Public Water Systems: Temporary Conversions to Free Chlorine

Prepared by:
Water Supply Division
TCEQ RG-631
August 2023

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY • PO BOX 13087 • AUSTIN, TX 78711-3087

Contents

Introduction

Disinfection is a critical step in treating and maintaining safe drinking water. In Texas, public water systems (PWSs) are required to maintain a disinfectant residual throughout the entire distribution system so that every customer receives safe water. All water systems must maintain residuals of either:

- free chlorine
- chloramines—specifically monochloramine.

In areas with warm climates, bacteria grow more quickly and disinfectants, like chloramine, degrade more quickly. This can lead to nitrification events within distribution system piping. PWSs that use chloramine usually perform periodic, temporary conversions to free chlorine as either a maintenance measure or as a response to nitrification.

The purpose of this guidance is to assist PWSs that normally carry a chloramine residual within their distribution system to perform successful temporary conversions to free chlorine.

This guidance is not a substitute for the rules. If there is a discrepancy between this guidance and the rules, follow the rules.

Acronyms and Definitions

Term	Definition
AOB	ammonia oxidizing bacteria
DBP	disinfection byproduct
EPRS	Emergency Preparedness and Response Section
FMT	Financial, Managerial and Technical
HAA5	haloacetic acid
NaOCl	sodium hypochlorite (bleach)
NOB	nitrite oxidizing bacteria
PTRS	Plan and Technical Review Section
PWS	public water system
SOP	standard operating procedure
TCEQ	Texas Commission on Environmental Quality
TOP	Texas Optimization Program
TTHM	total trihalomethane
WSD	Water Supply Division

Overview of Chloramines and Nitrification

Monochloramine is the desired disinfectant species present with the use of chloramines. It is formed when ammonia and free chlorine are mixed at the correct ratios. Nitrification occurs when nitrifying bacteria consume the ammonia that is always present in small amounts with monochloramine.

Note: Chloramine chemistry and nitrification biology are complicated topics. This guidance will focus on temporary conversions to free chlorine and will not describe the details of chloramines and nitrification. **See the Contact section for more information on trainings.**

Normal chloramine reactions, in the monochloramine zone: there is always some amount of ammonia present.

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

$$2\ NH_2Cl \leftrightarrow NHCl_2 + NH_3$$

where:

$HOCl$ = hypochlorous acid (formed when free chlorine is dissolved in water, strongest disinfectant)

NH_3 = ammonia

NH_2Cl = monochloramine (desired chloramine species)

H_2O = water

$NHCl_2$ = dichloramine (undesirable chloramine species, non-disinfecting, smelly)

Nitrification can occur when ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), together known as nitrifying bacteria, are present with available ammonia. These nitrifying bacteria consume ammonia and nitrite as a food source and the resulting products are nitrite and nitrate. As nitrifying bacteria populations grow, they exert a demand on monochloramine and cause the total chlorine and monochloramine residuals to drop.

Nitrification Reactions:

$$NH_3 + O_2 + AOB \rightarrow NO_2^- + 3\ H^+ + 2\ e^- + \text{more AOB growth}$$

$$NO_2^- + H_2O + NOB \rightarrow NO_3^- + 2\ H^+ + 2\ e^- + \text{more NOB growth}$$

where:

NH_3 = ammonia
O_2 = oxygen
NO_2- = nitrite
H^+ = hydrogen
e^- = electron
NO_3^- = nitrate

Nitrifying bacteria live in biofilm along pipe walls where they convert ammonia in water to nitrite and then to nitrate. Ammonia can be present in water naturally, through addition as part of the water treatment process, or from the decomposition and decay of chloramines. Figure 1 depicts this process.

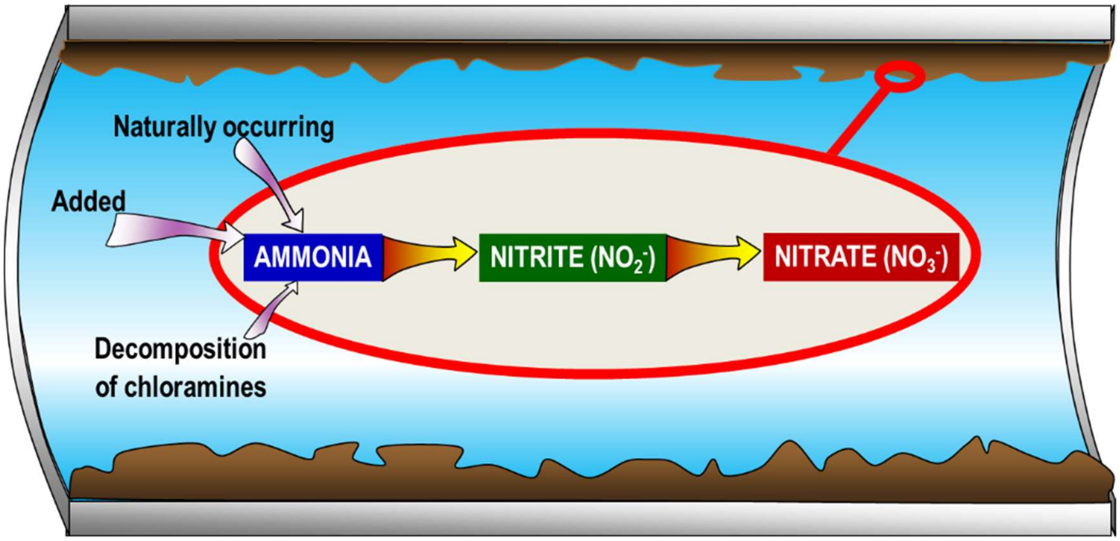


Figure 1. Nitrification in water pipes.

Nitrification and Low Residuals

Nitrification causes loss of total chlorine and monochloramine residual. Low or no disinfectant residual may allow regrowth and persistence of bacteria which can lead to positive coliform tests, potential illness, and violations.

Without nitrification, monochloramine residuals may last for weeks throughout the distribution system. With nitrification, residuals can be destroyed quickly. Figure 2 shows the difference in total chlorine, monochloramine, ammonia, nitrite and nitrate in the water from in a distribution system under normal conditions and nitrification conditions.

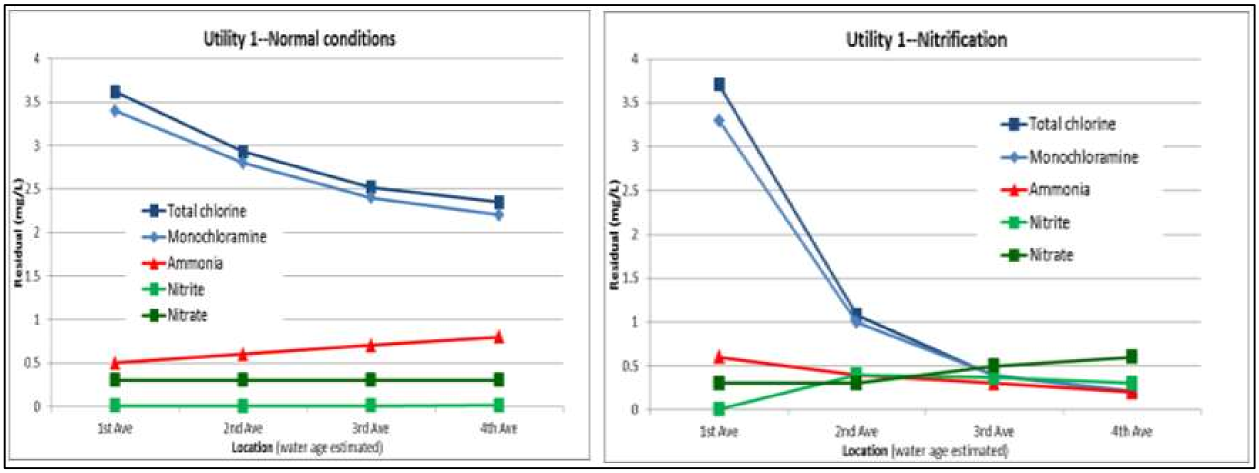


Figure 2. Total chlorine, monochloramine, ammonia, nitrite and nitrate in the water from a utility under normal conditions and nitrification conditions.

