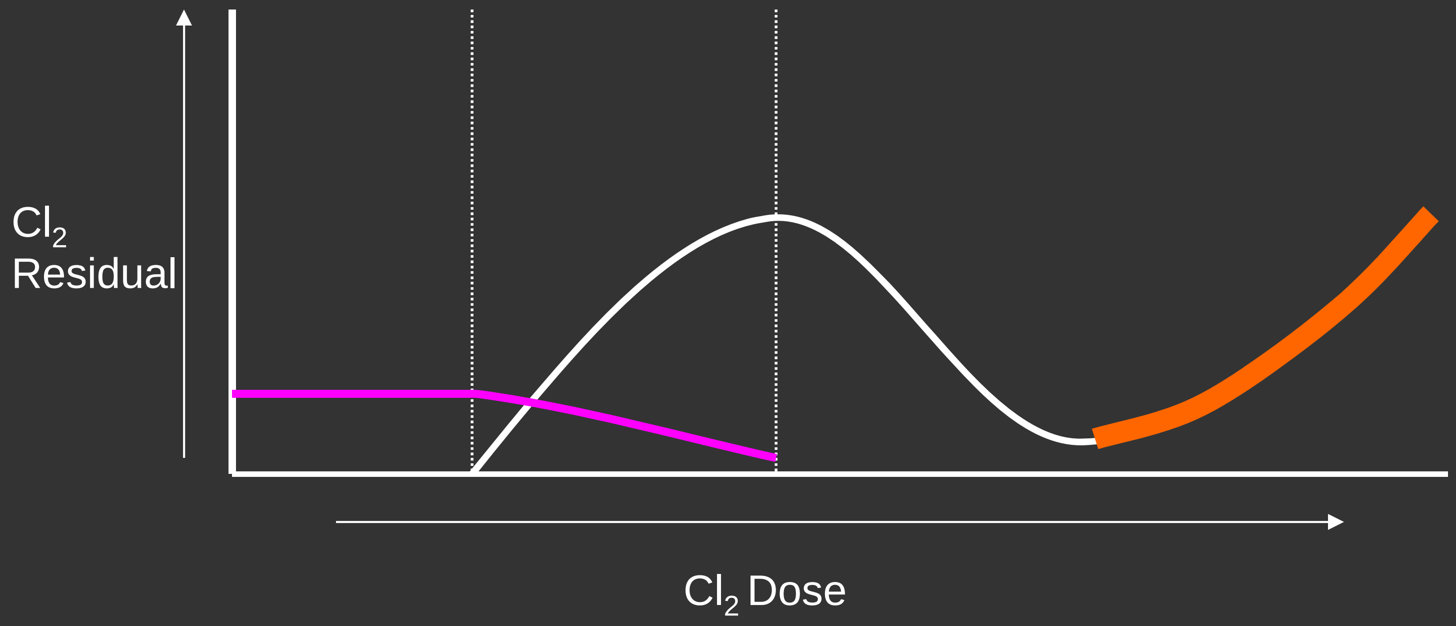
Destruction of Chloramine

- 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.



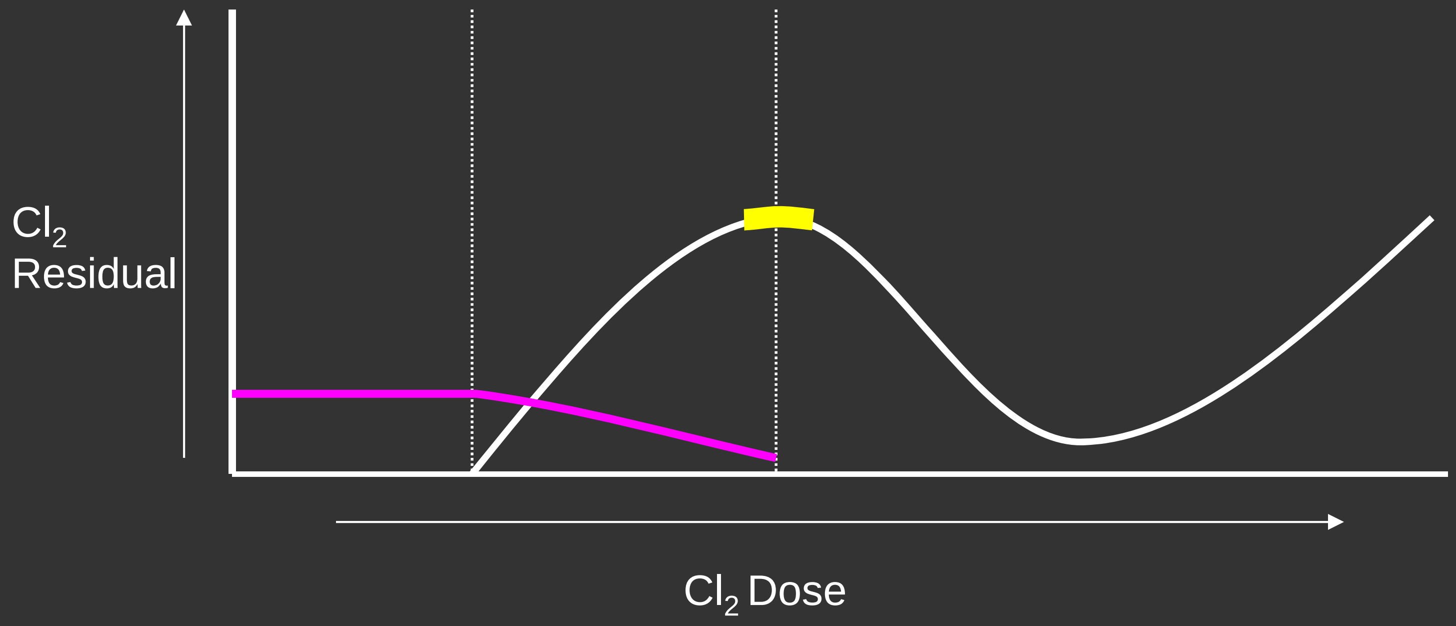
Increasing Free Chlorine

- 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.



Free Cl_2 Exposure

- Limited use of free Cl_2 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_2 is possible then the Cl_2:NH_3 ratio can be determined by comparing the measured free Cl_2 residual to the NH_3 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_2. In such a case NH_3 must be added upstream from Cl_2 and setting NH_3 dosage based on free Cl_2 is not possible.

Cl_2:NH_3 Ratio

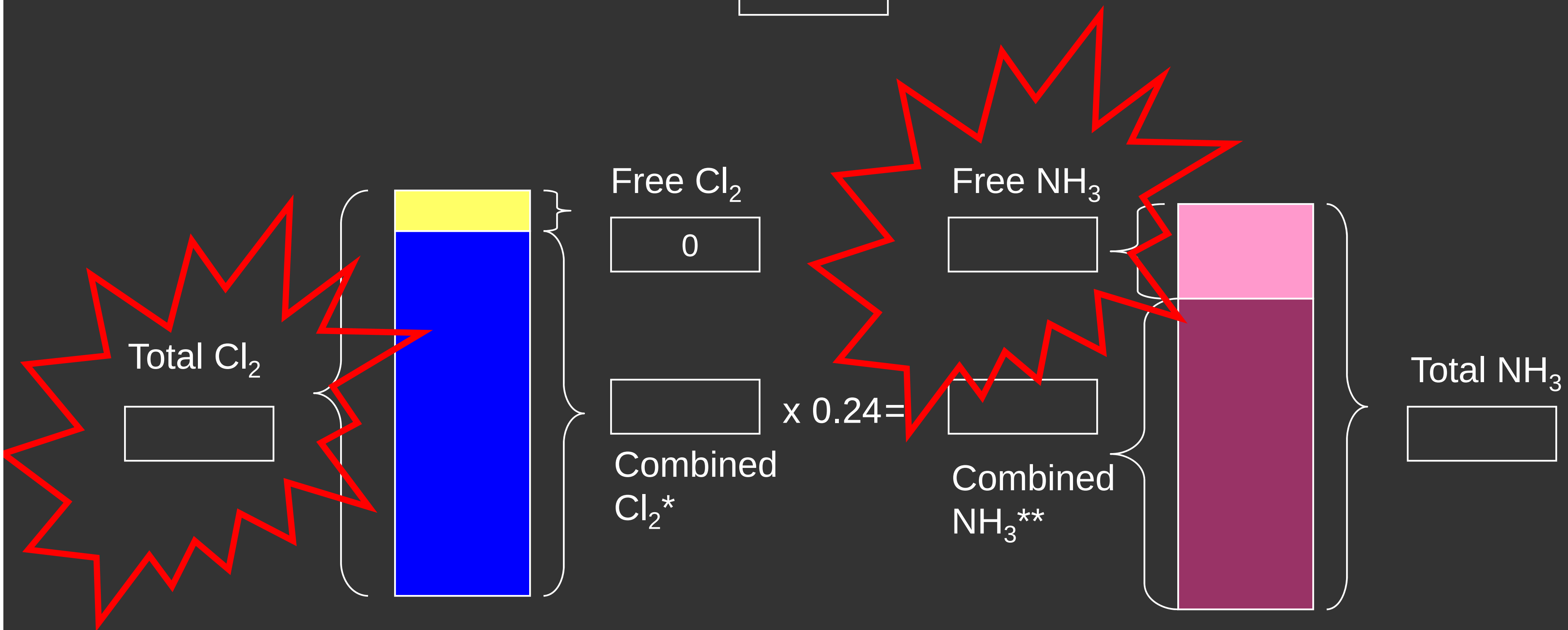
- Two ways to determine Cl_2:NH_3
- Method used is dependent on the NH_3 application point in reference to the Cl_2 application point
- It is possible to use both methods in systems that apply Cl_2 upstream from NH_3 and sustain a free chlorine zone
- Only one method available to systems applying NH_3 upstream from the Cl_2 application point

