TEXAS OPTIMIZATION PROGRAM (TOP)
DIRECTED ASSISTANCE MODULE (DAM) 5

PROCESS MANAGEMENT FOR SYSTEMS USING CHLORAMINES

STUDENT GUIDE

TCEQ Course # 524

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Notes

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Notes

Definitions, acronyms, abbreviations, symbols, and chemicals

Definitions

Anhydrous: Without water. For example, anhydrous ammonia is sold as a pressurized gas/liquid and contains no water.

Applied dose: the amount of chemical we add divided by the amount of water we put it in. For example, if we add 1 milligram (mg) of a chemical to 1 liter (L) of water, we have an applied dose of 1 mg/L.

Atom: The smallest amount of an element. For example, the symbol "H" stands for one atom of hydrogen. (The symbol H_2 stands for one molecule of hydrogen gas).

Atomic weight: The weight of a single atom of an element. For example, the atomic weight of chlorine is the weight of a single chlorine atom: 35.45 atomic mass units.

Calculated flush time (CFT)—The amount of time it takes water to get from the main to the sample tap

Compliance samples—Samples that must be used to determine whether the levels at a PWS comply with the TCEQ regulations. Compliance samples differ from process management samples because the latter do not get included in compliance calculations.

Effective reactant dose: The amount of the reactant (contained in the chemical we add) that (after any competing reactions) is actually available to form product we want divided by the amount of water we put it in

Equilibrium: In some chemical reactions, products and reactants may both remain present and the species that dominate may depend on some outside influence like pH. For example, in free chlorine, hypochlorous acid (HOCl) and hypochlorite ion (OCl-) are in equilibrium.

Free ammonia: The sum of ammonia and ammonium ion normalized to be measured as the equivalent amount of N (nitrogen) in milligrams per liter. The free ammonia does not include organic amines.

Free chlorine: The sum of hypochlorous acid, hypochlorite ion, and dissolved chlorine gas (at pH <4) normalized to be measured as the equivalent amount of Cl_2 (elemental chlorine) in milligrams per liter. The free chlorine measurement does not include chloramines.

Mole: The number 6.02×10^{23}. This is the number of atoms (or molecules), as there are atoms in 12 grams of carbon-12 ($_{12}C$), the isotope of carbon with standard atomic weight 12 by definition.

This is important, because 1 mole of a chemical is the quantity identical to the substance's atomic or molecular mass (atomic or molecular weight).

Molecule: A group of atoms bonded together, representing the smallest fundamental unit of a chemical compound that can take part in a chemical reaction.

Molecular weight: The weight of a molecule is the weight of all the atoms in the molecule. For example, the weight of water is two times the weight of hydrogen plus the weight of one oxygen:

Nitrification: The two-stage biological process of converting ammonia first into nitrite and then into nitrate. Nitrification can occur in drinking water systems containing natural ammonia, in chloraminated systems where free ammonia exists in excess from the chloramination process, or from decomposition of the chloramines themselves.

Quality assurance (QA): Quality assurance (QA) is the management-level policy and requirements for following QA programs and adhering to quality control (QC) tools, such as SOPs.

Quality control (QC): Quality control (QC) includes the specific activities, standards, and protocols implemented by staff in accordance with management's QA program: SOPs, inspection, compliance criteria, testing procedures and passing requirements, methods, etc.

pH: The negative log concentration of hydrogen ions in water. Low pH occurs when there are lots of hydrogen ions—called acidic conditions. High pH occurs when there are few hydrogen ions, called basic conditions.

Public water system (PWS): An entity that provides water for human consumption to at least 25 people at least 60 days a year (see §290.38)

Process control: The term 'process control' is widely used to describe actions taken to make sure that a process or procedure gives successful results—not necessarily for regulatory compliance. However, in Texas, the Texas Health and Safety Code defines 'process control monitoring' as monitoring performed to meet regulations—just the opposite of how it is often used informally. Therefore, the term 'process management' is used to describe non-regulatory samples in this guide.

Process management: Actions taken to manage the results of a process or procedure, such as sampling. Process management samples refer to samples that are not used for determining regulatory compliance.

Products: In a chemical reaction, the products are the chemicals on the right-hand side. For example, in the reaction $A + B \rightarrow C + D$, C and D are the products.

Reactants: In a chemical reaction, the reactants are the chemicals on the left-hand side. For example, in the reaction A + B → C + D, A and B are the reactants.

Total ammonia: All species of amine-containing species, including organic amines that do not provide available nitrogen (N) for forming chloramines when mixed with chlorine.

Total chlorine: The sum of all 'active' chlorine species: hypochlorous acid (HOCl), hypochlorite ion (OCl-), monochloramine (NH_2Cl), dichloramine ($NHCl_2$), trichloramine (NCl_3), and organic amines.

Acronyms and abbreviations

This is not an exhaustive list of acronyms and abbreviations, but includes a variety that are used in the context of chloramination.

CFT Calculated flush time

DAM Directed Assistance Module

DI Deionized

DPD N,N diethyl-1,4 phenylenediamine sulfate

DWW Drinking Water Watch (dww2.tceq.texas.gov/DWW/)

FAA Free available ammonia

FAC Free available chlorine

fps Feet-per-second (velocity measurement)

LAS Liquid ammonium sulfate

mg/L Milligrams per liter

Mono Monochloramine

NAP Nitrification action plan (or the half hour after lunch)

ppb Parts per billion (generally equivalent to micrograms per liter (ug/L) in water)

ppd Pounds per day (dosing measurement)

ppm Parts per million (generally equivalent to mg/L in water)

ppt Parts per trillion (generally equivalent to nanograms per liter (ng/L) in water)

psi Pounds per square inch (pressure measurement)

PWS Public water system

SOP Standard operating procedure

TAC Total available chlorine (or Texas Administrative Code)

TCEQ Texas Commission on Environmental Quality

TLA Three-letter acronym

TOP Texas Optimization Program

w/w Weight-to-weight

Mathematical and chemical symbols

These are some of the symbols used in this manual.

< Means "less than."
For example, 2 < 3. (2 is less than 3)

> Means "greater than."
For example, 4 > 1. (4 is greater than 1)

≤ Means "less-than-or-equal-to."
For example, the group of numbers 1, 2, and 3 are all less-than-or-equal-to (≤) 3

≥ Means "greater-than-or-equal-to."
For example, the group of numbers 1, 2, and 3 are all greater-than-or-equal-to (≥) 1.

→ Means that a reaction proceeds in the direction of the arrow. For example, $NaCl \rightarrow Na^{+} + Cl^{-}$ (in water)

← → Means that a chemical reaction reaches an equilibrium between the reactants (on the left) and the products (on the right). For example, $HOCl \leftrightarrow H^{+} + OCl^{-}$

← → Means that a chemical reaction reaches an equilibrium between the reactants (on the left) and the products (on the right)—but MOST of the material stays in the reactant form.

← → Means that a chemical reaction reaches an equilibrium between the reactants (on the left) and the products (on the right) but MOST of the material goes to the product form.

DAM 5: Process Management for Systems Using Chloramines

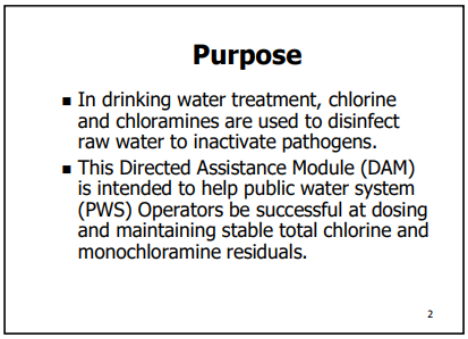
Disclaimer: This Directed Assistance Module (DAM) describes the regulatory requirements of Title 30, Texas Administrative Code (30 TAC) Chapter 290, relating to public water systems (PWSs). Should there be any inadvertent discrepancy between this training and the rules of 30 TAC Chapter 290, the rules shall apply.

