FAQs For Groundwater Supplies with Ammonia in Well Water

Useful references materials

IRWA Homepage: http://www.ilrwa.org/
For VA/ERP and NAP: http://www.ilrwa.org/Downloads.htm
For Building flushing (reopening) directions (1st box on page): http://www.ilrwa.org/index.htm
For Illinois EPA Drinking Water Watch: http://water.epa.state.il.us/dww/
For Illinois EPA Sample Collector Handbook NAP Chapter:
https://www2.illinois.gov/epa/topics/compliance-enforcement/drinking-water/Documents/NAP-Handbook-final.pdf
For Subtitle F: Public Water Supplies, Chapter I Pollution Control Board:
https://pcb.illinois.gov/SLR/IPCBandIEPAEnvironmentalRegulationsTitle35
2018, Julie Sievers, Iowa DNR Presentation:
http://www.iowaruralwater.org/presentations/2018/IRWA-AmmoniaChlorine2018.pdf

Ammonia complicates chlorination practices

You must either **"burn" the ammonia out** (remove it) **OR** form chloramines.

- Removal of ammonia can be accomplished through biological treatment and cation exchange following removal of hardness (e.g., Reverse Osmosis followed by a cation exchange resign cartridge).

Most Plants – **should** breakpoint to remove ammonia.

- Keep in mind ammonia levels **WILL** vary based upon source water quality (e.g., which well, time of year, etc.). Therefore, chlorine levels **MUST** be adjusted based upon testing.
- Competition exists for chlorine and you must overcome these competing reactions.
  - Generally, chlorine reactions follow this sequence:
    - Iron, Manganese, Hydrogen Sulfide, etc.
      - Iron will consume 0.64 times its concentration (mg/l) in Cl_2.
      - Manganese will consume 1.3 times its concentration (mg/l) in Cl_2.
      - Hydrogen Sulfide will consume 2.2 times its concentration (mg/l) in Cl_2.
    - Free Ammonia.
    - Monochloramine and Dichloramine.

Establish a "Free" chlorine residual.

- Theoretical: It takes 7.6 mg/L of chlorine to burn out 1.0 mg/l of ammonia and establish a free chlorine residual.
  - Remember you must overcome other reactions with things like Iron, Manganese, and Hydrogen Sulfide.
- Must maintain a minimum of 0.5 mg/l free chlorine residual in all areas of the distribution system.

Maximum NSF chlorine feed = 30 mg/l (as Cl_2) for gas and 10 mg/l (as Cl_2) for Sodium Hypochlorite (80 mg/l for 12.5% solution as product).

- This feed rate includes the sum of all points of application (pre, in process and post) and is based upon contaminants present when the gas or solution is made by the manufacturer.
- In round numbers, if using sodium hypochlorite anything over 1.3 mg/l of free ammonia in the source water and chloramine formation is needed. Likewise, if using gas Cl_2 anything over 3.9 mg/l of free ammonia in the source water and chloramine formation is needed.
  - Experience in IL is that, competition for Cl_2, maximum free ammonia of 1.0 and 3.0 mg/l for hypo and gas respectively.

Optimize chemical addition through review of water quality parameters and testing.

- Gradually increase chemical dosage without exceeding NSF feed rates.

Too much ammonia to establish a free residual

Must form chloramines (specifically, monochloramine).