Determining Ratios

- For systems that apply NH_3 upstream from the Cl_2 application point measurable total Cl_2 and measurable free NH_3 must be present to accurately determine the $Cl_2:NH_3$ ratio

Determining Cl_2:NH_3 Ratio

Cl_2: NH_3 Ratio = $\frac{\text{Total } Cl_2}{\text{Total } NH_3}$ = $\frac{\square}{\square}$ = $\square$



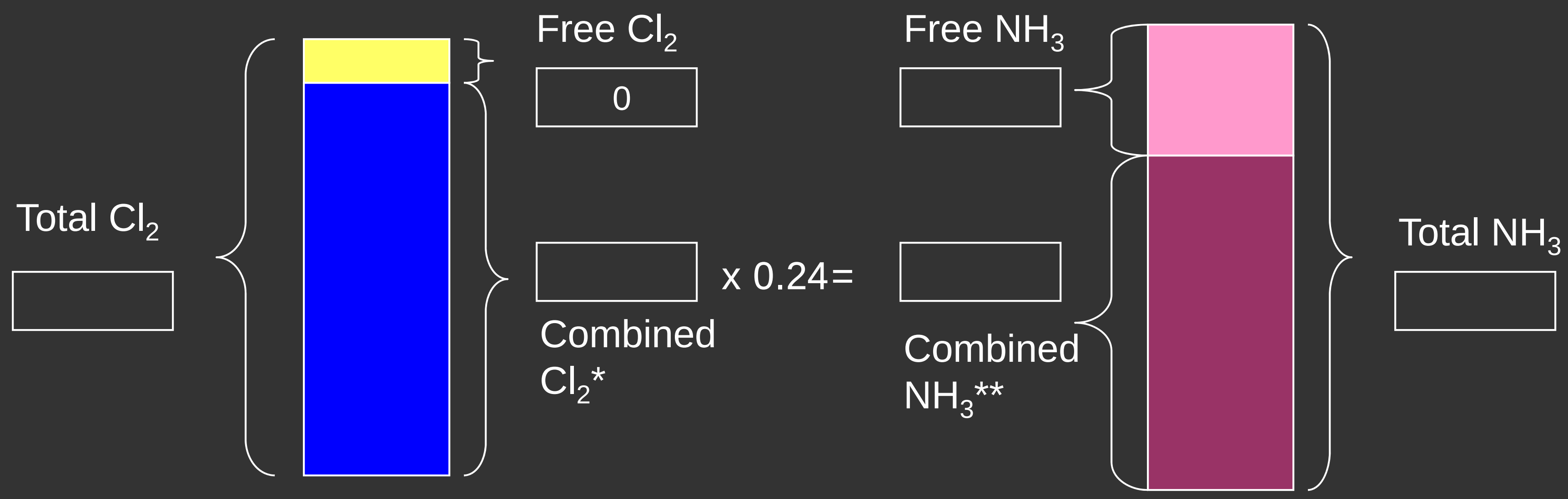
**Note: With Free NH_3 greater than 0*
Combined Cl_2 = Total Cl_2

Determining $Cl_2:NH_3$ 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 $Cl_2:NH_3$ ratio for this water

Determining $Cl_2:NH_3$ Ratio

Cl_2: NH_3 Ratio = $\dfrac{\text{Total } Cl_2}{\text{Total } NH_3}$ = $\dfrac{\square}{\square}$ = $\square$



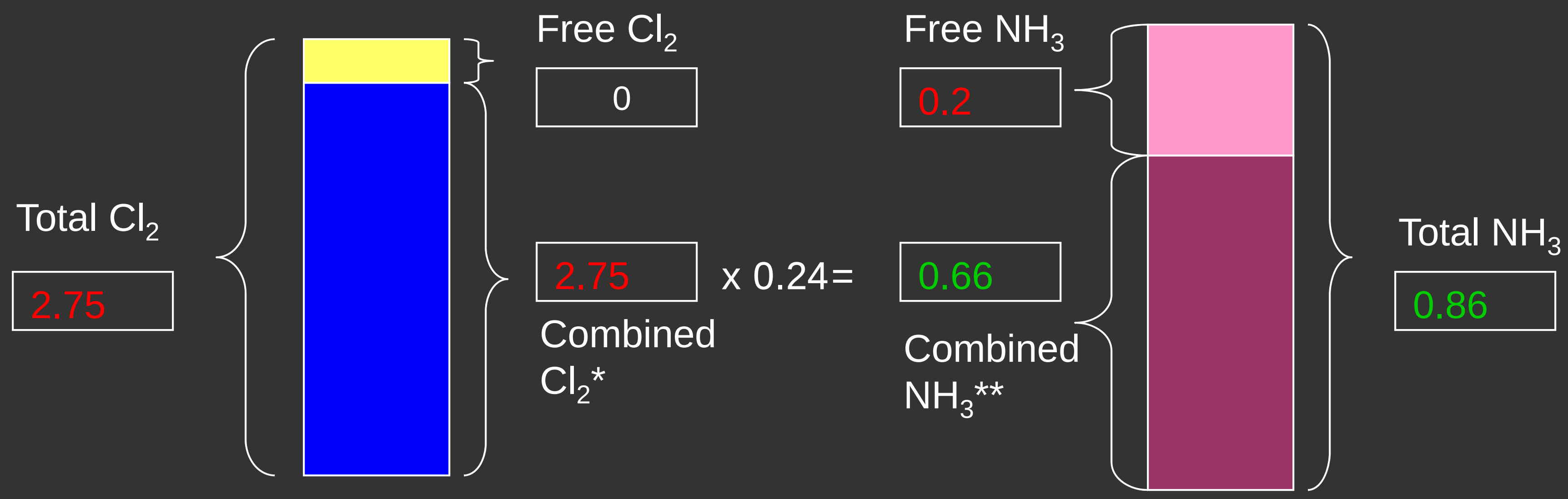
Note: With Measured Free NH_3 present Combined Cl_2 = Total Cl_2

Example 1

- 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 1/5th of the total chlorine residual so...
    - 2.75 mg/L Cl_2 x 0.24 = 0.66 mg/L combined NH_3
    - 0.2 mg/L free NH_3 + 0.66 combined NH_3 = 0.86 total NH_3
    - 2.75 mg/L Cl_2 ÷ 0.86 total NH_3 = 3.2:1 Cl_2:NH_3 Ratio

Determining $Cl_2:NH_3$ Ratio

$Cl_2: NH_3$ Ratio = $\frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{2.75}{0.86} = 3.2$