Introduction

This Directed Assistance Module (DAM) is part of the TCEQ's Capacity Development program which helps public water systems (PWSs) develop the technical capacity needed to provide safe water. This DAM has been developed by the TCEQ's Water Supply Division (WSD) Texas Optimization Program (TOP) to help PWSs that use chloramines.

This training is available through the TCEQ's Financial, Managerial, and Technical (FMT) Assistance Program (512-239-4691).

Purpose



Chloramination chemistry is more complex than free chlorine chemistry, but chloramination is a very important tool for some PWSs, so learning more about it is useful and important.

Every PWS is required to maintain a disinfectant residual throughout the distribution system at all times. Disinfectant residuals protect against pathogens that may enter the distribution system through leaks, cross-connections, backflow/backpressure events. Disinfectant residuals also protect against pathogens that may be harbored or spawned in biofilms found in pipe tuberculation.

What is chloramination?

Chloramination is a form of disinfection. All water is required to be disinfected before it can be used as drinking water. Water in its natural environment contains pathogens that must be removed and/or inactivated before the water is safe for human consumption.

Even if the water is treated to stringent standards at the entry point, its quality can degrade in the distribution system. For example, contaminants can enter

through leaks when pressure is low, or high water-age can allow microbial growth. Luckily for Texans, TCEQ requires that systems disinfect the water throughout the entire distribution system.

Disinfection processes need to be maintained and operated correctly, or there is a potential risk that they will fail, leading to the introduction of harmful microbes and pathogens into the distribution system. For example, if you don't change the oil in an engine, it will break sooner than if you did.

Chloramination is disinfecting drinking water using monochloramine (NH_2Cl). PWSs typically use chloramination to:

- Successfully disinfect without forming regulated disinfection byproducts, and/or
- To ensure that they maintain a long-lasting residual throughout their entire distribution system.

The TCEQ has more information about chloramination on the web at:

www.tceq.texas.gov/drinkingwater/

The EPA has more information on their web site at:

www.epa.gov/dwreginfo/chloramines-drinking-water

What TCEQ rules apply to chloramination?

All of the rules related to chloramination are listed in Attachment 1.

These include rules for how to design and build chloramination facilities in 30 TAC 290 Subchapter D, and rules for monitoring and maintaining residuals in Subchapter F. Rules related to analysis, reporting, and recordkeeping are also shown.

Nitrification Action Plan (NAP)

A NAP is a plan for detecting and correcting nitrification, which can destroy total chlorine residuals. A NAP includes:

1. Map of compliance and process management sites,
2. Schedule for sampling,
3. List of Analytical Methods,
4. Goals/baselines and triggers,
5. Actions, and action plans or SOPs.

The first three items will be discussed and developed in this DAM.

The follow up—"**DAM 8: Creating a NAP for a Public Water System**" —will provide training on the last two items.

When were the rules for monochloramine and ammonia monitoring adopted?

The rules for chloramination monitoring became effective July 30, 2015. Before that, the same requirements were applied on a case-by-case basis to all systems using chloramines through the TCEQ's 'exception' process.

What monitoring is required?

Systems that use chloramines must monitor according to 30 TAC §290.110(c)(5). The specific requirements are described in detail in Chapter 3.

Getting started: Training logistics and system summary

In drinking water treatment, chloramines are an important tool used to disinfect raw water to inactivate pathogens, and to keep them inactivated throughout the distribution system.

This Directed Assistance Module (DAM) is intended to help public water system (PWS) operators be successful at dosing and maintaining stable chloramines throughout their system. We will cover:

- Basic chemistry review;
    - Chloramine chemistry and the breakpoint curve;
- Sample collection and analysis;
- Monitoring for compliance and for process management—at the source, plant, entry point and in the distribution system;
- Mixing and dosing; and
- How to apply those concepts in a treatment plant,

Training location

This training includes slides and desktop exercises. The classroom portion of the training should be held in a room or office that is clean, dry, and not too noisy. It is helpful to have a blackboard or whiteboard, and a place to project slides.

The two main hands-on activities are analyzing samples and working with the systems map. Additionally, if time permits, we may do a plant tour or take samples in distribution.

Prerequisites for attending this DAM

This DAM is intended for people who have some familiarity with chloramination at a PWS. For example: the chief operator at a city, a utility manager, or an owner of a campground. A person does not need to be a licensed water operator to benefit from this training.

No single training event can create an expert. People who need to use chloramines successfully should be ready to seek expert assistance on items outside their expertise.

CEUs

Instructors for this workshop who are subject-matter-experts (SMEs) approved through the TCEQ's Occupational Licensing process described in Regulatory Guidance (RG) 373 may provide continuing educational units (CEUs) for this training. In order to receive CEUs, attendees must provide a list of the names of staff to be trained, with their license numbers.

For any questions about the instructor approval process, contact the trainer at their number or the TCEQ Occupational Licensing Section at 512 239-1000.

What the system needs to bring to the DAM

Before this DAM training occurs, a system must gather some materials.

The PWS should have the following ready before the training starts:

- **Analytical instruments** for analyzing total chlorine, monochloramine, and ammonia, with
  - Instrument manuals, and
  - SOP for collecting and analyzing samples *(if available);*
- **Monitoring plan**, specifically:
  - Distribution map showing with sample sites,
  - Schedules for chloramine-effectiveness monitoring, and
  - The entire NAP *(if available);* and
- Sampling results for total chlorine, monochloramine, free ammonia (as N), nitrite, and nitrate *(if available).*

DAM schedule

Today's training has an ambitious schedule. Please work with the instructor to stay on time. The presentations and activities are organized in the following order. Students should think about which topics are of greatest interest to them.

Latitude

The instructor can use latitude to emphasize topics of greatest importance to the PWS where the training is held. However, the overall length of time should not be shortened.

System review/plant tour

In terms of latitude, a system with a surface water treatment plant (SWTP) may need to arrange to spend more time on the plant tour and Chapter 5.

A system without a SWTP may want to spend more time on the earlier chapters.

Basic schedule

Let's review the basic schedule and then talk about what areas need more or less time.

Agenda for DAM 5—Chloramination (see slide)

Time	Activity
8:30-8:45	Introductions, sign-in (15 minutes)
8:45-9:00	**Pre-Test (**15 minutes)
9:00-9:15	**Getting started**—Review today's schedule. **System Summary Table**—Plant tour or desk-top review
9:15-10:15	**Chapter 1—Chemistry review and breakpoint curve** (1 hour)
10:15-10:30	*Break*
10:30-12:00	**Chapter 2—Sample collection and analysis** (1 hour) ***Activity:*** Hands on sample analysis using system's equipment ***Activity:*** Complete List of Analytical Methods
12:00-1:00	*Lunch*
1:00-2:00	**Chapter 3—Distribution sampling**—Sites and Schedules ***Activity:*** Evaluate distribution sample locations (1 hour)
2:00-2:15	*Break*
2:15-3:00	**Chapter 4—Dosing calculations** (45 minutes)
3:00-3:45	**Chapter 5—Treatment plant scenarios** (45 minutes)
3:45-4:00	**Wrapping it up: Post-Test** and review of answers (15 minutes)
4:00-4:30	**Review Plan of Action and Evaluations** Review recommendations, Plan of Action, and complete evaluation,

Students will need to commit a full work day to participate in this DAM.

Training materials

The instructor of this DAM will provide copies of the most current versions of this Student Guide. If this training is performed at a PWS, the system will also have to gather some materials, described above.