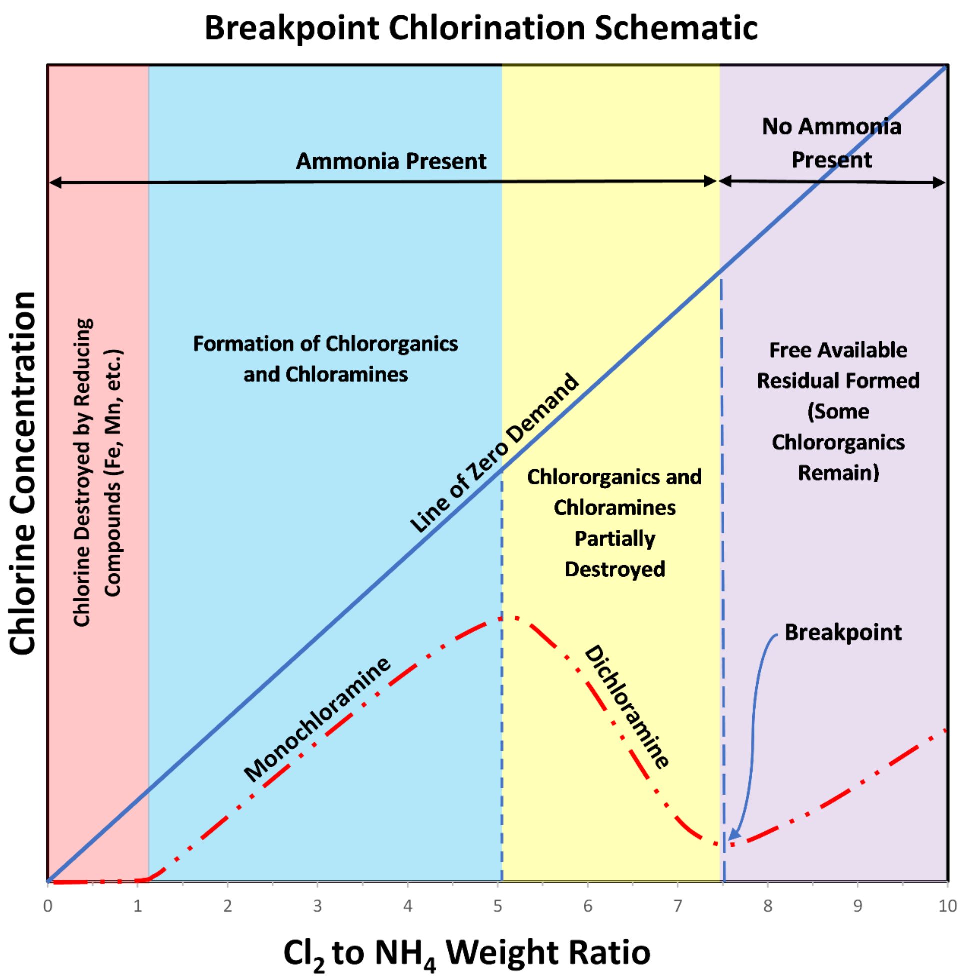
- As a starting point use the correct chlorine dosage to react with the ammonia present in the water, establish a chlorine to ammonia-N ratio of 5.06 to 1.
    - Remember, there is competition for chlorine and presence of iron and H_2S (etc.) is a factor.
- Must maintain 1.0 mg/l of total chlorine in all areas of the distribution system.
    - IMPORTANT NOTE: IF YOU ARE CHLORAMINATING YOU **WILL NOT** HAVE 'FREE CHLORINE" PRESENT.
        - Discontinue testing and reporting!

Optimize chemical addition through reviewing water quality parameters and testing.

- Remember NSF maximums still apply.
    - This feed rate includes the sum of all points of application (pre, in process and post) and is based upon contaminants present when the gas or solution is made by the manufacturer.
    - In round numbers, if using sodium hypochlorite anything over 2.0 mg/l of free ammonia in the source water and ammonia will not be bound up in the formation of monochloramine. Likewise, if using gas Cl_2 anything over 5.9 mg/l of free ammonia will not be bound up in the formation of monochloramine.
        - IF AMMONIA IS TOO HIGH, YOU PHYSICALLY **CANNOT FEED ENOUGH CHLORINE TO BREAKPOINT – EXCESS FREE AMMONIA WILL GET INTO THE DISTRIBUTION SYSTEM**

Optimize chemical addition through reviewing water quality parameters and testing.

- Gradually increase chemical dosage without exceeding NSF feed rates.
- Do not get on the wrong side of the curve by overfeeding Cl_2 **residual will go down.**



Refresher on the breakpoint curve

Until you reach breakpoint (7.6 to 1), **adding chlorine to water containing monochloramines with no free ammonia, will form dichloramine** (moving to the right on the breakpoint curve). Once dichloramine is formed, the reaction cannot be reversed to form monochloramine.

In this situation, increasing chlorine after monochloramine has been formed can adversely affect water stability, increase nitrification and decrease the ability to maintain residual disinfectant in distribution systems.

Optimize your chloramination practices

Measure Free Ammonia in your source water

- Start with a 5 to 1 chlorine to Ammonia-N ratio.