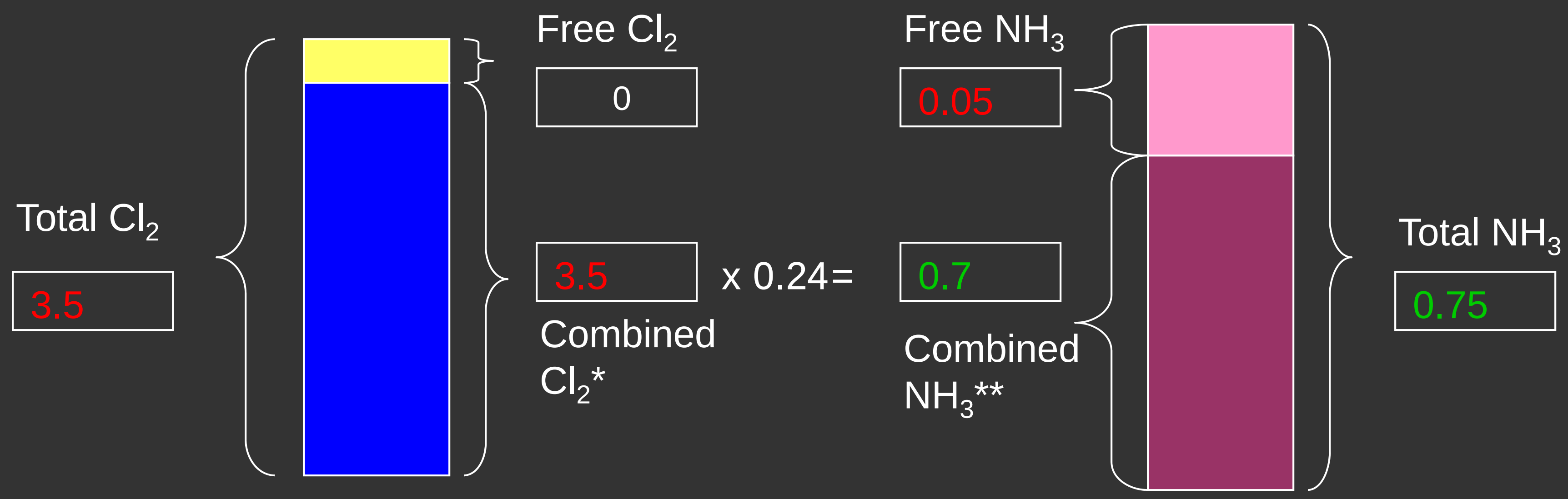
Note: With Measured Free NH_3 present
Combined Cl_2 = Total Cl_2

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 mg/L Cl_2 x 0.24 = 0.84 mg/L combined NH_3
    - 0.05 mg/L free NH_3 + 0.84 combined NH_3 = 0.89 total NH_3
    - 3.50 mg/L Cl_2 ÷ 0.89 total NH_3 = 3.9:1 Cl_2:NH_3 Ratio

Determining $Cl_2:NH_3$ Ratio

$$Cl_2: NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{3.5}{0.75} = 4.7$$



Note: With Measured Free NH_3 present Combined Cl_2 = Total Cl_2

Excess Chlorine

- When excess Cl_2 is applied in the chloramination process (above a 4.2:1 ratio) excess chlorine destroys monochloramine at a 1:1 ratio

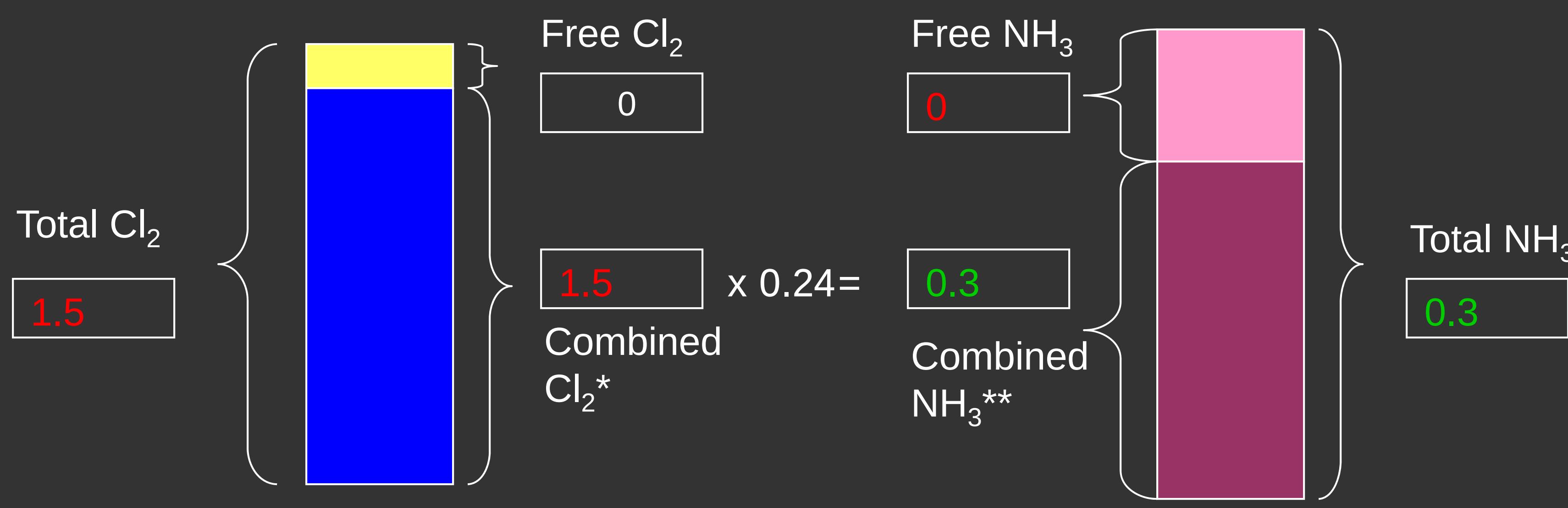
- Each part of Cl_2 added above the 4.2:1 ratio will destroy a part of monochloramine (1 mg/L Cl_2 will destroy 1 mg/L NH_2Cl)

Example 3

- 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 NH_3 feed set at 0.75 mg/L we have sufficient NH_3 present to give a total Cl_2 residual of 3.75 mg/L (0.75 x 5 = 3.75).
  - We see only a 1.5 mg/L total Cl2 residual which amounts to 0.3 mg/L total NH_3

Determining $Cl_2:NH_3$ Ratio

$Cl_2: NH_3$ Ratio = $\frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{1.5}{?} = ?$



**Note: With Measured Free NH_3 present*
Combined Cl_2 = Total Cl_2

Example 3-continued

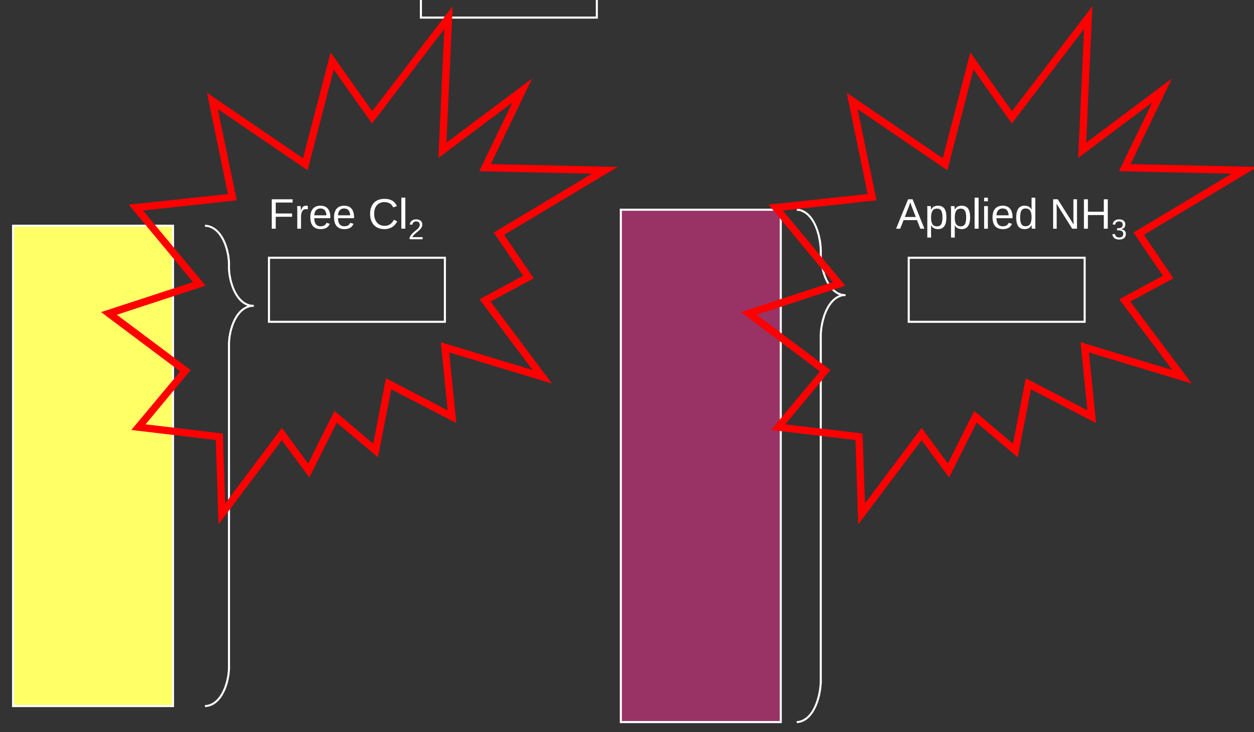
- We subtract combined NH_3 from applied NH_3 to give an indication of the excess Cl_2 feed (0.75 applied NH_3 – 0.3 combined NH_3 = 0.45 NH_3 lost).
- We now know we're losing 0.45 mg/L of the applied NH_3
- 0.45 mg/L applied NH_3 represented 2.25 mg/L of lost NH_2Cl
- Since excess Cl_2 destroys NH_2Cl at a 1:1 rate we know now that we're overfeeding about 2.25 mg/L Cl_2