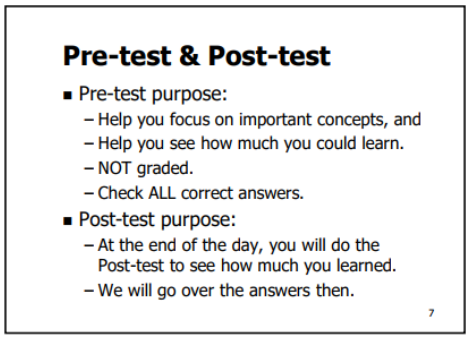
Student Guide—Use it today and in the future

This DAM is intended to use the data for the PWS that it is being given at. Please try to have a way to share the distribution map with all the students. For example, make several copies.

In order for your Student Guide to be useful as a reference, you need to become familiar with it. As you go through the workshops:

- **Open** the Student Guide to see what information is provided.
    - **Tab** areas you need to study more.
- Start writing down things you need to **follow up** on.

Pre- and Post-Test



This DAM includes a Pre- and Post-Test intended to help the student's learning process. These tests will NOT be graded.

Check ALL correct answers—there may be MORE THAN ONE correct answer.

When you take the Pre-Test, note the questions that were puzzling—the answers will be covered in the course. If they are not—make sure to ask about them. At the end of the day, we will go through the answers.

Training Evaluation Form

A Training Evaluation Form is included in this Student Guide. Students will complete this evaluation and return it to the instructor who will collect those to route securely to the TCEQ's Water Supply Division, who developed this training. By submitting your input, the TCEQ can continue to improve the training we develop.

You may complete the Training Evaluation Form anonymously, but please note the date and location at the top of the form. If you have items of concern which you wish to communicate anonymously by phone, please contact the Texas Optimization Program (TOP) at 512-239-4691.

Plan of Action

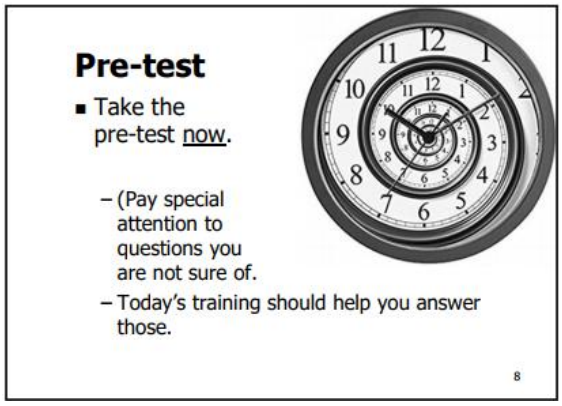
On-site assistance

This DAM should result in actions by the participants to develop or improve the chloramine management at this PWS. During the day, note your ideas about what to do on the Plan of Action provided in Attachment 7.

Classroom training

When this training is given in a large group, it may not be possible to go through a specific system's data. In that case, examples are provided for doing table-top exercises in small groups.

Each student, in this case, should think about how they can take the knowledge gained back to their system to achieve their goals.



System Summary Table: Getting to know this system

Before getting into the details of the training, it is important for the instructor and participants to focus on the PWS that needs assistance, so that the most important topics can be emphasized.

Note: *If the PWS plans to participate in "DAM 8: Creating a Nitrification Action Plan" you only need to do this once.*

System name/PWS ID:
Population
Comments:
Source(s)—Does the plant use wells, surface water, or purchase?
Treatment—Does the plant treat water? Where? With what chemicals?
Entry Points—Does water from sources or plants blend before entering distribution?
Distribution system: What type(s) of disinfectant(s) are in distribution? Where?

Note: Use additional paper if needed.

System Summary

System name/PWS ID:
Additional notes:

Chapter 1: Basic chemistry review and breakpoint curve

Before we begin discussing how to control the chloramination process, we may need to review basic chemistry so that we can understand chloramine chemistry. Then, by understanding the breakpoint curve, we can figure out what zone on the curve our water is in.

Scope

This chapter covers the chemistry that we need to know to be successful with chloramination.

Supporting documentation

For this chapter, the student should look at:

- ✓ The Student Guide,
- ✓ Slides presented by instructor (and printed in the chapter).

Learning goals

The learning goals for this workshop are:

- Understand basic chlorine chemistry,
  - Be able to define pH, equilibrium, and chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) mass ratios,
- Understand chloramine chemistry,
  - Be able to list the three members of the chloramine family,
  - Understand the chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) conditions that allow formation of monochloramine,
- Be able to identify the different zones on the breakpoint curve, and
- Be able to figure out which zone a water is in based on the concentrations of total chlorine, monochloramine, ammonia, and free chlorine.

Part 1—Basic chemistry review

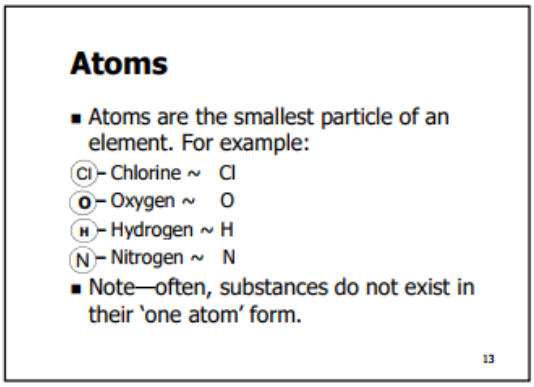
To understand chloramine chemistry, the first step is to review the basic chemistry you may have learned in high school, college, or operator training.

Atoms, molecules, etc.

An atom is the smallest unit of an element that is still recognizable as that chemical element. Everything around us—water, trees, people—is composed of atoms. They are incredibly small; around a ten-billionth of a meter (0.1 nanometers).

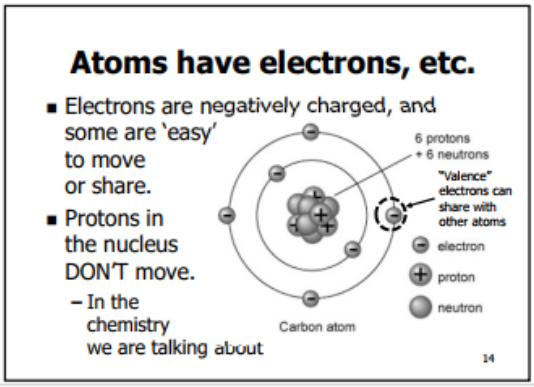
Atoms are made up of even tinier particles:

- Protons,
- Neutrons, and
- Electrons.



The protons and neutrons are in the middle, stuck closely together in the 'nucleus'. The protons have a positive charge, and the neutrons have a negative charge. Electrons are negatively charged and are less tightly stuck to the atom. Most of the reactions we will discuss involve electrons moving around or being 'shared'.

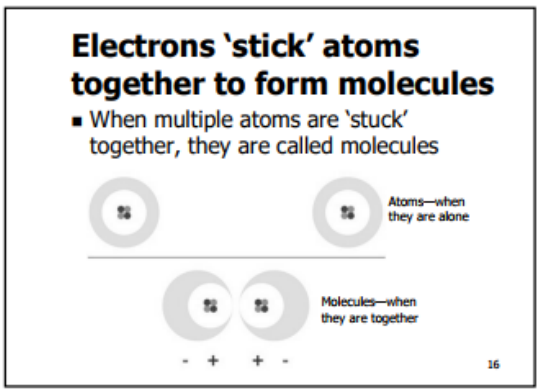
Even though the 'solar system' model of an atom is not exactly right, we are not theoretical physicists, so it is good enough for us.



Atoms are not the smallest particles—just the smallest particles that still have attributes of an element. When atoms are stuck together, we call them molecules.

Electrons

Electrons are the glue that sticks many molecules together. The protons in the center of atoms have a strong positive charge, and so the atom wants enough electrons—which are negatively charged—to balance that positive charge.