Measure Free Ammonia throughout your treatment process and know the vulnerabilities of your treatment train

- Ion exchange can actually "dump" free ammonia prior to regeneration based upon hardness, may have to begin regenerating based upon free ammonia rather than hardness
- Existing filter media may be removing some free ammonia (may be biologically active)
- Corrosion inhibiters may be a food source for nitrifying bacteria

Measure Monochloramine, Total Chlorine, and Free Ammonia following treatment.

- If Mono = Total and no free ammonia you have optimized.
- If free ammonia is still present, increase chlorine feed (up to NSF limit) and remeasure.
    - Remember you can only feed so much Cl_2, you may be stuck with some free ammonia.
- If total higher than mono and no free ammonia, decrease chlorine feed and remeasure.

Chloramines are more stable (long lasting) at higher pH.

- Also, nitrifying bacteria growth rate declines as pH increases, and declines significantly at pH's approaches 9 and above.

What happens after chloramines are formed

After chloramines are formed, they begin to decay and release ammonia back into the water.

- As decay occurs, monochloramine is converting to dichloramine and then dichloramine begins to dissipate.
- As pH drops, the rate of dichloramine formation is more rapid and it lasts longer in the water. (Wahman 2017).
    - Note: Dichloramine is a precursor in formation of NDMA (Nitroso-dimethylamine). NDMA is a carcinogen that will likely be regulated in drinking water in the future.

MUST deal any free ammonia that may be present in the distribution system – the result of which is **<u>nitrification</u>**.

- Nitrification is the process where ammonia is broken down to form nitrite (MCL=1.0 mg/l) and nitrate (MCL=10.0 mg/l).

Dealing with nitrification

Limit nitrification:

- Control chloramination process
- Maintain monochloramine residual above 1.5 mg/L, AWWA M-56
- Increase flushing (directional flushing with scouring velocity),
- Decrease dead-ends in distribution system (looping mains and auto-flushers)
- Manage stored water (If you don't have capability to increase turnover, you need to plan to spend money on such things as mixers, altitude valves, electrically controlled valves, simple SCADA, etc.)
- Consider alternative disinfectants (e.g., chlorine dioxide), pH adjustment and biocides (jury still out).
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Effects if not controlled	
Chemical:	**Biological:**
Depletes Chlorine Residuals	Increase in HPC (If Tested)
Nitrites/Nitrates Increase	Formation of Ammonia Oxidizing Bacteria
pH & Alkalinity go Down	Formation of Nitrite Oxidizing Bacteria
Potential to Create Lead/Copper Corrosion	
Increased Chemical Usage	
Potential for Increased DBP Formation	

Considerations:		
Nitrifiers WILL develop especially in the presence of:	Opportunistic and WILL develop anywhere and everywhere:	Must DECREASE water age wherever and whenever possible:
High Ammonia	Raw Water Lines	Frequent Flushing
pH > 7	Aerator/Reaction Basin	Remove Tuberculation in Pipes
Warmer Temperatures	Clarifiers/Cones – Sludge Blanket	Water Storage Management
Sufficient Alkalinity, Oxygen and Nutrients	Filters/Softeners	De-Stratify Towers Deep Cycle Towers
	Storage Tanks	Reduce Excess Stored Water
	Distribution Piping	

If supplemental disinfection becomes necessary

REMOTE CHEMICAL FEED LOCATIONS: Add Ammonia first, establish a SAMPLE POINT WELL DOWNSTREAM TO CHECK concentrations, THEN CHLORINE FEED, and another SAMPLE POINT WELL DOWNSTREAM TO CHECK effects.

- If good monochloramine residual present:
  1. TYPICALLY ADD AMMONIA FIRST – ADD upstream far enough to assure good mixing prior to next step.
  2. Provide Sample Point to measure ACTUAL FREE AMMONIA in the water – make sure target free ammonia is present to hit target monochloramine residual.
  3. ADD Chlorine to form monochloramine residual.
  4. May require 15 to 60 seconds mixing and reaction time downstream of chlorine feed before adding sample point for CHLORINE ANALYZER, or grab samples. If you have a little pump station – this means you have to tap the water main outside of the building, and run a line back into the building for proper sampling or to hook to an analyzer.

What can happen if nitrification takes control?