Other Causes of Low Residuals

Temporary conversions to free chlorine only work on nitrification. Nitrification is not the only thing that can cause low residuals. Other issues that can cause low residuals and will not be helped by a conversion to free chlorine:

Water age—characterized by decreased total chlorine and monochloramine residuals; increased free ammonia residuals; no change to nitrite and nitrate concentrations from treatment plant to distribution sample sites.

Cross-connections—characterized by decreased total chlorine and monochloramine residuals; potential increase to total inorganic nitrogen (sum of nitrogen in monochloramine, free ammonia, nitrite, and nitrate), especially if wastewater is involved; potential higher inorganic levels (metals, salts, TDS, etc.) in distribution than leaving plant.

Non-nitrifying microbiological growth—characterized by decreased total chlorine and monochloramine residuals; potential increases in heterotrophic plate counts (HPCs).

Treatment failure—characterized by low total chlorine and monochloramine residuals leaving the treatment plant.

Increased oxidant demand in source water—characterized by lower total chlorine and monochloramine residuals leaving the treatment plant and/or rapid decay at distribution sites near the plant.

Unstable chloramines—characterized by chlorine to ammonia-nitrogen weight ratio greater than 5:1; zero free ammonia leaving plant; monochloramine residual much less than total chlorine residual.

Other TCEQ training courses and presentations describe clues to detect whether low residuals are caused by nitrification or something else. **See the Contact section for more information on trainings.**

Pros and Cons of Free Chlorine Conversions

Pro: It Works!

A temporary conversion to free chlorine is the only way to ‘starve’ AOB. Otherwise, bacterial colonies continue to bloom because they constantly have access to food in the form of ammonia. Free available ammonia cannot be present in the water if there is a free chlorine residual.

Con: It Is More Work

When a free chlorine conversion is planned and performed correctly, there will be extra work for the operators from start to finish. The operators must determine the required chlorine dose or coordinate with a wholesale supplier to receive free chlorine residuals. Operators must verify that all valves required to conduct the conversion are operable and fix any that aren’t working properly. Flushing free chlorine quickly and efficiently through a distribution system may require additional labor hours, and flushing monochloramine quickly and efficiently into the distribution system at the end of the conversion requires the same level of effort. Remember—the free chlorine conversion may not work if it is not planned and performed correctly.

Con: Potential Taste and Odor Complaints from Customers

If the free chlorine is not flushed through your distribution system quickly, there could be areas of unstable chloramines (dichloramine and trichloramine) that smell bad. As Figure 3 illustrates, there will always be some dichloramine and trichloramine where free chlorine and monochloramine meet in the distribution system, but a fast, efficient conversion to free chlorine minimizes dichloramine and trichloramine and is better for your customers.

Some customers may notice the difference in taste and odor from free chlorine once the conversion is fully established. Attempt to set customer expectations before the start of the conversion to reduce complaints.

Figure 3. Unstable chloramines in a pipe at the boundary between water with a free chlorine residual and water with a monochloramine residual.

Con: Potential Color Complaints from Customers

Extra flushing at the start of a free chlorine conversion can stir up sediments that have deposited in the distribution system and cause color complaints. Some PWSs, particularly those with iron and manganese issues, don’t flush regularly because it stirs up sediments that have deposited in the distribution system. A lack of regular flushing builds up sediments that nitrifying bacteria live within and can promote nitrification. The distribution system will have a better chance of resisting nitrification after the conversion if it is thoroughly scoured and cleaned before the conversion.

During the conversion free chlorine residuals may oxidize more of the naturally occurring metals, like iron and manganese, resulting in additional color. Attempt to set customer expectations before the conversion to reduce complaints.

Planning a Free Chlorine Conversion

There is more to a temporary free chlorine conversion than just turning off the ammonia feed. Planning will differ for:

- Systems that inject chlorine and ammonia to form chloramines.
- Systems with source water that contains free ammonia.
- Systems that purchase water with a chloramine residual and do not have the capability to inject chlorine on their own.

Planning Topics

There are several topics and planning questions to address before you can begin your free chlorine conversion, helping both your staff and customers.

What is your **source of free chlorine** water?
What is your **schedule** going to look like?
Where and when will you **monitor**?
Who should you **communicate** with prior to beginning, during, and at the end of the conversion?

These topics will be discussed in detail in the following sections.

Source

A source of free chlorine is needed in order to perform a successful conversion to free chlorine. The following scenarios describe possible sources of free chlorine.

Scenario 1—System treats raw source water by injecting free chlorine and free ammonia.

- Solution: Turn off the ammonia feed. This is the simplest scenario.

Scenario 2—System purchases water with a chloramine residual and has the ability to inject free chlorine and free ammonia.

- Solution: Turn off the ammonia feed and turn up the free chlorine feed.

  Note: See **Amount of Free Chlorine** (below) and Attachment 1 for help determining if your chlorine injection system has enough capacity for a free chlorine conversion.

Scenario 3—System is purchasing water with a chloramine residual and has no ability to inject free chlorine.

- Solution: Work with the water supplier to schedule a free chlorine conversion.

Scenario 4—System uses a raw water source that contains natural ammonia and injects free chlorine.

- Solution: Turn up the free chlorine feed.

  Note: See Amount of Free Chlorine and Attachment 1 for help determining if your chlorine injection system has enough capacity for a free chlorine conversion.

Amount of Free Chlorine

If your PWS receives water with a chloramine residual and/or free ammonia, the dose of free chlorine must be high enough to overcome any ammonia and chloramine that is present in the water. There may also be some unmet chlorine demand in the water from chemicals like iron, manganese, total organic carbon, hydrogen sulfide, and nitrite.

Attachment 1 of this document describes how to calculate the required chlorine dose and feed rate for a free chlorine conversion.

Schedule

It is important to plan your schedule before the conversion begins. The following sections contain information that will help develop a schedule.

Sequence of Flushing

Free chlorine must be flushed through your distribution system as efficiently as possible, beginning at the entry point, then to the nearest flush points, then to the farthest flush points. This procedure should be discussed and planned at length prior to beginning. Do not wait to plan out this sequence and timing in the field.

All distribution valves must be operable. Before starting the conversion, find and fix any inoperable valves that you will need to move free chlorine through your distribution system.

Do not open the farthest valves first. Figure 4 illustrates a distribution system. Each branch represents a different part of your system with a flush location at the end of each branch. Starting the flush at the farthest point in the distribution system may promote the formation of stinky di- and tri-chloramine at points closer to the source.

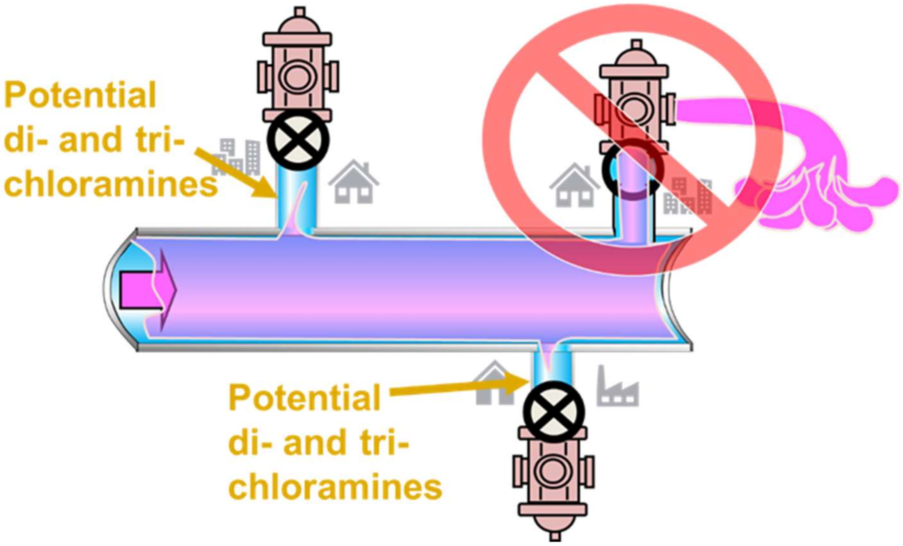


Figure 4. A distribution system with three branches and flush points at the end of each branch.

Flush sequentially, beginning nearest the entry point, followed by intermediate flush points, then to the far reaches of the distribution system. Doing so will allow the free chlorine to move evenly and efficiently through the entire distribution system. Figure 5 shows this strategy.