Determining Ratios

- 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 NH_3 present
- Requires knowing free chlorine residual at the ammonia application point and ammonia dose

Determining Cl_2:NH_3 Ratio

$$Cl_2:NH_3\text{ Ratio} = \frac{\text{Free }Cl_2}{\text{Applied }NH_3} = \frac{\square}{\square} = \square$$

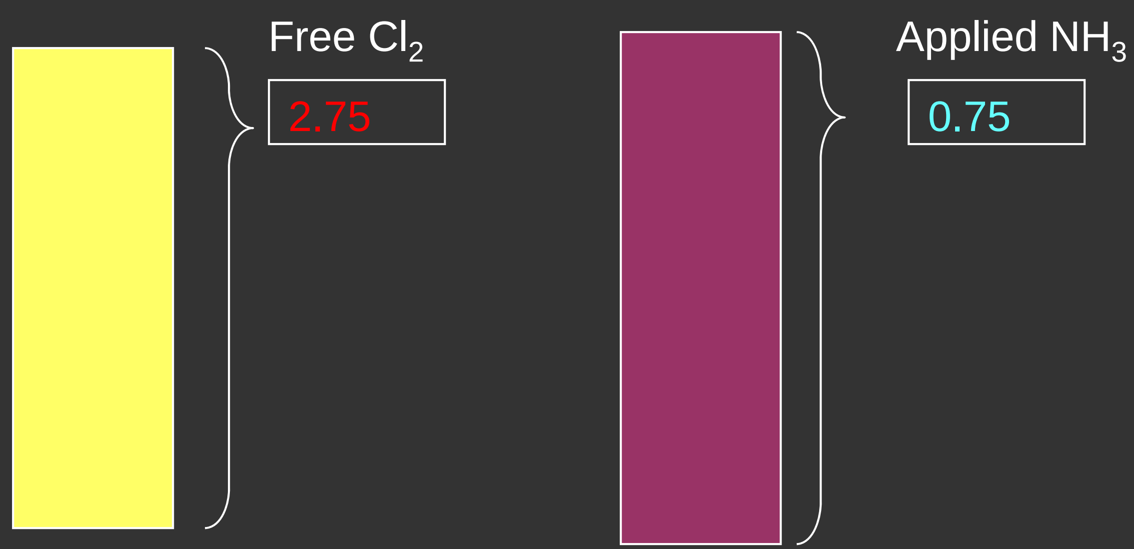


Example 4

- Water just upstream from the NH_3 application point has a free Cl_2 residual of 2.75 mg/L and 0.75 mg/L NH_3 - nitrogen is added at the NH_3 application point
  - To determine Cl_2:NH_3 Ratio free Cl_2 is divided by applied NH_3
    - 2.75 mg/L Cl_2 ÷ 0.75 applied NH_3 = 3.7:1 Cl_2:NH_3 Ratio
    - The 2.75 mg/L Cl_2 will combine with 0.55 mg/L NH_3 (2.75 ÷ 5)
    - 0.75 applied NH_3 - 0.55 mg/L combined NH_3 = 0.20 mg/L free NH_3

Determining $Cl_2:NH_3$ Ratio

$$Cl_2: NH_3 \text{ Ratio} = \frac{\text{Free } Cl_2}{\text{Applied } NH_3} = \frac{2.75}{0.75} = 3.7$$

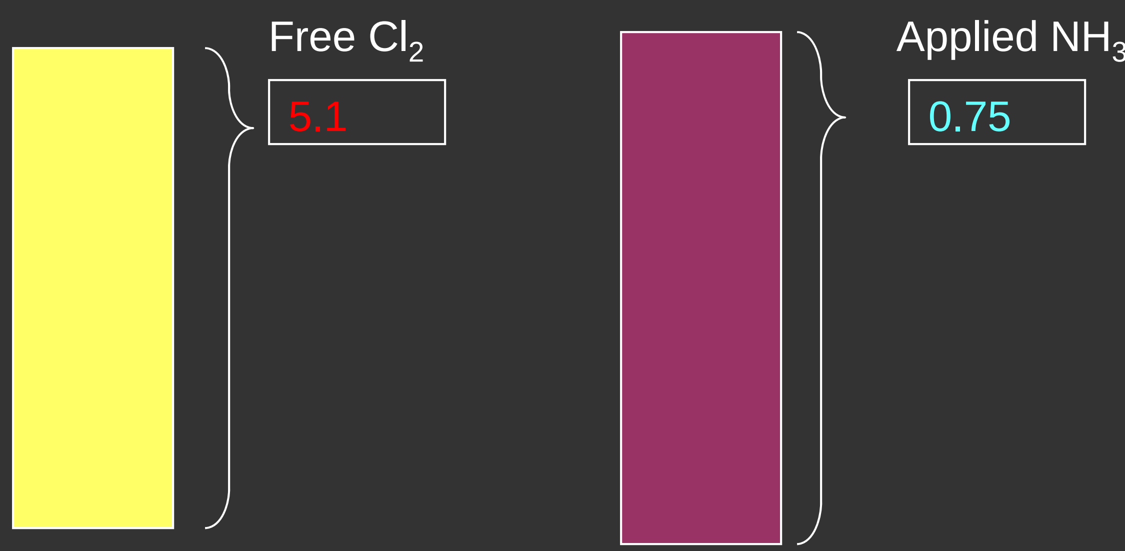


Example 6

- Water just upstream from the NH_3 application point has a free Cl_2 residual of 5.10 mg/L and 0.75 mg/L NH_3 - nitrogen is added at the NH_3 application point
  - To determine Cl_2:NH_3 Ratio free Cl_2 is divided by applied NH_3
    - 5.10 mg/L Cl_2 ÷ 0.75 applied NH_3 = 6.7:1 Cl_2:NH_3 Ratio
    - The 5.10 mg/L Cl_2 will combine with 1.02 mg/L NH_3 (5.10 ÷ 5) but only 0.75 mg/L NH_3 was applied
    - 0.75 mg/L applied NH_3 is consumed by the Cl_2 residual and the excess free chlorine residual then begins to oxidize monochloramine and the total chlorine residual drops...headed towards breakpoint

Determining $Cl_2:NH_3$ Ratio

$$Cl_2 : NH_3 \text{ Ratio} = \frac{\text{Free } Cl_2}{\text{Applied } NH_3} = \frac{5.1}{0.75} = 6.7$$