Loss of disinfection residual WILL lead to:

- Violation of State Regulation
- TCR Violation of Federal/State Regulation
- Vulnerability to pathogens including Legionella and naegleria fowleri
    - Legionella at Illinois Veteran's Home in Quincy
    - Naegleria outbreaks in Louisiana and recently in Texas
        - Lake Jackson, Texas

Nitrification action plan monitoring

Measure free and total ammonia along with nitrite and nitrate in the distribution system to confirm the level of nitrification that is occurring.

- In distribution, increase free Ammonia-N indicates monochloramine residual is being decayed and ammonia is being release.
- If total Ammonia-N is decreasing, it is likely being "consumed" by Ammonia-Oxidizing Bacteria (nitrification is occurring).

Measuring total chlorine along with monochloramine.

- Will indicate the decay of mono to di prior to reverting to ammonia.

Check pH.

- Lowered pH will also indicate decay of mono.

MATH REFRESHER

Special Reminder- The pounds formula equation works directly if the chemical is 100% pure (such as chlorine gas). If the chemical is not 100% pure, divide the pounds of chemical by the purity percentage (in decimal form).

EXAMPLE 1

What is the feed rate (mg/l) if 10 lbs of chlorine gas is added to 500,000 gallons of water?

$$lbs/Day = (MGD)(mg/l)(8.34) \equiv mg/l = \frac{\text{lbs/Day}}{(\text{MGD})(8.34)}$$

$$mg/l = \frac{10 \text{ lbs}}{(0.5 \text{ MGD})(8.34)} = \frac{10}{4.17} = 2.398$$

EXAMPLE 2

What is the feed rate (mg/l) if 10 lbs of 12% Sodium Hypochlorite is added to 500,000 gallons of water?

$$lbs/Day = \frac{(MGD)(mg/l)(8.34)}{Purity\ (\%\ as\ a\ Decimal)} \equiv mg/l = \left(\frac{\text{lbs/Day}}{\text{(MGD)(8.34)}}\right) * (Purity\ as\ a\ Decimal)$$

$$mg/l = \frac{\text{10 lbs}}{\text{(0.5 MGD)(8.34)}} * .12 = \frac{10}{4.17} * .12 = .288$$

EXAMPLE 3

Over a seven-day period, a system produced 40,000 gallons of water. In that time period, the system used 41.64 liters of 5% NaOCl solution (w/v). What is the average chlorine dosage in mg/L?

Convert Liters of NaOCL solution to Gallons: 1 gallon NaOCl = 10 lbs

1 gallon = 3.785 liters: $Gallons = \frac{\text{Liters}}{\text{Liters/Gal.}} = \frac{41.64}{3.785}$ = 11.0

$$lbs/Day = \frac{(MGD)(mg/l)(8.34)}{Purity\ (\%\ as\ a\ Decimal)} \equiv mg/l = \left(\frac{\text{lbs/Day}}{\text{(MGD)(8.34)}}\right) * (Purity\ as\ a\ Decimal)$$

$$mg/l = \frac{\text{110 lbs}}{\text{(0.04 MGD)(8.34)}} * .005 = \frac{110}{.333} * .005 = 1.65$$

EXAMPLE 4

The chemical feed rate is 40 mL/min of 0.25% NaOCl solution (w/v) and the flow is 35 gpm. What is the chlorine dosage in mg/L as Cl2?

Convert mL to Gallons: 1mL = 0.000264172 Gal. 1-gallon NaOCl = 10 lbs 1440 Minutes/Day

Convert feed rate to a 24-hour period: $(40) * (1440) * (.000264) = 15.21\ Gallons$

Convert flow rate to a 24-hour period: $(35) * (1440) = 50{,}400\ Gallons$

$$lbs/Day = \frac{(MGD)(mg/l)(8.34)}{Purity\ (\%\ as\ a\ Decimal)} \equiv mg/l = \left(\frac{\text{lbs/Day}}{\text{(MGD)(8.34)}}\right) * (Purity\ as\ a\ Decimal)$$

$$mg/l = \frac{\text{15.21 (Gal)} * \text{10 (lbs)}}{\text{(0.0504 MGD)(8.34)}} * .0025 = \frac{152.1}{.420} * .0025 = 0.905$$