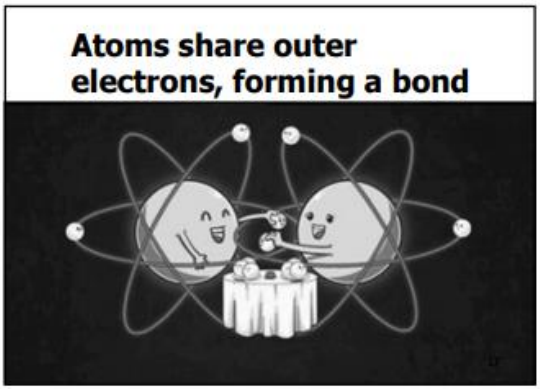


Electrons that are close to the nucleus are usually safe from being 'stolen' by other molecules to balance out their protons. But, the electrons in the outer (valance) ring are at risk! Most of the molecules we deal with want to have eight (8) electrons in their outer ring.

Thus, one could say that electrons are the glue that sticks molecules together.

Bonds

When atoms share electrons, we say that they form a 'bond.'



Bonds can be weak or strong.

Bonds between atoms can be strong or not.

- "Covalent" bonds are very strong —like **family**—they SHARE electrons.
  - For example: Oxygen (O_2) or nitrogen (N_2)
- "Ionic" bonds are not as strong —like **friends**—they TRANSFER electrons.
  - For example: Table salt (Na+ Cl-), sodium hypochlorite (Na+ Ocl-) or hydrochloric acid *(in water)* (H+ Cl-)

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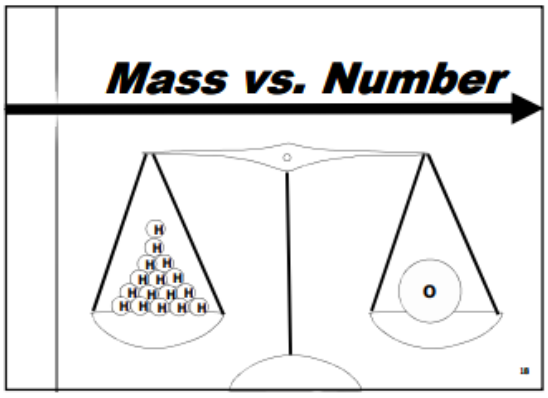
In a compound that easily breaks up, that is a weak bond. For example, the bond between sodium and chloride in sodium chloride (NaCl, or normal table salt) is weak enough that just putting salt into water lets those two atoms split apart. Or, in sodium hypochlorite (NaOCl), the bond between the sodium atom (Na+) and the hypochlorite ion (OCl-) splits apart easily, but the bond between oxygen (O) and chlorine (Cl) in the hypochlorite ion is stronger, and harder to break.

Mass vs. Number

Number ("moles") versus mass

When we talk about chemical reactions, we need to talk about the number of atoms and molecules. However, we usually talk about residual or dosage of chemicals, which is the mass concentration—like milligrams per liter (mg/L) or pounds-per-day (ppd).



For example, the illustration in the slide shows a balance with hydrogen atoms (H) on one side, and one oxygen atom (O) on the other side. Oxygen is much bigger than hydrogen—one oxygen weighs the same as 16 hydrogen atoms.

Not all atoms or molecules weigh the same amount

- When we talk about chemical reactions, we need to talk in 'numbers'—like "one oxygen and two hydrogens make water"
- But! When we talk about dosing in the 'real' world, we need to talk about pounds-per-day, and residuals of milligrams-per liter,
- So we need to be able to convert between weight (mass) and number.

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Talking about 'one atom' doing something is silly, because we can't see, feel, or touch a single atom—we just deal with them in large numbers. Therefore, scientists invented a term to make it easier to talk about huge numbers of atoms and molecules.

Moles ain't nothin' but a number

When we talk about the number of atoms or molecules in something, there are a lot. Instead of using a big number to count them (like trillions or kajillions) we use the number "mole."

Moles per gram

- Luckily, we have a conversion factor: The atomic weight.
- The atomic weight of a molecule is in the units of "GRAMS PER MOLE"
  - Where a "MOLE" is just a number… a really big number.
  - This allows the chemist to weigh out amounts of two substances, such that equal numbers of atoms are obtained.

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The word "mole" just means a certain number—6.0221415×10^{23} to be precise (like a dozen means 12). One mole of something is equal to 6.022×10^{23} of it.

10^{23} means 1-with-23-zeros-after-it =
100,000,000,000,000,000,000,000

Therefore, one mole of something is that looooong number times 6.022:

602,214,150,000,000,000,000,000

So, "One mole of hydrogen atoms" means 6.022×10^{23} hydrogen atoms.

Another way to say it is 602 trillion billion.

Moles per gram

- Luckily, we have a conversion factor: The atomic weight.
- The atomic weight of a molecule is in the units of "GRAMS PER MOLE"
  - Where a "MOLE" is just a number… a really big number.
  - This allows the chemist to weigh out amounts of two substances, such that equal numbers of atoms are obtained.

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Important: Mass matters! (but so do moles)

The **number** of molecules is a way of figuring out the chemistry.
The amount of chemicals present, *or needed*, is determined from **mass**.

The cool thing about moles

The cool thing about moles is that they make it easy to convert from the number of atoms or molecules to their mass. They 'translate' from chemistry to practical use.

You need to know the number of things to figure out chemistry, since that is how reactions work, but it would take a long time to count all those atoms. However, the mass is easier to measure, and more important when dosing chemicals.

Example—chlorine and nitrogen

Chlorine and nitrogen have different atomic weights.

The atomic weight of the **chlorine** atom (Cl) is **35.45** grams per mole of Cl, so the atomic weight of elemental chlorine—Cl_2—is **71** grams per mole.

The atomic weight of the **nitrogen** atom is **14.01** grams per mole of N

We are going to find it helpful in translating chloramine chemistry to dosing that:

One mole of chlorine (atom) weighs 35.45 grams—and one mole of elemental chlorine (Cl_2) weights 71 grams, and

One mole of free available ammonia-as nitrogen (N)-weighs 14.01 grams.

Conversion factor: molecular weight

- If you know the molecular weight, (in grams per mole) you can convert from number to mass:
  - The atomic weight of H is 1.0079 grams per mole, therefore 1 mole of H atoms weigh 1.0079 grams.
  - The atomic weight of Cl is 35.45, therefore 1 mole of Cl has a mass of 35.45 grams.

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So now we can calculate how to dose.

The thing about moles is that one mole of anything weighs its atomic or molecular weight. Tables 1 and 2 show the weight of various atoms and molecules of interest.

So, for example, one mole of H weighs 1.008 grams, and one mole of Cl_2 weighs 71 grams. This is incredibly helpful in converting chemistry into pounds and milligrams—much more useful units. We will get into this more when we talk about dosing in Chapters 4 and 5.

From this, we can figure out the mass ratio if we know the 'number ratio. For example, if there is *one* Cl_2 mole and *one* N mole, we can figure out their mass ratio.

1 mole of Cl_2 weighs 71 grams

1 mole of N weighs 14 grams.

So the ratio is:

1 mole Cl_2:1 mole N = 71 grams: 14 grams = **5.06**

(unitless mass ratio)

Table 1 lists the chemicals of interest to us for discussing chloramines, and gives their size and weight.

Table 1. Atomic number, weights, and radius of some elements of interest

Atom *		Atomic weight (grams per mole)	Atomic radius (picometers)
1	Hydrogen (H)	1.008	37
6	Carbon (C)	12.01	77
7	***Nitrogen (N)***	***14.01***	74
8	Oxygen (O)	16.0	73
11	Sodium (Na)	22.94	186
17	Chlorine (Cl)	35.5	100
20	Calcium (Ca)	40.8	197
25	Manganese (Mn)	54.94	205
35	Bromine (Br)	79.90	114

* The most important use for this table is dosing calculations, which we will do later in the DAM.