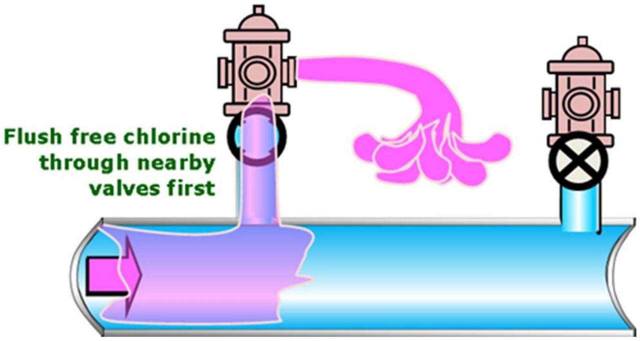


Figure 5. Flush through the nearest points first.

Tank Levels

Before you start the conversion, decrease the amount of water in all storage tanks. If possible, start with the tanks nearest the source of free chlorine, followed by the farthest tanks. The purpose is to make it quicker for the free chlorine to be distributed throughout the distribution system. If the storage tanks are full, it will take longer for monochloramine to be replaced by free chlorine. You will also use up more of your chlorine supply overcoming monochloramine residuals in full tanks.

Figure 6 is an example of how free chlorine mixes into a tank full of monochloramine. Water enters the tank at the lower right-hand corner and tank water exits to the lower left. Time increases from left to right. If the tank had started at half its volume, the conversion of the tank to free chlorine would have been much faster.

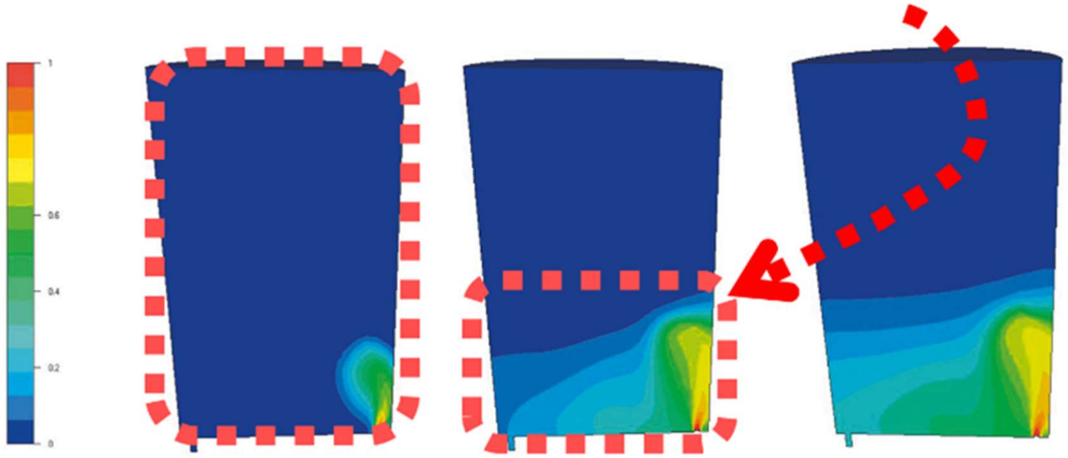


Figure 6. Replacement of monochloramine by free chlorine inside a storage tank over time.

Monitoring

In order to track the spread of free chlorine through your distribution system, you must monitor for four parameters at each flush point:

- Total chlorine
- Free chlorine
- Monochloramine
- Free ammonia

You can be certain that you have a monochloramine residual when both of the following are true:

- Total chlorine is about equal to monochloramine.
- Free ammonia is greater than zero.

Note: the free chlorine residual may appear to be above zero at this point; however, this is a false positive caused by monochloramine interference with the free chlorine test. Free chlorine cannot be present when free ammonia levels are significantly above zero.

You can be certain that you have a free chlorine residual when all of the following are true:

- Total chlorine is about equal to free chlorine.
- Monochloramine is about equal to zero.
- Free ammonia is about equal to zero.

Once you have converted the entire distribution system to free chlorine, you can just monitor free chlorine until it is time to switch back to monochloramine.

Note: Some water will have small concentrations of chlorine-based constituents left after breakpoint chlorination is achieved that is measured by a total chorine test but is not free chlorine—for example, organochloramines. Free chlorine may never equal total chlorine exactly. Free chlorine and free ammonia cannot occur together to any measurable degree. If you find that you have a substantial free chlorine result and a free ammonia result near zero, the free ammonia is a false positive. With the free ammonia test methods that are commonly available, a free ammonia reading less than or equal to 0.05 mg/L as nitrogen should be considered a zero reading.

Communication

While we strongly recommended that you disclose your conversion schedule to everyone that may be impacted, it is not a TCEQ requirement that you do so. Keep in mind that communication with both internal and external entities will help to make your temporary conversion to free chlorine a success.

The following is a list of potential people and entities that you should inform of the conversion.

Internal Communication

- Utility managers
- Licensed operators
- Utility personnel who will help with the conversion

External Communication

- TCEQ
- Chemical suppliers
- Downstream customer systems
- Residential and commercial customers, particularly medical facilities and dialysis centers because they may use filters that are sensitive to free chlorine residuals.

Notifying TCEQ

You should always notify TCEQ at least 30 days prior to beginning of a free chlorine conversion, or as soon as possible, so that, if necessary, we can coordinate the collection of your quarterly disinfection byproduct (DBP) samples. At systems with source water that contains organic matter, it is normal for DBP levels to spike in the distribution system during a temporary conversion to free chlorine. For this reason, TCEQ will allow a delay in the collection of DBP samples for up to 30 days during a calendar year since water quality during this time does not represent normal operating conditions. If a system continues to use free chlorine for longer than 30 days in a calendar year, the use of this type of disinfectant is no longer considered temporary and thus **no additional DBP sampling delay will be allowed**.

To notify TCEQ of a temporary conversion to free chlorine, please send an email to DBP@tceq.texas.gov or call 512-239-4691 and ask to speak to a member of the Drinking Water Quality team. Be prepared to include:

- PWS Name
- PWS ID
- Point of Contact Name
- Point of Contact Phone Number
- Point of Contact Email
- Begin and End dates of the conversion (this should include the time that it takes to flush the distribution system and return to chloramines)
- Reason for the conversion (for example, annual maintenance, nitrification, low residuals)

Once your temporary conversion is complete, you should contact TCEQ again to confirm that you have returned to normal treatment conditions.

Contacting Customers and Suppliers

It may be helpful to contact your chemical suppliers prior to beginning your conversion, especially if you will need to schedule additional deliveries to meet increased usage. Additionally, your wholesale customers should take advantage of your conversion to free chlorine as well as coordinate with TCEQ to delay quarterly collection of their DBP samples.

To limit the number of retail customer complaints or questions about changes to water taste and odor, we recommend that you notify your customers of the scheduled conversion. Set their expectations for potential odor, taste, and color issues. **Do not refer to the conversion as a chlorine “burn” or “burnout”**—it is not an accurate representation of the process and does not instill confidence with customers if you to tell them you are “burning” their water. You may use the announcement template on our Temporary Free-Chlorine Conversion webpage.[1]

Ending the Conversion

After the conversion, reverse the process to return to monochloramine.

Repeat the sequential flushing process to push the normal monochloramine water through the system.

- Repeat deep-cycling tanks.
- Repeat monitoring to ensure all areas are returned to monochloramine.
- Write down ‘lessons learned’ for next time.

Monitoring the End of the Conversion

While you are switching back to monochloramine, monitor all four parameters:

- Total chlorine
- Free chlorine
- Monochloramine
- Free ammonia

After the conversion, you will know that you are back to monochloramine when the following occur:

- Total chlorine is about equal to monochloramine
- Free ammonia is greater than zero
- Free chlorine does not matter. If monochloramine is present, free chlorine readings are false positives.

Example: Smallville Purchased Water with Chloramines and Booster Treatment

Questions for consideration:

- Where are “critical” control points for this system?

---

[1] www.tceq.texas.gov/drinkingwater/disinfection/temporary-free-chlorine-conversion

- What would the sequence of flushing locations look like?
- What are some critical monitoring locations for this system?

In the map of Smallville below, the source water comes in at the lower left and booster treatment occurs at the same spot. This is the kind of map used for a nitrification action plan (NAP) or coliform sample siting plan.

In Figure 7, pipes are designated by blue lines—larger diameter pipes are drawn with thicker lines. The pressure plane boundary includes all customers inside and outside the city limit served by the PWS. One elevated tank is shown at the lower left corner. Valves are not shown here but should be included in your distribution map.