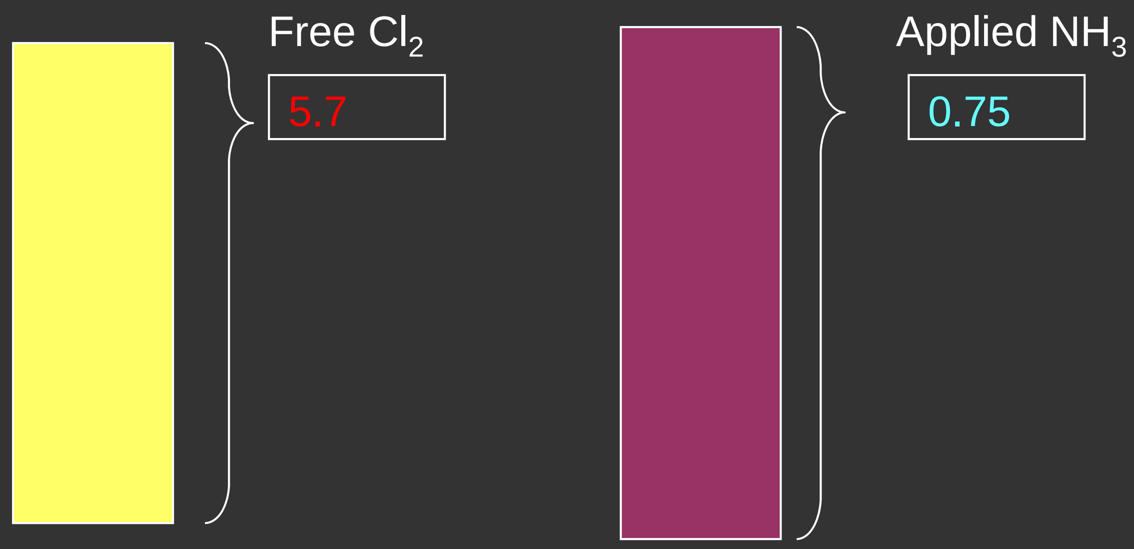


Example 7

- Water just upstream from the NH_3 application point has a free Cl_2 residual of 5.70 mg/L and 0.75 mg/L NH_3 -nitrogen is added at the NH_3 application point
  - To determine Cl_2:NH_3 Ratio free Cl_2 is divided by applied NH_3
    - 5.70 mg/L Cl_2 ÷ 0.75 applied NH_3 = 7.6:1 Cl_2:NH_3 Ratio
    - The 5.70 mg/L Cl_2 will combine with 1.14 mg/L NH_3 (5.70 ÷ 5) but only 0.75 mg/L NH_3 was applied
    - 0.75 applied NH_3 is consumed by the 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 $Cl_2:NH_3$ Ratio

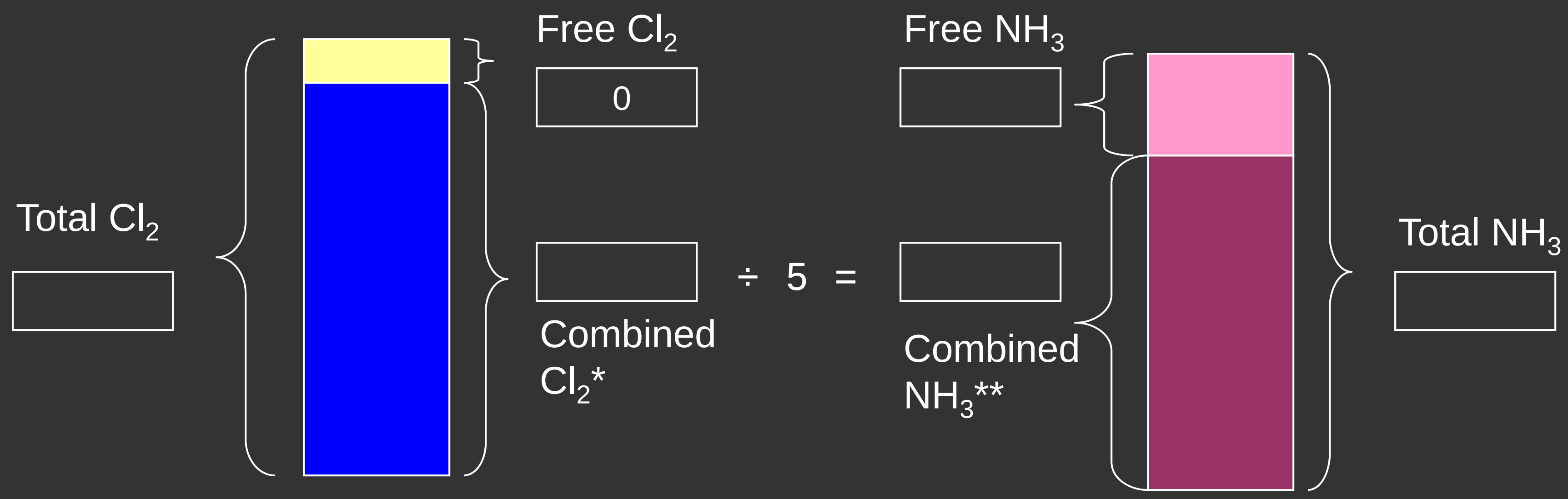
$$Cl_2:NH_3\ \text{Ratio} = \frac{\text{Free } Cl_2}{\text{Applied } NH_3} = \frac{5.7}{0.75} = 7.6$$



Summary of Examples

Cl_2:NH_3 Ratio Calculation

$$Cl_2: NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{\square}{\square} = \square$$



Note: With Free NH_3 greater than 0 Combined Cl_2 = Total Cl_2

***Note: Combined NH_3 = Total Cl_2 ÷ 5*

Process Control Summary

- To keep a stable total chlorine residual the $Cl_2:NH_3$ 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)

- When NH_3 is not a limiting factor and some excess free NH_3 is available:
  - The total chlorine residual represents monochloramine.
  - Combined NH_3 = ~1/5th of the total chlorine residual
  - Total NH_3 = combined NH_3 + free NH_3
- When some free NH_3 is present we can divide the measured total chlorine by the total NH_3 to determine the Cl_2:NH_3 ratio.
- When free NH_3 is not present the only reliable means to determine the Cl_2:NH_3 Ratio is applying NH_3 to water with a free Cl_2 residual

Process Control Summary (cont)

- 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 NH_3 in the system.
- If chlorine feed is increased and the total chlorine residual drops then there was insufficient NH_3 in the system.

Nitrification

- What is it?
- Detection
- Prevention
- Correction

Nitrification

- 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

- 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

- 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

- 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

- 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

- If nitrification problems are suspected as a result of low chlorine readings follow-up sampling can be used to confirm suspicions
  - Free 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 NO_2-N to confirm

Nitrification Prevention

- 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

- 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 Cl_2:NH_3 ratio in the range of 4:1 to 4.5:1 to minimize free NH_3 levels in the finished water
  - Maintaining pH in finished water at 8.8+

Nitrification Prevention

- 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

- 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

- 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

- 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

- 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

"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

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

Analytical Methods

- Free Chlorine
- Total Chlorine
- Free Ammonia
- Monochloramine
- Nitrite

Free Chlorine Analytical

- TCEQ accepted methods to measure free chlorine
  - DPD Colorimetric
  - DPD Ferrous Titration
  - Amperometric Titration
  - Syringaldizine
- When operating at chlorine :NH_3 ratio of less than 7.6:1 (in the presence of chloramines) DPD Free Chlorine measurement is inaccurate

Free Chlorine Analytical (cont)

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

NH_2CL (as Cl2)	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; 4th Edition*

Free Chlorine Analytical (cont)

- Equipment
  - Colorimeter or spectrophotometer for DPD Colorimetric

    or

  - Titration assembly

Analytical Methods

- Free Chlorine
- Total Chlorine
- Free Ammonia
- Monochloramine
- Nitrite

Total Chlorine Analytical

- Methods to measure
  - DPD Colorimetric
  - DPD Ferrous Titration
  - Amperometric Titration

Total Chlorine Analytical (cont)

- Equipment
  - Colorimeter or spectrophotometer

    or

  - Titration assembly

Analytical Methods

- Free Chlorine
- Total Chlorine
- Free Ammonia
- Monochloramine
- Nitrite

Free Ammonia Analytical

- Methods to measure
  - Modified Phenate
  - Indophenol
  - Ion Selective Electrode
  - Salicylate
  - Others...