Molecules are groups of atoms, atoms are the smallest single particle of an elemental substance.

Table 2. Molecular weights of some molecules of interest

Molecule *	Molecular weight (grams per mole)
Chlorine gas (Cl_2)	***71***
Nitrogen gas (N_2)	28
Ammonia (NH_3)	17
Ammonium (NH_4)	18
Monochloramine (NH_2Cl)	51
Dichloramine ($NHCl_2$)	85
Trichloramine (NCl_3)	119

Chemicals of interest—the basics

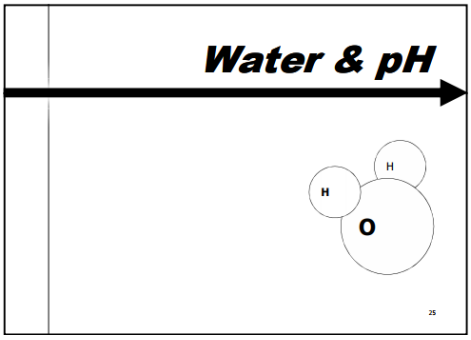
We don't need to know everything about every chemical to treat water. We just need to know a few chemicals pretty well.

These include:

- Water and pH,
- Chlorine in its free form,
- Ammonia,
- The chloramine family:
    - Monochloramine,
    - Dichloramine, and
    - Trichloramine

The Student Guide also has a review of nitrite and nitrate, for completeness, but we won't go into those in depth till we talk about nitrification in DAM 8: Nitrification Action Plans (NAPs).

Water and pH



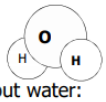
It may seem silly, or obvious, to start by talking about water, but there are a couple of points that are important. The first is that all of the chemistry we talk about here is in the context of water—specifically drinking water.

If you look on the web, you can find references that seem to conflict with one another. Often that is because the important chemistry for boiler water, process water, swimming pools, and drinking water is all a little bit different, because of the different goals, and different potential issues.

Just as a reminder, water is H2O. If you are feeling particularly science-y, you could call it 'di-hydrogen monoxide' and see if anyone can figure out what you are talking about.

Water

- Water is one oxygen and two hydrogens.



  - Important things about water:
    - It is strongly bound together,
    - It is polar,
    - It can be acidic or alkaline (basic),
      - Based on the concentration of hydrogen ions (H+) or hydroxide ions (OH-).

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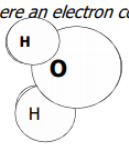
Water has very strong bonds between the hydrogen atoms and the oxygen atom… it is fairly easy for it to lose one hydrogen, but not two.

Water is held together by covalent bonds

- Covalent bond:

  - Oxygen likes to have 2 extra electrons.
    - *The "-" is an electron.*
  - Hydrogen loses its outer electron easy, so it is happy being H+.

    - *The "+" is a hole where an electron could be.*
  - So one oxygen can fit together with two hydrogens.



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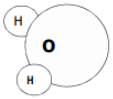
Where the hydrogens are, water has a slight plus charge, and where the oxygen is water has a slight negative charge. This means that water is slightly polar, even though it does not actually have a plus or minus charge as a molecule.

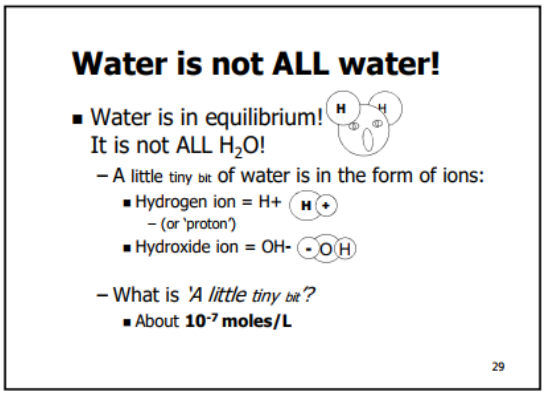
Water is polar

- Water is slightly polar (like a magnet):
  - *But not fully charged–not an ion*
  - One end is *slightly* positive, one is negative.
    - Water can attract oppositely charged molecules
      - The slightly positive end can attract negative ions, etc.
      - The slightly negative end can attract positive ions, etc.
    - *(And NOT get pulled apart)*



28

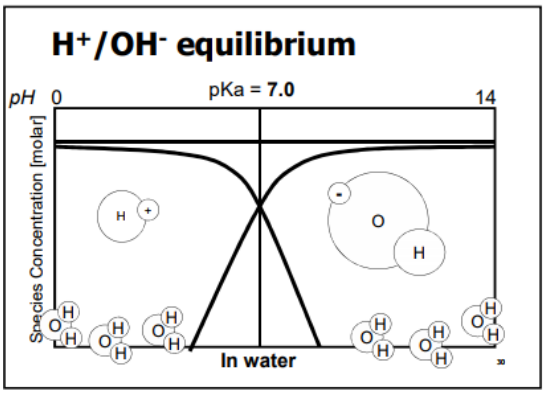
A tiny bit of water is always broken into H+ and OCl-, which is described by pH.



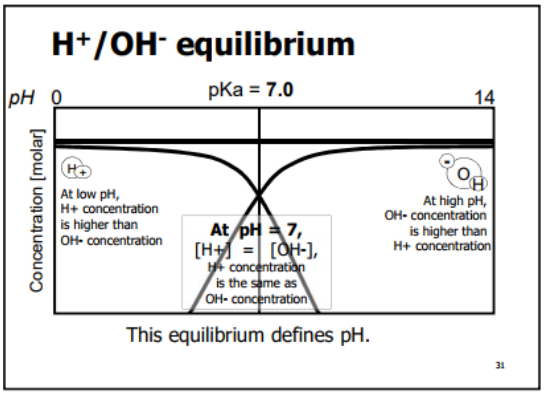
pH (equilibrium between hydrogen ion and hypochlorite ions)

For discussing chloramines, one of the most important topics about water is pH. Depending on the pH, chemical reactions may work or not work. Knowing the pH is one clue to what is going on in your drinking water.

A tiny bit of water is present not as H2O, but as H+ and OH- in equilibrium.



On the equilibrium graph, the horizontal line represents a concentration of 10-7 (ten to the negative seven)—a pretty tiny amount. The sum of the concentration of H+ and OH- always adds up to that number… but sometimes one or the other is dominant.



When H+ is dominant, we call that acidic.

When OH- is dominant, we call that basic.

Literally, pH is "the negative log of the concentration of hydrogen ions"

$$pH = -\log_{10} [H^+]$$

Where:

Hydrogen ions are H^+

(Hydrogen ions are also called "protons")

[H+] is their concentration in moles per liter (not mass per liter)

Log_{10} is the logarithm with base 10, that is, the number is the exponent.

For example:

If the molar concentration of H+ is 10^{-7},

Then:

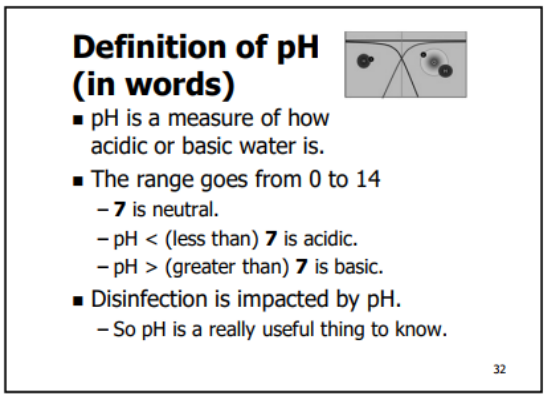
$$pH = -\log_{10} [10^{-7}] = 7 \text{ pH units}$$

This can be said as

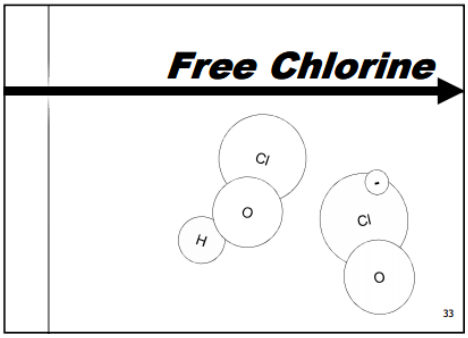
"when the concentration of hydrogen ions is [10^{-7} molar], the pH is 7."