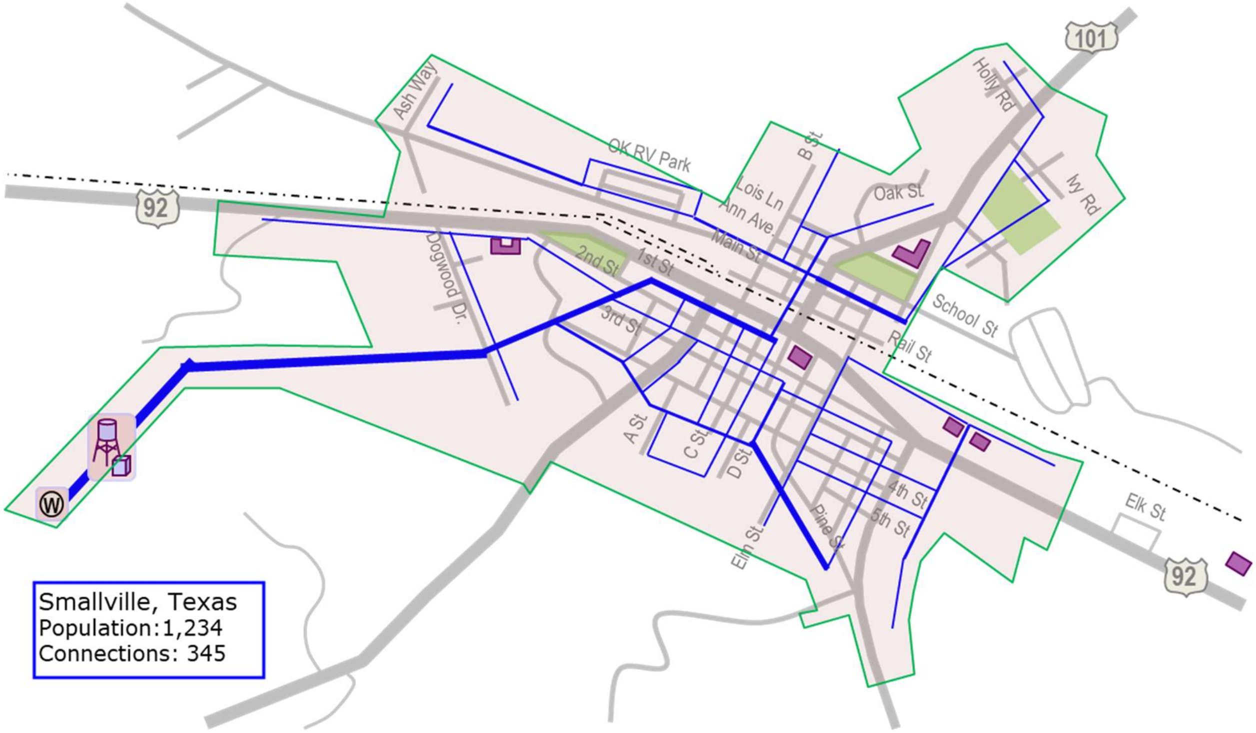


Figure 7. Map of example public water system, Smallville.

Before the Conversion

Check the flushing strategy.

- Identify the flush locations and draw them on a map (see Figure 8).
- Do all the valves that are needed to direct flow and flush work?
- Do all operators understand which locations to flush first, second, etc.?
- Do the operators understand what tests to run?

Plan how low to drop the tank levels.

- Calculate the required chlorine dose and chlorine feed rate for the conversion.
- Does the chlorine injection system have enough capacity (See Attachment 1)?

Communicate externally.

- Contact TCEQ.
- Contact wholesale water supplier and downstream wholesale customers.
- Coordinate with chlorine vendor.
- Send notice of conversion to retail customers.

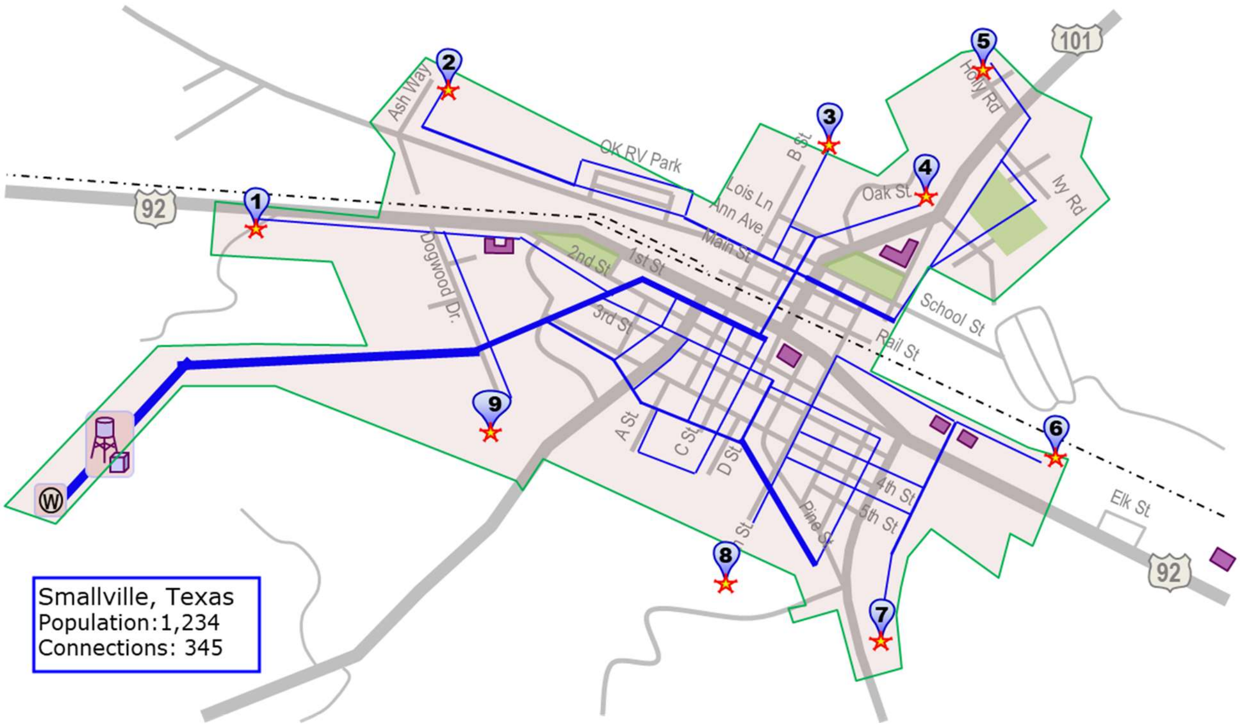


Figure 8. Map of example public water system, Smallville, containing all the identified flush locations.

Smallville staff add flush locations to their map and decide on the following flush sequence, beginning at the booster station and moving outward.

1. #9
2. #8 and #1
3. #6 and #7
4. #3 and #4
5. #5 and #2

Starting the Conversion

Smallville staff lower the elevated tank level. Flush location #9 is opened up, the ammonia feed is turned off in the booster station, and the chlorine feed rate is adjusted to the desired free chlorine residual leaving the booster station. Smallville staff begin to slowly raise the elevated tank level to draw in and mix more free chlorine into the tank and monitor flush location #9.

After Smallville staff have determined that total chlorine ≈ free chlorine, monochloramine ≈ 0, and free ammonia ≈ 0 at flush location #9, they notice that there is more chlorine demand than they had anticipated. They adjust the chlorine feed rate again to overcome the excess chlorine demand.

Smallville staff allow the elevated tank level to drop again to clear out some of the mixed water from the tank. The residuals they measure leaving the elevated tank indicate that the tank water is in Zone 3 on the breakpoint curve. (See Attachment 1 of this document for a discussion of the breakpoint curve and its zones.)

Soon after that, the free chlorine and total chlorine residuals drop at flush location #9 and the monochloramine residual begins to rise. Free ammonia remains at zero. After the elevated tank has dropped as low as they want it to and the tank begins filling again, the total chlorine and free chlorine residuals start rising and the monochloramine residual drops to zero again at flush location #9.

Once the residuals are back to desired levels at flush location #9, Smallville staff open flush locations #8 and #1, close flush location #9, and repeat the monitoring process at #8 and #1. This pattern is followed for the remaining sequence of flush locations.