- Methods to be avoided due to interference by chloramines and other
  - Nessler
  - Whatever is not working for you

Free Ammonia Analytical (cont)

- Equipment
  - Ion selective electrode with meter
  - Colorimeter
  - Other

Analytical Methods

- Free Chlorine
- Total Chlorine
- Free Ammonia
- Monochloramine
- Nitrite

Monochloramine Analytical

- Methods to measure:
  - Indophenol or Monochlor F

Monochloramine Analytical (cont)

- Equipment
  - Colorimeter or spectrophotometer

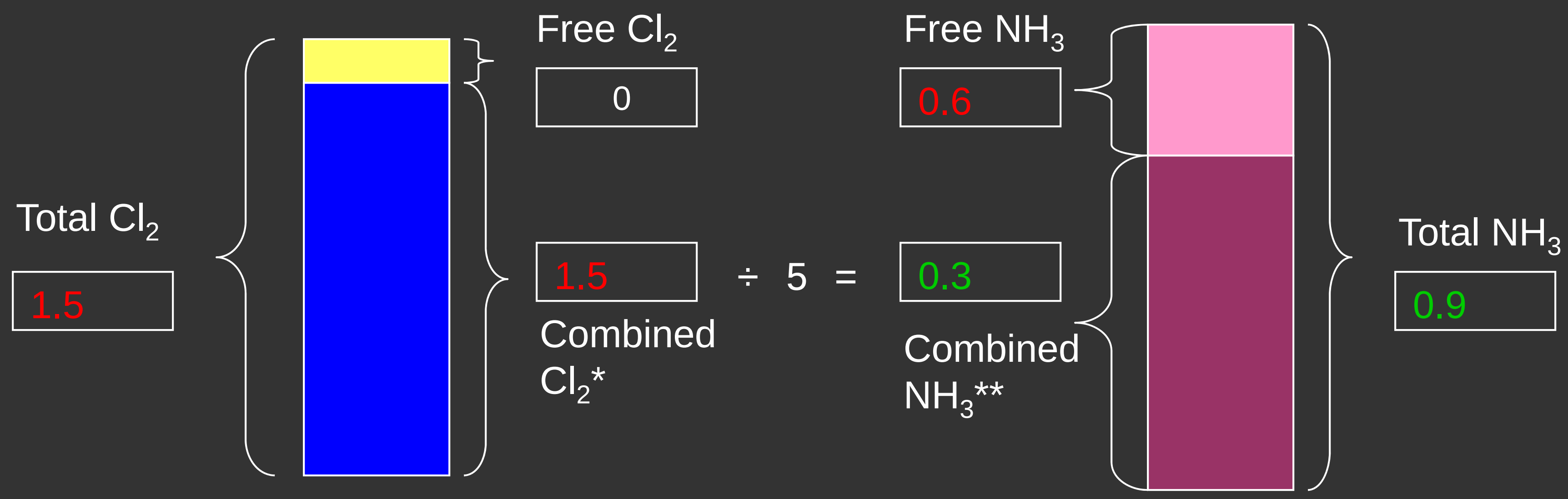
Practice Problems

Practice Problem 1

- A ground storage tank in the distribution system receives water with a total Cl_2 residual of 1.5 mg/L and a free NH_3 residual of 0.6 mg/L
  - What is the Cl_2:NH_3 ratio in the water reaching the tank?
    - 1.5 mg/l Cl_2 ÷ 5 = 0.3 mg/L combined NH_3
    - 0.3 mg/L combined NH_3 + 0.6 mg/L free NH_3 = 0.9 mg/L total NH_3
    - 1.5 mg/L Cl_2 ÷ 0.9 mg/L total NH_3 = 1.7:1

Determining Cl_2: NH_3 Ratio

$$Cl_2 : NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{1.5}{0.9} = 1.7$$



**Note: With Measured Free NH_3 present*
Combined Cl_2 = Total Cl_2

Practice Problem 1 (cont)

- You would like to increase the total chlorine residual to 3.5 mg/L at the tank
  - Can you do that without adding more NH_3?
    - Yes...0.6 mg/L free NH_3 x 5 = 3.0 mg/L 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 Cl_2

Practice Problem 1 (cont)

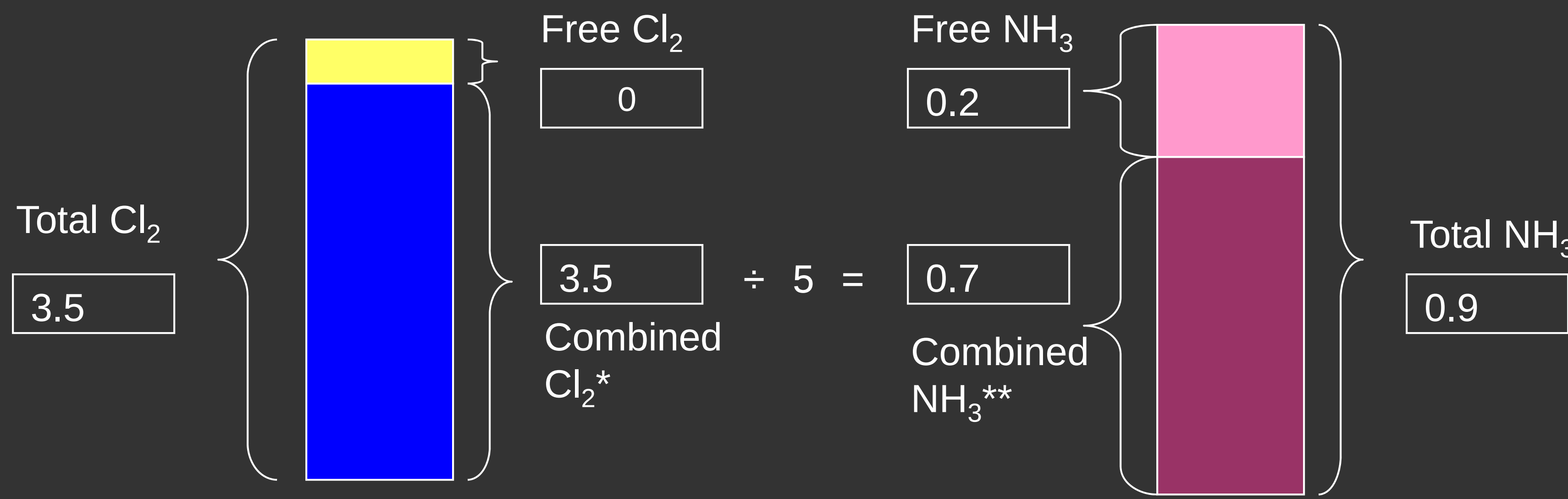
- You adjust the chlorine dosage to feed 2.0 mg/L Cl_2 to the water at the tank which already has a 1.5 mg/L total Cl_2 residual and a free NH_3 residual of 0.6 mg/L (before your applied Cl_2)
  - What would you expect the total Cl_2 residual to do?
    - Would expect the total Cl_2 residual to increase 2.0 mg/L to 3.5 mg/L
  - What would you expect the free NH_3 residual to do?
    - Would expect the free NH_3 residual to drop from 0.6 mg/L to 0.2 mg/L (2.0 mg/L Cl_2 increase ÷ 5 = 0.4 mg/L free NH_3 to combined NH_3)

Practice Problem 1 (cont)

- If residuals respond as expected what will the new Cl_2:NH_3 ratio be in water leaving the tank?
  - 3.5 mg/l Cl_2 ÷ 5 = 0.7 mg/L combined NH_3
  - 0.7 mg/L combined NH_3 + 0.2 mg/L free NH_3 = 0.9 mg/L total NH_3 (Note that this did not change)
  - 3.5 mg/L total Cl_2 ÷ 0.9 mg/L total NH_3 = 3.9:1

Determining Cl_2: NH_3 Ratio

$$Cl_2 : NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{3.5}{0.9} = 3.9$$