When there are MORE hydrogen ions, the pH is LOWER. That is why an acid solution is low pH and a basic solution is high pH.

Units of pH are just 'units.' You can say "the pH is 7" or you can say "the pH is 7 pH units." Both are equally correct.



Free chlorine



When we talk about 'free chlorine' we are actually talking about two chemicals—free chlorine is the sum of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-).

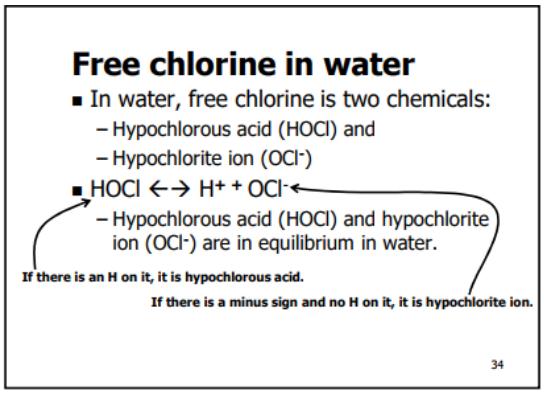
We need to talk about free chlorine because that is what we mix with ammonia to form chloramines.

Note: Dissolved chlorine gas

Chlorine gas is only dissolved in water at low pH.

At pH <4, dissolved chlorine gas may persist in water. At higher pH, it is not present.

Potable water should not be at pH <4. The TCEQ lower limit for pH is 7 because water is corrosive, even at pH 7. Therefore, off gassing chlorine is not a big problem in Texas.

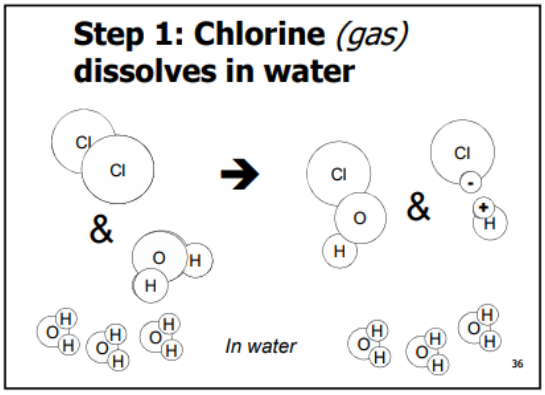


When chlorine gas (Cl2) is added to water that does not have ammonia in it, the instant reactions are:

First, gas chlorine reacts in water to form hypochlorous and hydrochloric acids:

$$Cl_2 + H2O \leftarrow\rightarrow\rightarrow\rightarrow HOCl + HCl$$

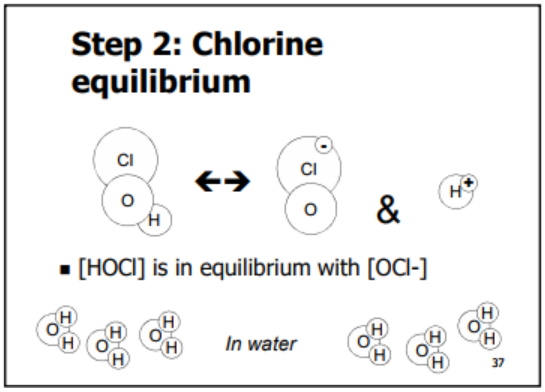
The three bold arrows $\leftarrow\rightarrow\rightarrow\rightarrow$) indicate that there is an equilibrium, but almost all of the chlorine is in the form shown on the right side of the equation.



Then the hypochlorous acid splits up into its two chemical forms:

$$HOCl \leftarrow \rightarrow OCl^{-} + H^{+}$$

.

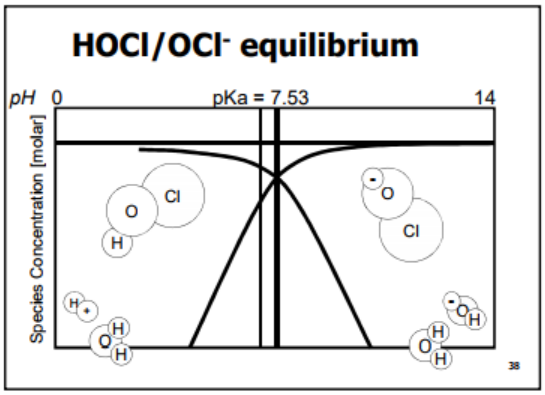


"Gaseous chlorine, when added to water,
forms mainly hypochlorous acid and hypochlorite ion."

When you measure free chlorine, you are measuring the sum of these two chemicals:

$$\text{Free chlorine (as } Cl_2\text{)} = \text{ the sum of } HOCl + OCl^{-}$$

Hypochlorous acid (HOCl) is the chemical with strong disinfecting power. It will be present in greater amounts at lower pH, because of the HOCl/OCl- equilibrium.



Forms of chlorine

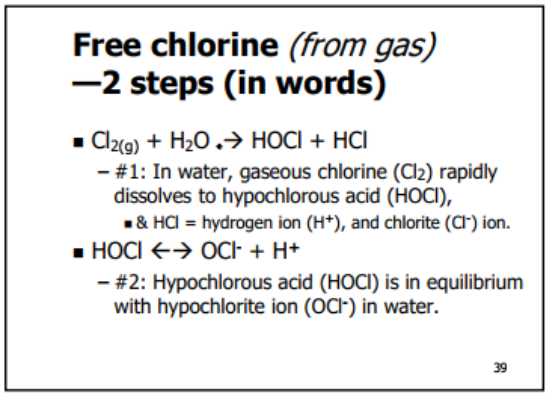
Chlorine is available in one of three forms:

- sodium hypochlorite (liquid),
- calcium hypochlorite (liquid), and
- gas chlorine (compressed into a liquid in metal gas bottles).

When comparing elemental chlorine as an oxidizing agent to powder (calcium hypochlorite) or solution (sodium hypochlorite), the oxidizing effect is the same. That is, all three produce hypochlorous acid, the oxidizing agent present for disinfection in water and waste water application.

Chlorine gas

Chlorine (Cl2) is a gas, heavier than air, toxic, non-flammable and an economically available oxidizing agent that provides properties desirable in disinfection usage.



Liquid chlorine, known also as “chlorine gas”, is straight chlorine at 100% strength. (It is a gas, but it is compressed to liquid form at high pressure when you buy the metal cylinders of chlorine.) The most common ways of adding chlorine to a water are to feed gas with a vacuum-operated solution feed system, or to feed the gas under pressure.

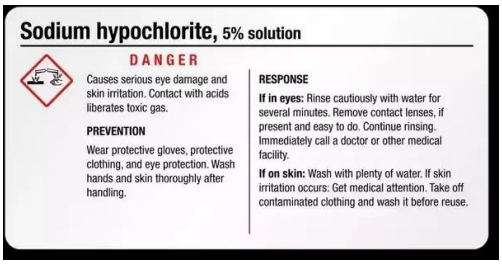
When chlorine gas is dissolved in water, it reacts with the water to form hypochlorous acid and hydrochloric acid (as shown above):

$$Cl2 + H2O = HOCl + HCl$$

The slight contribution of alkali when a hypochlorite is added or the slight contribution of acid when chlorine is added, generally, makes no difference in the final pH of the water except if the water is low alkalinity. The amount of chlorine added in either form is very small compared to the buffering power of most waters.