During the Conversion

Once free chlorine ≈ total chlorine throughout the distribution system and free chlorine residuals are up to the desired levels, Smallville staff end the heavy flushing. Smallville staff only monitor free chlorine until it is time to end the conversion. The elevated tank is returned to its normal fill settings.

Ending the Conversion

Smallville staff repeat the same processes as the start of the conversion, only now to draw monochloramine back through the system and all of the following:

- Dropping the elevated tank level.
- Resetting the booster station to feed chlorine and ammonia.
- Following the same sequence of flushing.
- Cycling the elevated tank.
- Monitoring total chlorine, free chlorine, monochloramine, and free ammonia.

The conversion is complete and heavy flushing ends when normal monochloramine and free ammonia residuals are established throughout the distribution system.

Free Chlorine Conversion Tips

Starving bacteria takes time. Plan to expose all locations in the distribution system to free chlorine for more than a few days. Two weeks of free chlorine exposure at the ends of the distribution system is a good rule of thumb.

Nitrifying bacteria can live in cracks and elbows—any areas where bulk water does not scour out the biofilm. These are slow growing organisms. Therefore, it is recommended that a temporary conversion to free chlorine be scheduled for 30 days for maximum benefit.

One reason that PWSs use chloramines is because their water tends to form regulated DBPs with free chlorine—specifically total trihalomethanes (TTHM) and haloacetic acids (HAA5). During a temporary conversion to free chlorine, those levels will be higher than usual for systems that normally use chloramines.

TCEQ is reluctant to promote free chlorine conversions that last longer than 30 days unless absolutely necessary to fully convert the system.

We can reschedule TTHM and HAA5 sampling around abnormal operating conditions, generally setting an upper limit of 30 days per year for abnormal operating conditions. If you conduct a free chlorine conversion for longer than 30 days, TCEQ considers that to be a normal operating condition, subject to any and all DBP compliance sampling.

The bottom line—pull the free chlorine through your system as quickly and efficiently as possible to maximize the benefit of the free chlorine conversion.

Long-term Actions

What if free chlorine conversions are not enough to control nitrification?

In a system that has long-term issues with nitrification that can't be controlled by periodic free-chlorine conversions, longer term solutions may be needed. Examples include:

Looping mains and eliminating stagnant areas in the distribution system.
Adding tank mixers or modifying tank inlets and outlets.
Changing or adding chlorine and ammonia injection stations.
Converting to free chlorine permanently in the distribution system with aeration for trihalomethane removal.

These longer-term solutions are outside the scope of this guidance document. Seek professional help to consider these or similar changes.

TCEQ must approve plan and specification submittals from a licensed engineer before a PWS is allowed to change the chemical injection capacity of an existing treatment plant like a booster station. Make sure to provide the engineer with the highest possible monochloramine and free ammonia residuals entering the treatment plant so that the engineer sizes the chemical injection system appropriately for all expected conditions.

Regulatory Reference

TCEQ established rules and regulations for public water systems (PWS) in Title 30, Texas Administrative Code (30 TAC), Chapter 290.

The rules in 30 TAC, Subsection 290.42(e) specify disinfection equipment design requirements. The rules in 30 TAC, Section 290.110 specify disinfectant residual requirements. Find these rules and others on the webpage Rules and Regulations for Public Water Systems.[2]

TCEQ Contact Information

Financial, Managerial and Technical (FMT) Assistance program can provide free, on-site assistance while you plan your conversion. While you plan your conversion, FMT representatives may assist with:

- Tank cycling
- Distribution system flushing
- Customer notification

Contact us at:

FMT@tceq.texas.gov or 512-239-4691

Also contact FMT for free training opportunities on chlorine chemistry and nitrification biology.

Texas Optimization Program and Response team can answer your questions about:

- chloramination

---

[2] www.tceq.texas.gov/drinkingwater/pdw_rules.html

- nitrification
- breakpoint curves
- unidirectional flushing practices
- disinfection byproducts
- any other topic discussed in this guidance]

Contact us at:

TOP@tceq.texas.gov or 512-239-4691

Also see our Controlling Nitrification webpage.[3]

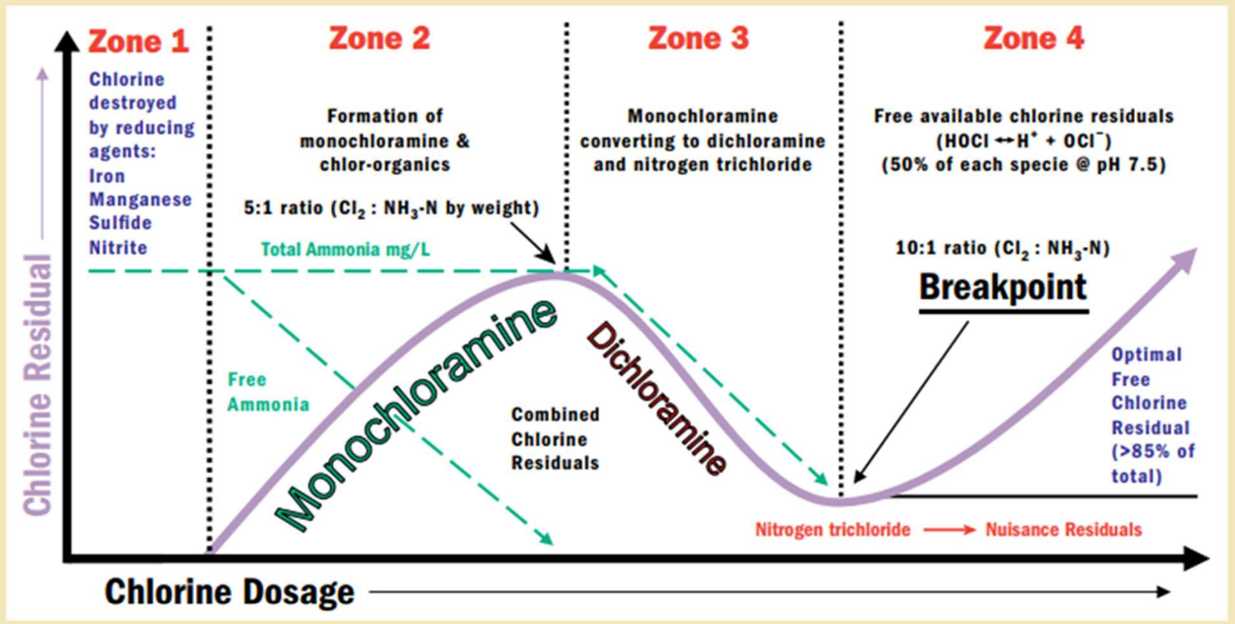
---

[3] www.tceq.texas.gov/drinkingwater/disinfection/nitrification.html

Attachment 1: Free Chlorine Conversion Calculations

A goal of a free chlorine conversion is to breakpoint chlorinate the source water so a free chlorine residual can occur.

Chloramine chemistry is described by the chlorine breakpoint curve. Here is an example of a breakpoint curve published in the June 2008 edition of the American Water Works Association’s (AWWA’s) OpFlow magazine in an article titled, “Do You Really Have a Free Chlorine Residual?” The curve shows the residual that would be measured by a total chlorine test as the chlorine dose is increased in a source water.



***Zone 1:** Initial chlorine demand is caused by reducing agents (Fe^{+2}, Mn^{+2}, H_2S, NO_2^-) that consume most of the chlorine applied prior to forming combined residuals.

Zone 2: Additional chlorine combines with available total ammonia and reactive organics until forming maximum monochloramine residual. At the same time, uncombined free ammonia is being depleted until it reaches zero.

Zone 3: More chlorine dosage converts monochloramine into odorous dichloramine and nitrogen trichloride. Total combined chloramine residual decreases and ammonia concentration approaches zero at the breakpoint.

Zone 4: True free chlorine residual is obtained and provides the least nuisance odor when free residuals make up 85 percent of the total chlorine concentration. Nuisance combined chlorine residuals survive and the potential for disinfection by-products (trihalomethane and haloacetic acid) formation remains, as free chlorine residual develops further.

Figure 9. AWWA Breakpoint Chlorination Curve

As indicated in the figure above, breakpoint occurs at an approximate chlorine to ammonia-nitrogen weight ratio of 10:1 after other chlorine demands have been met.

At chlorine to ammonia-nitrogen weight ratios below the breakpoint (dip), all chlorine is in a combined form with nitrogen and can only be measured by a total chlorine test. (A free chlorine test may show a positive result below the breakpoint; however, it is a false positive because monochloramine interferes with the method.)