**Note: With Measured Free NH_3 present Combined Cl_2 = Total Cl_2*

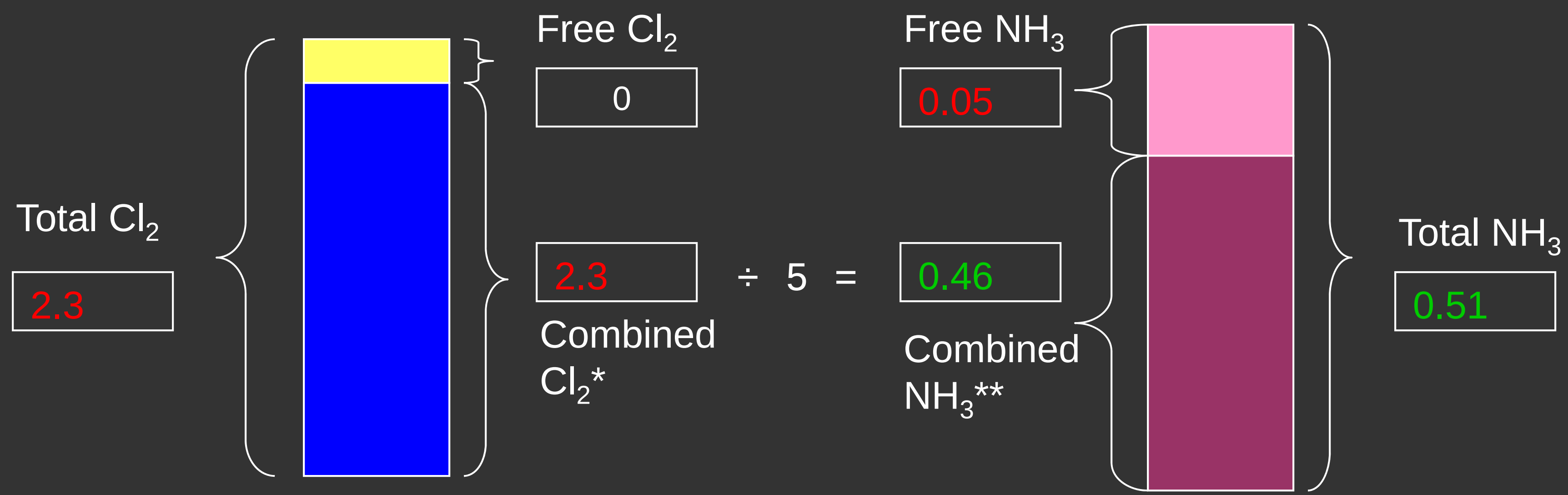
***Note: Combined NH_3 = Total Cl_2 ÷ 5*

Practice Problem 2

- The finished water leaving your plant shows a total Cl_2 residual of 2.3 mg/L and free NH_3 of 0.05 mg/L.
  - What is the present Cl_2:NH_3 ratio?
    - 2.3 mg/l Cl_2 ÷ 5 = 0.46 mg/L combined NH_3
    - 0.46 mg/L combined NH_3 + 0.05 mg/L free NH_3 = 0.51 mg/L total NH_3
    - 2.3 mg/L total Cl_2 ÷ 0.51 mg/L total NH_3 = 4.5:1

Determining Cl_2: NH_3 Ratio

$$Cl_2:NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{2.3}{0.5} = 4.5$$



Note: With Measured Free NH_3 present Combined Cl_2 = Total Cl_2

***Note: Combined NH_3 = Total Cl_2 ÷ 5*

Practice Problem 2 (cont)

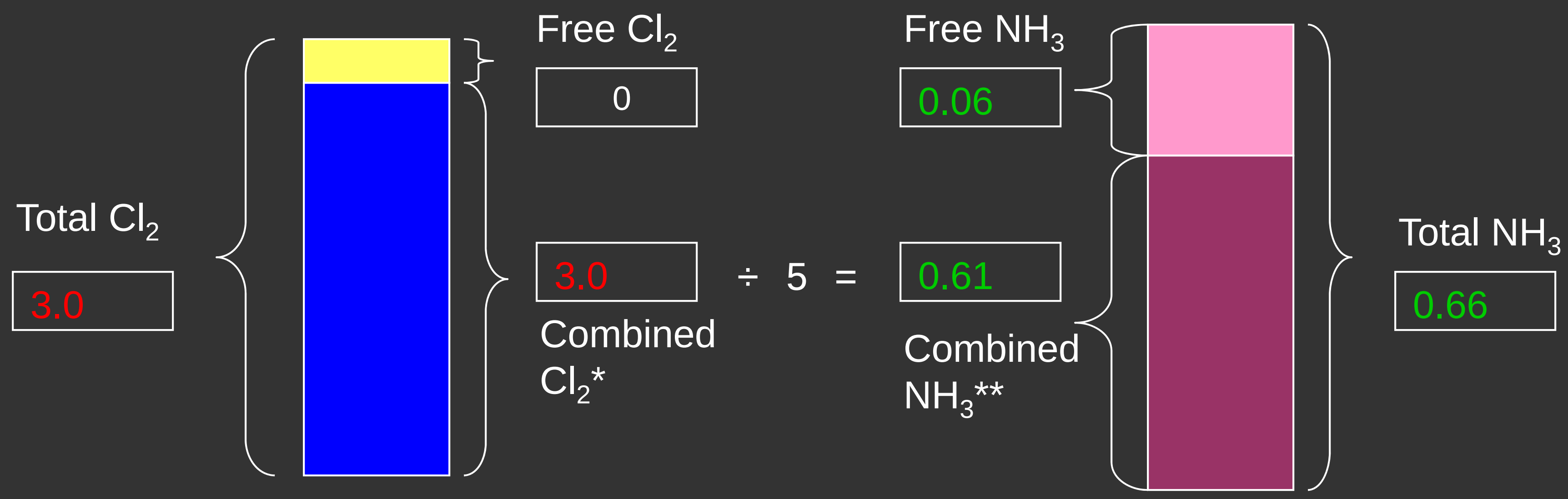
- You would like to boost the total Cl_2 residual from to 2.3 mg/L to 3.0 mg/L which represents a 0.7 mg/L boost.
  - Can you do that without adding more NH_3?
    - No...0.05 mg/L free ammonia x 5 = 0.25 mg/L Cl_2
    - You can increase the Cl_2 dosage by only 0.25 mg/L which only gives you about 2.5 mg/L total Cl_2 and you will no longer have any free NH_3 to cushion your process
  - What do you do?

Practice Problem 2 (cont)

- You must first raise the NH_3 dose by 0.15 mg/L. After raising the NH_3 dose the Cl_2 dose is then raised by 0.7 mg/L.
  - What will you expect the finished water total Cl_2 residual to do?
    - Would expect to see it increase to 3.0 mg/L
  - What will you expect the finished water NH_3 to do?
    - New total Cl_2 of 3.0 mg/L ÷ 5 = 0.60 mg/L combined NH_3
    - Had 0.51 mg/L total NH_3 so if we increase NH_3 feed by 0.15 mg/L would expect a new total NH_3 of 0.66 mg/L
    - Total NH_3 of 0.66 mg/L - combined of 0.60 mg/L = 0.06 mg/L free NH_3

Determining Cl_2: NH_3 Ratio

$$Cl_2 : NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{3.0}{0.66} = 4.5$$



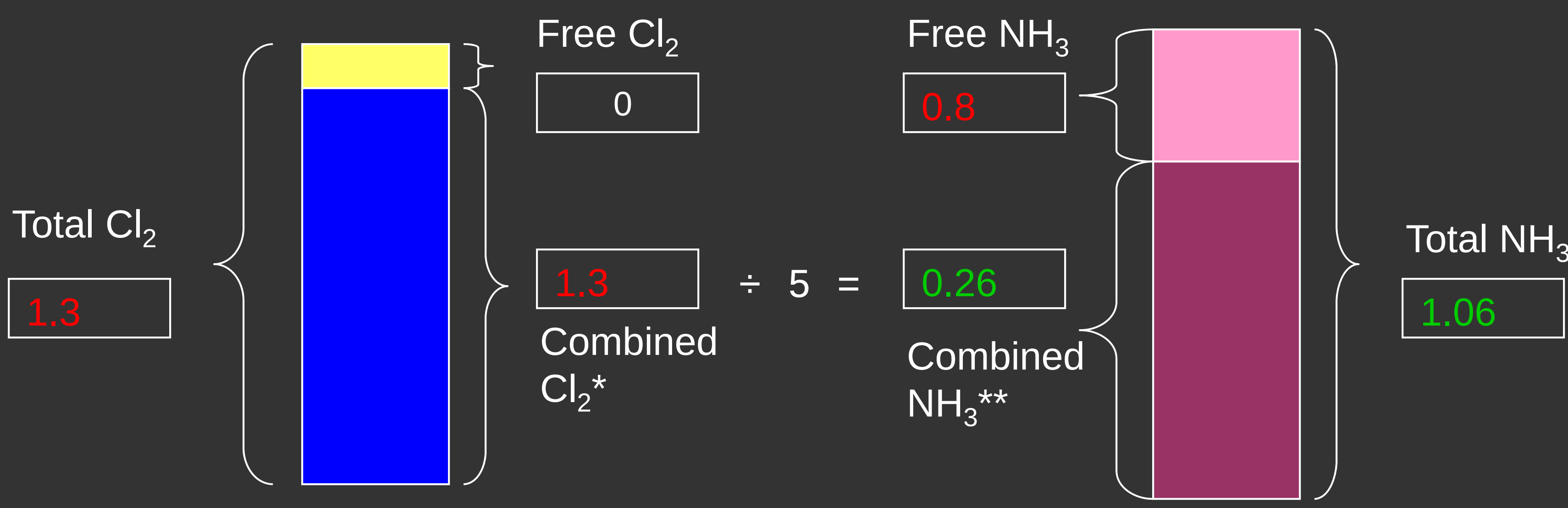
**Note: With Measured Free NH_3 present*
Combined Cl_2 = Total Cl_2