Liquid bleach

Sodium hypochlorite, commonly called "liquid bleach", is commercially available in strengths approximately 15% by weight. It can be added to the receiving stream by gravity, by the use of a chemical metering pump, or by physically dumping it.



When a 'hypo' is added to water, it reacts to form hypochlorite ion and hydroxide:

$$NaOCl = OCl^- + Na+$$

Free chlorine–*from sodium hypochlorite* (NaOCl)

- $NaOCl \rightarrow OCl^- + Na^+$
  - #1: In water, sodium hypochlorite (NaOCl) dissociates into hypochlorite ion (OCl^-) and sodium ion (Na^+)
- $OCl^- + H^+ \leftrightarrow HOCl$
  - #2: Hypochlorite ion (OCl^-) and hypochlorous acid (HOCl) are in equilibrium in water.
    - (Same step #2 as with gas chlorine)

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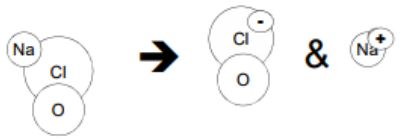
The reactions are similar—but not identical—to the reactions with gas.

In the first step, the sodium chloride dissolves in water, just like salt or sugar.

Free chlorine – from NaOCl



- Solid NaOCl dissolves in water
  - A concentrated solution is used for dosing
- (Calcium chloride ($Ca(OCl)_2$) is also used)

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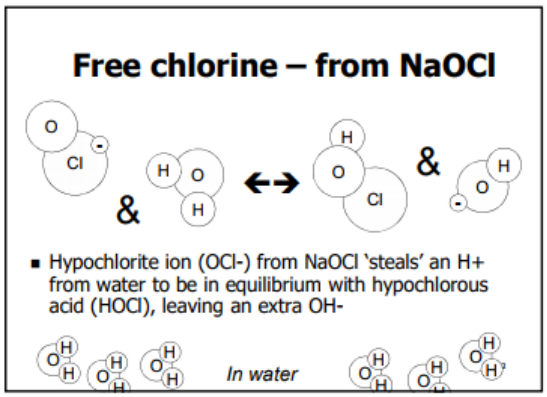
Then, in the second step, the OCl- enters the equilibrium with HOCl.



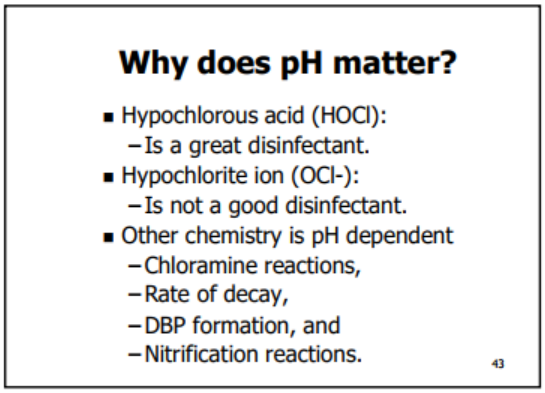
However, since the reaction forms OH-, NaOCl is more likely to make the water slightly more basic, rather than slightly more acidic like with gas.

Calcium hypochlorite

Calcium hypochlorite, generally referred to as "powder chlorine". It contains 70% available chlorine. It can be added to the receiving stream by use of pellets or by mixing a solution of water and calcium hypochlorite, decanting the solution into a tank and using a small chemical feed pump.

Importance of pH to free chlorine

One of the main reasons that we usually stress pH when we are discussing disinfecting with free chlorine is that hypochlorous acid (HOCl) is a great disinfectant but hypochlorite ion (OCl-) is not that good.



In the context of chloramination, other chemistry is more important, like the formation of chloramine, which we will talk about in the next part of this Chapter, when we look at the breakpoint curve.

Also, pH impacts the rate of decay of both free chlorine and chloramines and is important in nitrification reactions (which are discussed in "DAM 8: Creating a Nitrification Action Plan (NAP) for a Public Water System (PWS)."

Total chlorine

Total chlorine measures the sum of all active chlorine species.

Total chlorine = HOCl + OCl- + NH2Cl + NHCl2 + NCl3

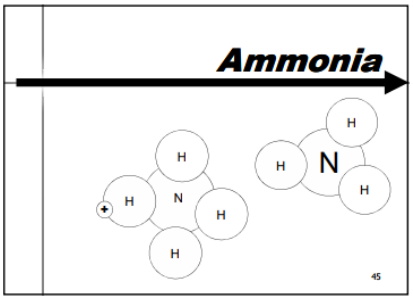
In English, this says:

> *"Total chlorine is the sum of hypochlorous acid, hypochlorous ion, monochloramine, dichloramine, and trichloramine."*

In natural waters, total chlorine will also measure organic amines, even though they have no disinfecting power.

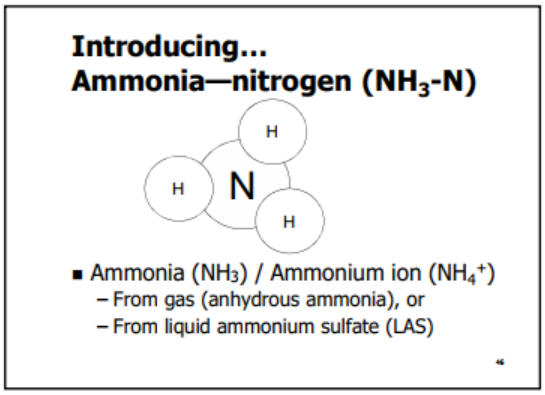
When you use free chlorine, the total chlorine measurement is just free chlorine; but, when you use chloramines, the total chlorine measurement is the sum of all the chloramine species—mono, di, and tri.

Free ammonia (as nitrogen)



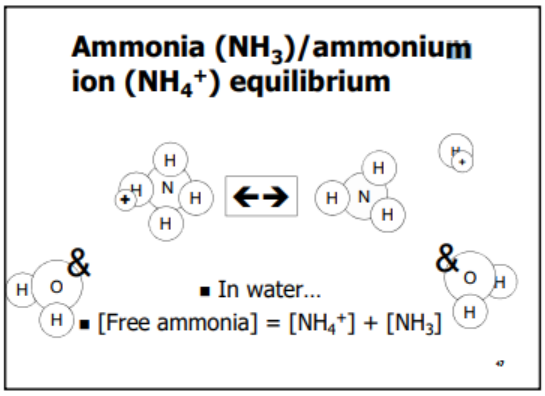
For chloramination, ammonia is important because ammonia plus chlorine equals chloramines.

Ammonia for chloramination is usually fed as liquid ammonium sulfate (LAS). Pressurized gas is also available, generally for larger facilities.

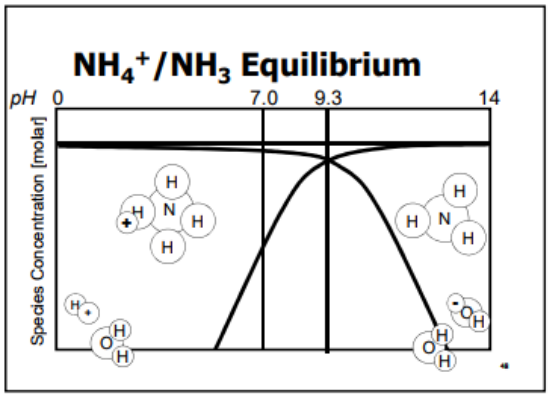


In water, ammonia is present as an equilibrium of ammonia (NH3) and ammonium ion (NH4+) depending on the pH.