Beyond the breakpoint, adding more chlorine establishes a free chlorine residual.

If there are both monochloramine and free ammonia in the water you are receiving, the received water must be somewhere in Zone 2 on the breakpoint curve and the chlorine to ammonia-nitrogen weight ratio must be less than about 5:1.

Calculation is required to determine the chlorine dose and chlorine feed rate for a free chlorine conversion. This is particularly important for PWSs that boost chloramines as opposed to providing the primary treatment of a raw water source. Chlorine injection systems in booster stations are often undersized for reliable breakpoint chlorination of the water they receive.

The breakpoint reactions between free chlorine and monochloramine to go from Zone 2 to Zone 4 take time to complete. The amount of time is dependent on many factors, water temperature and pH being among the most important. Generally, these breakpoint reactions complete within 1 hour. Reactions of chlorine with other reducing agents and organics in the source water (unmet chlorine demand) can also take some time to complete.

Measure free chlorine residuals at least an hour downstream of the chlorine injection point to confirm that the chlorine feed rate has been set appropriately.

Methodology: Monochloramine in Source Water

If your source water has both monochloramine and free ammonia, the water is somewhere in Zone 2 in the breakpoint curve. The water should be converted to Zone 4, as shown in Figure 10.

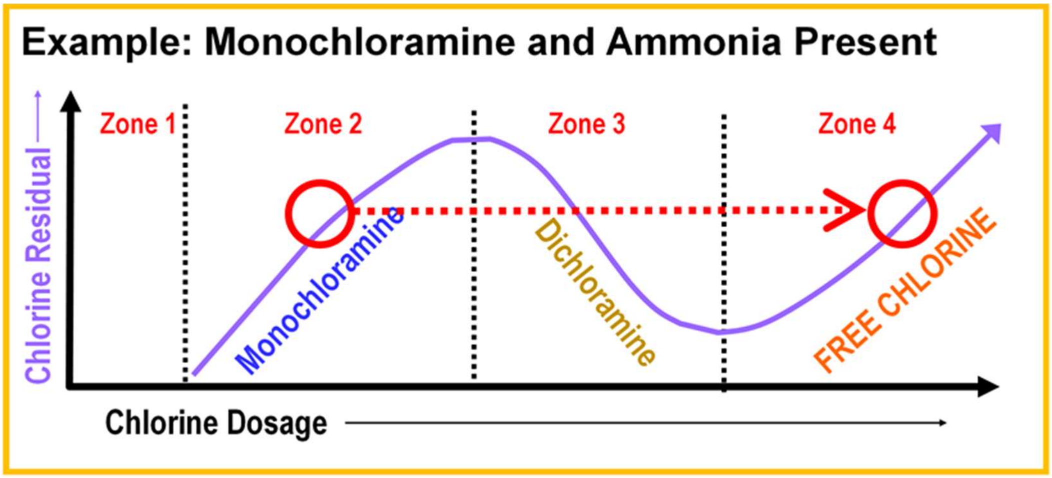


Figure 10. Breakpoint Curve. Beginning your conversion from Zone 2.

If your source water has monochloramine but no free ammonia, the water is somewhere in Zone 3 on the breakpoint curve, and you should convert it to Zone 4, as shown in Figure 11.

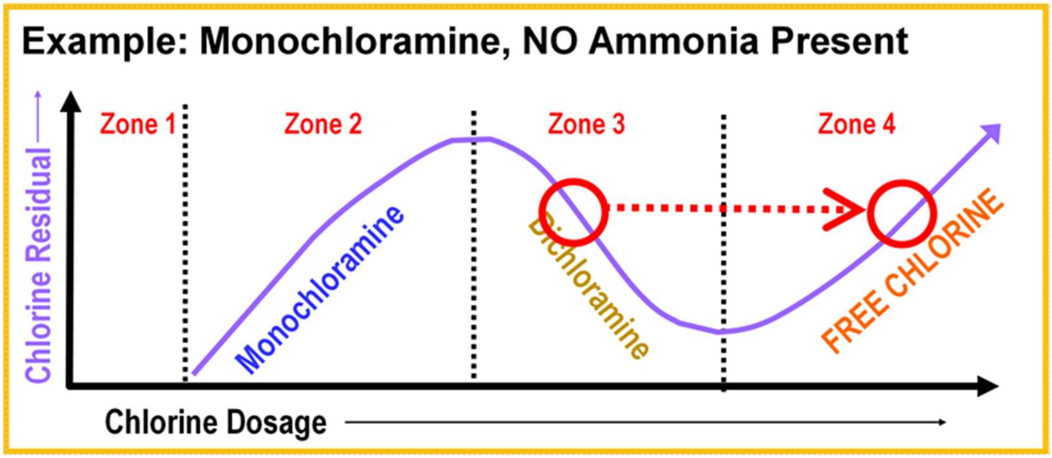


Figure 11. Breakpoint Curve. Beginning your conversion from Zone 3.

Procedure

1. Measure monochloramine in the source water. We will designate the monochloramine concentration as C_{mono} measured in units of mg/L as Cl2.
2. Measure free ammonia (as nitrogen) in the source water. We will designate the ammonia-nitrogen (NH3-N) concentration as $C_{NH3\text{-}N}$ measured in units of mg/L as nitrogen.

   Note: if the $C_{NH3\text{-}N}$ concentration is less than 0.1 mg/L as nitrogen, this could be a false positive free ammonia reading. Rerun the monochloramine and free ammonia analysis to confirm the results. A confirmed free ammonia test result less than 0.05 mg/L as nitrogen can be considered zero for the purposes of this scenario ($C_{NH3\text{-}N} \approx 0$).
3. Measure total chlorine in the source water. If the free ammonia test result is essentially zero and the difference between the results of the total chlorine test and monochloramine test are significant (monochloramine < 85% x total chlorine residual), the source water is probably well past the peak of the breakpoint curve in Zone 3.
4. Calculate the chlorine dose needed to overcome the free ammonia and monochloramine. We will designate this chlorine dose required to overcome the different forms of nitrogen in the water as DN in units of mg/L as Cl2.

   $$D_N = 10 \text{ x } C_{NH3\text{-}N} + C_{mono} \text{ (where } C_{NH3\text{-}N} > 0)$$

   Note: If free ammonia is essentially zero:

   $$D_N = C_{mono} \text{ (where } C_{NH3\text{-}N} \approx 0)$$
5. Determine your desired free chlorine residual leaving the plant, for example, 3 mg/L as Cl_2. Add a fudge factor for potential unmet chlorine demand in the water. We will designate these as C_{FCl} and C_{demand}, respectively, in units of mg/L as Cl_2.

   Note: Depending on how the source water was previously treated, unmet chlorine demand could be significant. We recommend that you initially estimate C_{demand} between 2 and 5 mg/L.
6. Estimate the total required chlorine dose to push the water past breakpoint and establish the desired free chlorine residual. We will designate the required chlorine dose as D_{Cl2} in units of mg/L as Cl_2.

   $$D_{Cl2} = D_N + C_{demand} + C_{FCl}$$

7. Estimate the maximum flow rate of water through the treatment plant. We will designate the treatment flow rate as Q_{H2O} in units of gallons per minute (gpm, or liters per second, L/s, metric).
8. Calculate the required chlorine feed rate to overcome the free ammonia, monochloramine, and chlorine demand and create the desired free chlorine residual in the flow of treated water. We will designate this chlorine feed rate with units as follows:
   a. If gas chlorine is being injected, Q_{Cl2} will be in units of pounds per day (ppd, or kilograms per hour, kg/hr, metric).

$$Q_{Cl2}\text{ (ppd)} = 0.012 \times D_{Cl2} \times Q_{H2O}\ \text{ (U.S. units)}$$

$$Q_{Cl2}\text{ (kg/hr)} = 0.0036 \times D_{Cl2} \times Q_{H2O}\ \text{ (metric units)}$$

   b. If chlorine bleach is being injected, find the strength of the bleach as a percentage of available chlorine and the specific gravity of the bleach solution (found in the safety data sheet, typically SG = 1.1). We will designate the strength of the bleach as $C_{bleach}\%$ in units of % available Cl_2 and the specific gravity of the bleach solution as SG_{bleach}. The liquid feed rate, Q_{bleach}, will be in units of milliliters per minute (mL/min).

$$Q_{bleach} = 0.38 \times D_{Cl2} \times Q_{H2O}\text{ (gpm)} / (C_{bleach}\% \times SG_{bleach})\ \text{ (U.S. units)}$$

$$Q_{bleach}\text{ (mL/min)} = 6 \times D_{Cl2} \times Q_{H2O}\text{ (L/s)} / (C_{bleach}\% \times SG_{bleach})\ \text{ (metric units)}$$

   Note: If the strength of the bleach is only provided as a percentage of sodium hypochlorite (for example, 10% sodium hypochlorite or NaOCl) and not as a percentage of available chlorine, substitute the percentage of sodium hypochlorite for $C_{bleach}\%$ (10% sodium hypochlorite ≈ 10% available chlorine). The error is insignificant for these calculations.