Practice Problem 3

- Purchased water entering your system arrives with 1.30 mg/L total Cl_2 and 0.80 mg/L free NH_3 . You'd like to raise your total chlorine residual and lower your free NH_3
  - What is the Cl_2:NH_3 ratio in the water reaching your system?
    - 1.30 mg/l Cl_2 ÷ 5 = 0.26 mg/L combined NH_3
    - 0.26 mg/L combined NH_3 + 0.80 mg/L free NH_3 = 1.06 mg/L total NH_3
    - 1.30 mg/L Cl_2 ÷ 1.06 mg/L total NH_3 = 1.2:1

Determining Cl_2: NH_3 Ratio

$$Cl_2:NH_3 \text{ Ratio} = \frac{\text{Total } Cl_2}{\text{Total } NH_3} = \frac{1.3}{1.06} = 1.2$$



**Note: With Measured Free NH_3 present*
Combined Cl_2 = Total Cl_2

Practice Problem 3 (cont)

- 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 NH_3?
    - Yes...0.8 mg/L free NH_3 x 5 = 4.0 mg/L 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 Cl_2

Practice Problem 3 (cont)

- You adjust the chlorine dosage to feed 2.7 mg/L Cl_2 to the water at your chlorination point where the water already has a 1.3 mg/L total Cl_2 residual and a free NH_3 residual of 0.8 mg/L (before your applied Cl_2)
  - What would you expect the total Cl_2 residual to do?
    - Would expect the total Cl_2 residual to increase 2.7 mg/L to 4.0 mg/L
  - What would you expect the free NH_3 residual to do?
    - Would expect the free NH_3 residual to drop from 0.8 mg/L to 0.26 mg/L

    (2.7 mg/L Cl_2 increase ÷ 5 = 0.54 mg/L free NH_3 to combined NH_3)

Practice Problem 3 (cont)

- If residuals respond as expected what will the new Cl_2:NH_3 ratio be in water downstream from your chlorination point?
  - 4.0 mg/l Cl_2 ÷ 5 = 0.8 mg/L combined NH_3
  - 0.8 mg/L combined NH_3 + 0.26 mg/L free NH_3 = 1.06 mg/L total NH_3 (Note that this did not change)
  - 4.0 mg/L total Cl_2 ÷ 1.06 mg/L total NH_3 = 3.8:1

Practice Problem 4

- Purchased water entering your system arrives at a GST with 1.30 mg/L total Cl_2 and 0.80 mg/L free 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 NH_3 present in the purchased water to chloraminate the groundwater flow as well?

    - Will have to determine overall pounds of available chlorine to overall pounds of available ammonia

Practice Problem 4 (cont)

- Let's start with total pounds of available chlorine...
  - lbs Cl_2 in PW = 1.30 mg/l Cl_2 x 2.0 mgd x 8.34 = 21.7 lbs Cl_2
  - lbs Cl_2 in GW = 1.00 mg/l Cl_2 x 0.5 mgd x 8.34 = 4.2 lbs Cl_2
  - Total lbs Cl_2 in Blended Water = 21.7 lbs + 4.2 lbs = 25.9 lbs Cl_2
- There are 25.9 lbs Cl_2 available for chloramination of the blended water

Practice Problem 4 (cont)

- Now let's look at lbs of NH_3...
  - Combined NH_3 in PW= 1.3 mg/l Cl_2 ÷ 5 = 0.26 mg/L Combined NH_3
  - Total NH_3 in PW= 0.26 mg/L combined NH_3 + 0.8 mg/L free NH_3 = 1.06 Total NH_3
  - lbs NH_3 in PW = 1.06 mg/l Cl_2 x 2.0 mgd x 8.34 = 17.7 lbs NH_3
- There are 17.7 lbs of total NH_3 available for chloramination of the blended water

Practice Problem 4 (cont)

- Now let's compare...
  - 25.9 lbs available Cl_2 ÷ 17.7 lbs of available NH_3 = 1.46 Cl_2:NH_3 ratio
  - Yes there is enough NH_3 present but what can we expect for blended water residuals?

Practice Problem 4 (cont)

- Blended water flow in mgd = 2.0 mgd + 0.5 mgd = 2.5 mgd
- Blended water Cl_2 in mg/L = 25.9 lbs available Cl_2 ÷ (2.5 mgd x 8.34) = 1.2 mg/L
- Blended water total NH_3 in mg/L = 17.7 lbs available NH_3 ÷ (2.5 mgd x 8.34) = 0.8 mg/L
- Blended water combined NH_3 in mg/L = 1.2 mg/L ÷ 5 mgd = 0.2 mg/L
- Blended water free NH_3 in mg/L = 0.8 mg/L total NH_3 – 0.2 mg/L free NH_3 = 0.6 mg/L free NH_3

Practice Problem 4 (cont)

- Given that we project blended water total Cl_2 residual to be 1.2 mg/L and blended water free NH_3 to be 0.6 mg/L free NH_3 can we safely boost our existing chlorine residual to a target of 3.0 mg/L without adding more NH_3?
  - 0.6 mg/L free NH_3 x 5 = 3.0 mg/L total Cl_2 boost
  - It is anticipated that there will be sufficient free 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 NH_3 is possible
  - But...

Practice Problem 4 (cont)

- 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

- 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 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)

- Let's first look at chlorine dose...
  - 185 lbs/day Cl_2 feed ÷ (2.5 mgd x 8.34) = 8.9 mg/L Cl_2 dosed
- Now look at measured Cl_2 residual in comparison to Cl_2 dose...
  - 8.9 mg/L Cl_2 dosed – 4.3 mg/L Cl_2 measured = 4.6 mg/L Cl_2 destroyed

Practice Problem 5 (cont)

- With a target $Cl_2:NH_3$ ratio of 4.2:1 how much NH_3 should be dosed?
  - 4.3 mg/L measured Cl_2 ÷ 4.2 $Cl_2:NH_3$ ratio = 1.0 mg/L NH_3 dose
- How much free NH_3 can we expect to see in the finished water?

Practice Problem 5 (cont)

- To answer that we'll first determine combined NH_3...
  - 4.3 mg/L measured Cl_2 ÷ 5 = 0.86 mg/L combined NH_3
  - 1.0 mg/L NH_3 dose - 0.86 mg/L combined NH_3 = 0.14 mg/L free NH_3

Practice Problem 5 (cont)

- Assuming we are still dosing 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 Cl_2 dose being destroyed to 5.6 mg/L of the Cl_2 dose destroyed?
  - 8.9 mg/L Cl_2 dosed – 5.6 mg/L Cl_2 destroyed = 3.3 mg/L Cl_2 destroyed

Practice Problem 5 (cont)

- Assuming we are still dosing NH_3 at 1.0 mg/L what would you expect to see happen to the finished water free NH_3 residual?

  - 3.3 mg/L Cl_2 ÷ 5 = 0.67 mg/L combined NH_3
  - 1.0 mg/L NH_3 dose - 0.67 mg/L combined NH_3 = 0.33 mg/L free NH_3