   Note: If your bleach is old, the strength of the bleach may be much less than the concentration indicated on the packaging. Consider purchasing fresh bleach for the free chlorine conversion. You could also estimate the strength of the bleach at half of the concentration on the packaging for the Q_{bleach} calculation.
9. Compare the capacity of your chlorine injection system to the required chlorine feed rate:
   a. For gas injection, compare the capacity of your chlorine rotameter in ppd (or kg/hr metric) to Q_{Cl2}.
      i. If the capacity of your rotameter is greater than Q_{Cl2}, then you should be able to conduct the free chlorine conversion with your existing chlorine injection system.
      ii. If the capacity of your rotameter is less than Q_{Cl2}, you cannot conduct a free chlorine conversion without making some changes at your treatment plant. Potential options include reducing the treatment flow rate, Q_{H2O}, during the conversion and installing a larger rotameter and chlorine eductor.
   b. For bleach injection, compare the capacity of your bleach pump in mL/min to Q_{bleach}.
      i. If the capacity of your bleach pump is greater than Q_{bleach}, then you should be able to conduct the free chlorine conversion with your existing chlorine injection system.
      ii. If the capacity of your bleach pump is less than Q_{bleach}, you cannot conduct a free chlorine conversion without making some changes at your treatment plant. Potential

options include reducing the treatment flow rate, Q_{H2O}, during the conversion and installing a larger bleach pump.

Conversion Factors

You might need some conversion factors for bleach pump capacities expressed in common units of L/hr, gal/hr or gal/day (gpd):

1 L/hr = 16.7 mL/min

Example—A pump rated as 5 L/hr is equivalent to 5 x 16.7 = 84 mL/min

1 gal/hr = 63 mL/min

Example—A pump rated as 10 gal/hr is equivalent to 10 x 63 = 630 mL/min

1 gpd = 2.63 mL/min

Example—A pump rated as 12 gpd is equivalent to 12 x 2.63 = 32 mL/min

Note: We recommend testing the installed capacity of your bleach pumps using a drawdown cylinder. Drawdown cylinders commonly include mL as a measurement unit. (Convert other units to mL.) Calculating a pump capacity in mL/min is straightforward—turn the pump to its maximum setting and time how long it takes to pump an observed volume from the drawdown cylinder. For example, a pump draws 350 mL in 2 minutes from the drawdown cylinder. The pump rate is 350/2 = 175 mL/min. Partial clogs in supply and injection lines and other potential factors could reduce the effective capacity of your chemical pumps below the rated capacity.

Use the following table to organize the steps in this procedure.

Table 1. Checklist for Calculating Chlorine Conversion Capacity

Step	Action	Symbol & Units	Your Result
1	Measure monochloramine in the source water.	C_{mono} mg/L as Cl_2	
2	Measure free ammonia (as nitrogen) in the source water. If $C_{NH3\text{-}N} < 0.1$ mg/L, rerun the test.	$C_{NH3\text{-}N}$ mg/L as NH_3-N	
3	Calculate the chorine dose needed to overcome the free ammonia and monochloramine. $D_N = 10 \times C_{NH3\text{-}N} + C_{mono}$	D_N mg/L as Cl_2	
4	Select your desired free chlorine residual after treatment.	C_{FCl} mg/L as Cl_2	
5	Estimate the unmet chlorine demand. If you do not have a better number, estimate C_{demand} between 2 and 5 mg/L	C_{demand} mg/L as Cl_2	

Step	Action	Symbol & Units	Your Result
6	Calculate the total required chlorine dose to push the water past breakpoint. $D_{Cl2} = D_N + C_{demand} + C_{FCl}$	D_{Cl2} mg/L as Cl_2	
7	Estimate the maximum flow rate of water through the treatment plant during the conversion period.	Q_{H2O} gpm (L/s metric)	

Proceed to the next step by matching the type of chlorine you use to the tables below.

Table 2. Gas Chlorine Feed

Step	Action	Symbol & Units	Your Result
8 (gas)	Calculate the required chlorine feed rate. Q_{CL2} (ppd) = 0.012 x D_{CL2} x Q_{H2O} (gpm) Q_{CL2} (kg/h**r**) = 0.0036 x D_{CL2} x Q_{H2O} (L/s)	Q_{CL2} (gas) ppd (kg/hr metric)	
9 (gas)	Estimate the capacity of your chlorine injection system.	Gas Cl_2 Capacity ppd (kg/hr metric)	

Step 10 (gas)

Compare the capacity of your gas chlorine injection system (Step 9) to the required chlorine feed rate (Step 8):

If the capacity of your chlorine injection system (Step 9) is greater the required chlorine feed rate (Step 8) you may **proceed with the conversion to free chlorine**.

If the capacity of your chlorine injection system (Step 9) is less than the required chlorine feed rate (Step 8), **do not proceed with the conversion to free chlorine.** Look into options that will help make your chlorine injection capacity greater than the required chlorine feed rate. For example, could you lower the treatment flow rate, Q_{H2O}, through the plant during the conversion?

Table 3. Bleach Chlorine Feed

Step	Action	Symbol & Units	Your Result
8 (bleach)	Find the strength of the bleach as a percentage of available chlorine [A B]	C_{bleach}%, % as available Cl_2	
9 (bleach)	Find the specific gravity of the bleach solution (look on your Safety Data Sheet or use 1.1)	SG_{bleach}. unitless	
10 (bleach)	Calculate the required bleach feed rate. $Q_{bleach} = 0.38 \times D_{Cl2} \times Q_{H2O}$ (gpm) / (C_{bleach}% x SG_{bleach}) $Q_{bleach} = 6 \times D_{Cl2} \times Q_{H2O}$ (L/s) / (C_{bleach}% x SG_{bleach})	Q_{bleach} mL/min	
11 (bleach)	Estimate (or Measure [C]) the capacity of your bleach injection system in mL/min.	Bleach Cl_2 Capacity mL/min	

Step 12 (bleach)

Compare the capacity of your bleach injection system (Step 11) to the required bleach feed rate (Step 10):

If the capacity of your bleach injection system (Step 11) is greater the required bleach feed rate (Step 10), you may **proceed with the conversion to free chlorine**.

If the capacity of your bleach injection system (Step 11) is less than the required bleach feed rate (Step 10), do not proceed with the conversion to free chlorine. Look into options that will help make your bleach injection capacity greater than the required chlorine feed rate. Potential options:

Could you lower the treatment flow rate, Q_{H2O}, through the plant during the conversion?

Could you use a higher strength bleach during the conversion?

Bleach Chlorine Feed Table Footnotes:

A - If the strength of the bleach is only provided as a percentage of sodium hypochlorite, for example, 10% NaOCl, not as a percentage of available chlorine, use the percentage of NaOCl for C_{bleach}. (10% NaOCl ≈ 10% available chlorine). The error is insignificant for these calculations.

B - Bleach loses strength over time. If you have fresh bleach, follow the instructions as written. If you have old bleach, estimate the strength at half the concentration on the container.

C - Testing bleach pump capacity: Use a drawdown cylinder labeled in milliliters (mL). Turn the pump to maximum and time how long it takes to remove a specific volume of bleach from the drawdown cylinder.

Example 1: Purchased Water

A PWS purchases water that normally has 2 mg/L of monochloramine and 0.5 mg/L of free ammonia as nitrogen. The PWS boosts monochloramine at the take point by injecting liquid ammonium sulfate (LAS) and gas chlorine. The maximum flow rate through the treatment plant is 500 gpm (32 L/s). The chlorine rotameter has a maximum capacity of 25 ppd (0.47 kg/hr). Plant staff estimate that there is unmet chlorine demand of 3 mg/L in the water. The desired free chlorine residual leaving the treatment station at the beginning of the free chlorine conversion is 4 mg/L.

Calculate the required gas chlorine feed rate to conduct the free chlorine conversion and determine if the existing chlorine injection system has enough capacity to deliver this feed rate.

C_{mono} = 2 mg/L as Cl_2

$C_{NH3\text{-}N}$ = 0.5 mg/L NH_3-N

$D_N = 10 \times C_{NH3\text{-}N} + C_{mono}$

$= 10 \times 0.5 + 2.0$

= 7 mg/L as Cl2

C_{demand} = 3 mg/L as Cl_2

C_{FCl} = 4 mg/L as Cl_2

$D_{Cl2} = D_N + C_{demand} + C_{FCl}$

$= 7 + 3 + 4$

= 14 mg/L as Cl_2

Q_{H2O} = 500 gpm (32 L/s)

Q_{Cl2} (ppd) $= 0.012 \times D_{Cl2} \times Q_{H2O}$

$= 0.012 \times 14 \times 500$

= 84 ppd (required chlorine feed rate)

Q_{Cl2} (kg/hr) $= 0.0036 \times D_{Cl2} \times Q_{H2O}$

$= 0.0036 \times 14 \times 32$

= 1.6 kg/hr (required chlorine feed rate)

Rotameter capacity = 25 ppd (0.47 kg/hr)

In this example, the existing chlorine injection system does not have the capacity to conduct a free chlorine conversion (rotameter capacity < Q_{Cl2}). This is common for chlorine injection systems that boost monochloramine; they are often undersized for breakpoint chlorination. There are a couple of options that the PWS could consider:

1. Discuss having the water wholesaler conduct a free chlorine conversion for the customer water system.
2. Install a larger rotameter and eductor.

The PWS decides that cutting the treated water flow rate by 70% during the conversion to free chlorine to use the existing 25 ppd (o.47 kg/hr) rotameter is not a reasonable option.

If the PWS elects to install a larger rotameter, note that chlorine usage could go up by 3 times or more during the conversion. The PWS should plan to have a larger number of chlorine gas cylinders available and to switch gas cylinders much more frequently than during normal conditions.

Example 2: Localized Nitrification

Water downstream of a PWS's chloramine booster station is showing signs of nitrification. PWS staff have not seen signs of nitrification in other parts of the distribution system, so they want to figure out how they can breakpoint chlorinate the water passing through this booster station.

The booster station is equipped only with a chlorine bleach injection system designed to combine any free ammonia in the upstream water; no ammonia injection facilities are provided at the booster station.

PWS staff begin by trying to turn up the chlorine bleach pump to its maximum setting; however, the water 1 hour downstream of the booster station (to allow breakpoint reactions to complete) ended up with:

- Total chlorine = 0.9 mg/L
- Free chlorine = 0.3 mg/L
- Monochloramine = 0.5 mg/L
- Free ammonia = 0.02 mg/L

PWS staff thought these were strange results since the total chlorine entering the booster plant was 2.5 mg/L. The color in the free chlorine test appeared to take a while to develop, so PWS staff let the test run a couple minutes longer to make sure they measured as much free chlorine as possible.

The maximum flow rate through the booster plant is 350 gpm (22 L/s). The chlorine bleach pump has a maximum capacity of 0.5 gallons per hour (1.9 L/hr). A bleach solution with 10% available chlorine and specific gravity of 1.1 is used in the booster station.

The PWS staff have no idea how much unmet chlorine demand is in the water at the booster plant, so they guess 2 mg/L of unmet demand. The desired free chlorine residual leaving the treatment station is 3 mg/L.

What should the PWS staff do?

1. First, let's take the data that they collected. Where is this boosted water on the breakpoint chlorination curve?
    a. Monochloramine interferes with the DPD free chlorine test. If monochloramine is present, it will react with the free DPD reagent and turn the color increasingly pink over time. **Assume that in the presence of monochloramine, any measured free chlorine residual is a false positive.**
    b. We can assume that the difference between the total chlorine and monochloramine test results around the distribution system are normally pretty small, within +/- 0.15 mg/L. The difference between the total chlorine and monochloramine in this sample, 0.9 mg/L-0.5 mg/L = 0.4 mg/L is abnormally large.

c. There is normally a significant amount of free ammonia, between 0.1 mg/L and 0.4 mg/L, in the distribution system samples downstream of the booster station. The 0.02 mg/L of free ammonia measured after the booster plans is at the lowest end of what the equipment and test method can accurately measure and could easily be a false positive within the normal error range of the test method. **We should assume that there is no actual free ammonia in the sample.**

d. Looking back at the breakpoint curve, Zone 3 is the part of the curve where there is no free chlorine, no free ammonia and monochloramine is a decreasing portion of the total chlorine residual as dichloramine is being formed.

What seemed like a strange data set now makes more sense when we realize that free chlorine and free ammonia were false positives.

2. Based on where the water is on the breakpoint curve, we know that the existing chlorine bleach pump does not have the capacity to push the water into Zone 4; thus, it is too small to perform the free chlorine conversion. They go back to measure the residuals in the water entering the booster station and use that data to follow the methodology described previously to determine how much bleach pump capacity is required.

Doing this, they measure:

C_{mono} = 2.37 mg/L as Cl_2

$C_{NH3\text{-}N}$ = 0.04 mg/L NH_3-N

They rerun the monochloramine and free ammonia tests to confirm the low free ammonia result and run a total chlorine test:

C_{mono} = 2.31 mg/L as Cl_2

$C_{NH3\text{-}N}$ = 0.02 mg/L NH_3-N

C_{total} = 2.45 mg/L as Cl_2

These results confirm that there is essentially zero free ammonia ($C_{NH3\text{-}N} \approx 0$) in the water entering the booster station. Monochloramine is pretty close to total chlorine (within 15%), so the water must be near the peak of the breakpoint curve.

Proceed with the calculations:

$D_N = C_{mono}$ = 2.37 mg/L as Cl_2 ($C_{NH3\text{-}N} \approx 0$)

C_{demand} = 2 mg/L as Cl2

C_{FCl} = 3 mg/L as Cl_2

$D_{Cl2} = DN + C_{demand} + C_{FCl} = 2.37 + 2 + 3 = 7.37$ mg/L as Cl_2

Q_{H2O} = 350 gpm (22 L/s)

$C_{bleach}\%$ = 10% available chlorine

SG_{bleach} = 1.1

Q_{bleach} (mL/min) = $0.38 \times D_{Cl2} \times Q_{H2O} / (C_{bleach}\% \times SG_{bleach})$ (U.S. units)

$$= 0.38 \times 7.37 \times 3.50 / (10 \times 1.1)$$

$$= 89 \text{ mL/min (required bleach feed rate)}$$

$$Q_{bleach} \text{ (mL/min)} = 6 \times (D_{Cl2} \times Q_{H2O}) / (C_{bleach} \times SG_{bleach}) \text{ (metric units)}$$

$$= 6 \times 7.37 \times 22 / (10 \times 1.1)$$

$$= 88 \text{ mL/min}$$

They compare the required bleach flow rate to the capacity of the existing bleach pump:

$$Q_{pump} = 0.5 \text{ gal/hr} \times (63 \text{ mL/min} / 1 \text{ gal/hr}) = 32 \text{ mL/min (U.S. units)}$$

$$Q_{pump} = 1.9 \text{ L/hr} \times (16.7 \text{ mL/min} / 1 \text{ L/hr}) = 32 \text{ mL/min (metric units)}$$

This confirms why the existing bleach pump was too small to push the water past breakpoint to the desired free chlorine residual. ($Q_{pump} < Q_{bleach}$)

In summary, it will take some work—sampling, looking up chemical properties, estimations, and a bunch of calculations—to figure out the required chlorine feed rate for a free chlorine conversion and to determine if your existing chlorine injection system has enough capacity.

If you need assistance, please contact TCEQ's Texas Optimization Program at 512-239-4691 or by email at TOP@tceq.texas.gov.

Note: TCEQ must approve plan and specification submittals from a licensed engineer before a PWS is allowed to change the chemical injection capacity of an existing treatment plant like a booster station. Make sure to provide the engineer with the highest possible monochloramine and free ammonia residuals entering the treatment plant so that the engineer sizes the chemical injection system appropriately for all expected conditions.