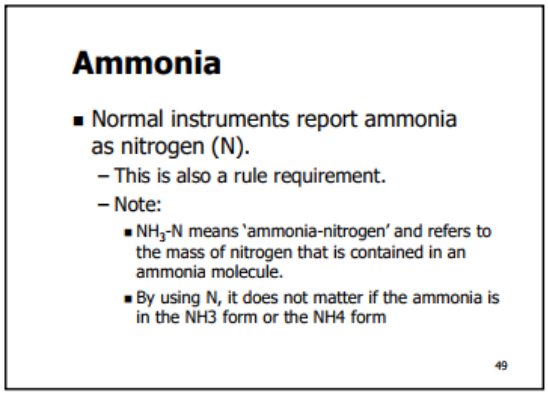
Free available ammonia = NH3 + NH4+



In water with a pH less than 9.3, ammonia is in the 'ammonium ion' form (NH4+). In water with a pH over 9.3, it is present as ammonia (NH3).



Luckily, the methods that we use to measure ammonia allow us to just read it all **'as nitrogen' (N)**. Just as with 'free chlorine', which measures both chlorine species **as 'Cl2'**. That makes it easier to compare amounts of chlorine and ammonia, which is a big deal in chloramination, as we will talk about soon.



Total chlorine

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Total chlorine = HOCl + OCl- + NH2Cl + NHCl2 + NCl3

In English, this says

> *"Total chlorine is the sum of*
> *hypochlorous acid, hypochlorous ion, monochloramine,*
> *dichloramine, and trichloramine."*

In natural waters, total chlorine will also measure organic amines, even though they have no disinfecting power.

When you use free chlorine, the total chlorine measurement is just free chlorine; but, when you use chloramines, the total chlorine measurement is the sum of all the chloramine species—mono, di, and tri.

Monochloramine

Monochloramine is the member of the chloramine family that provides disinfection.

Monochloramine is NH2Cl

Dichloramine and trichloramine

Dichloramine and trichloramine are unwanted members of the chloramine family that form when the ratio, or balance, of chlorine and ammonia is off.

Dichloramine is NHCl2

Trichloramine is NCl2

Note: In previous versions of this DAM, the term 'breakpoint chlorination' was used when describing chloramination. Strictly speaking, the term 'breakpoint chlorination' means adding enough chlorine to wastewater to overcome the ammonia (from urine) and create a free chlorine residual. This version has altered the wording to current usage.

The chemistry bottom line

When we chloraminate, we try to form monochloramine molecules. Monochloramine is our desired product because we know a lot about its effectiveness as a disinfectant and it produces the least offensive taste of any of the chloramine species.

Although some research indicates that dichloramine and trichloramine may be disinfectants, we try to avoid forming them because they are less stable than monochloramine and are associated with a variety taste and odor problems.

Figure 1 shows the reaction when gas chlorine is added to water to form free chlorine.

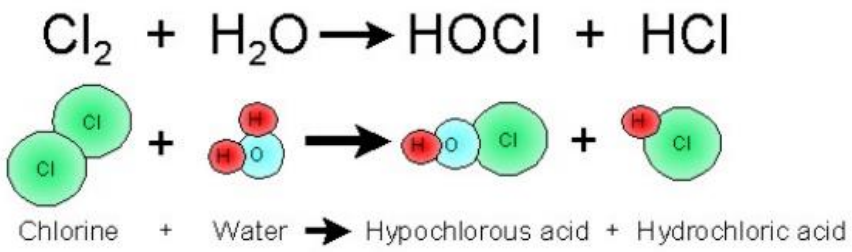


Figure 1. Gas chlorine added to water

Figure 2 shows the main chloramine formation reactions when chlorine is added to water that contains some free ammonia.

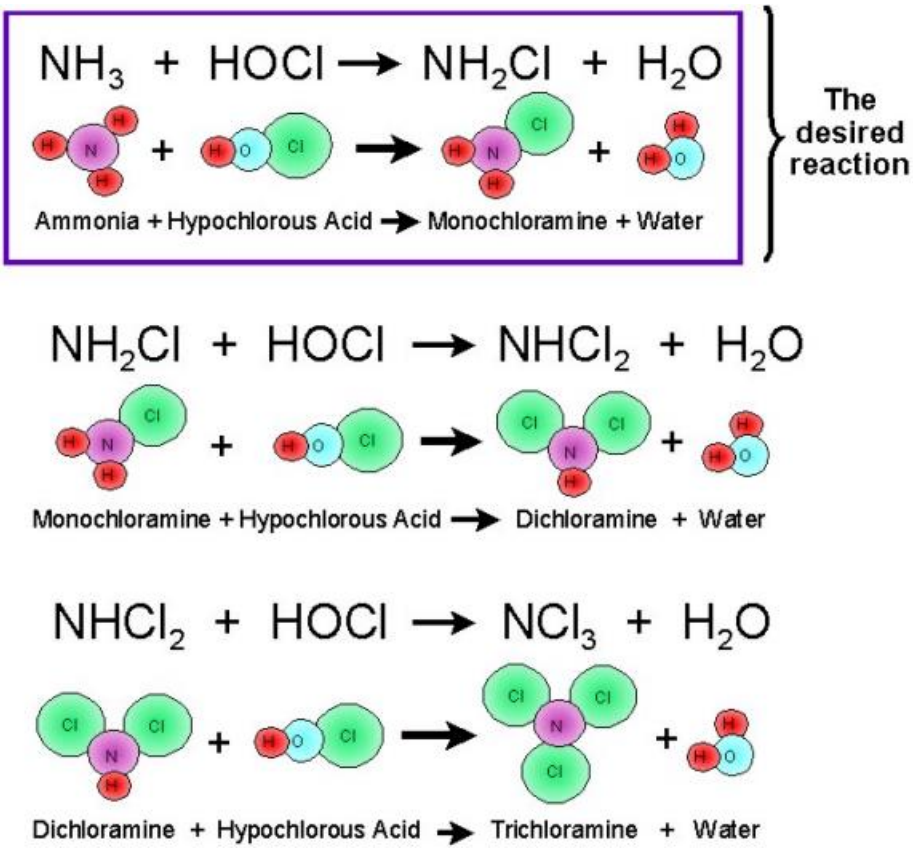


Figure 2. The three main reactions related to chloramine formation (autodecomposition of monochloramines is not shown).

This set of equations shows that one molecule of monochloramine will form when one molecule of chlorine reacts with one molecule of free available ammonia. However, if we have too much chlorine present, we run out of ammonia molecules and the excess chlorine reacts with our monochloramine molecules to form dichloramine. At really high chlorine levels, we can convert dichloramine molecules to trichloramine.

Organic chloramines can also form when chlorine reacts with organic compounds that contain an ammonia (amine) group. Organic chloramines will react with DPD to give a positive result but we don't know much about how effective they are as a disinfectant. Therefore, we consider organic chloramines to be interfering substances rather than a true disinfectant.

Finally, the equations show that free chlorine and free available ammonia cannot coexist to any significant degree because they will react with each other. Furthermore, it is extremely unlikely that free chlorine and monochloramine will exist in the same sample for very long since the free chlorine also reacts with monochloramine.

Part 2—Breakpoint curve

Chloramines

When we talk about mixing ammonia and chlorine—things get a little complicated.

Before we get into the specifics of the chlorine chemistry, we will talk about the breakpoint curve phenomenon.

The first time that people noticed how complicated chloramine chemistry was when wastewater operators in the 1930s-40s were trying to chlorinate wastewater, which tends to have a lot of ammonia in it. They would keep adding chlorine, and it just did not act normal.

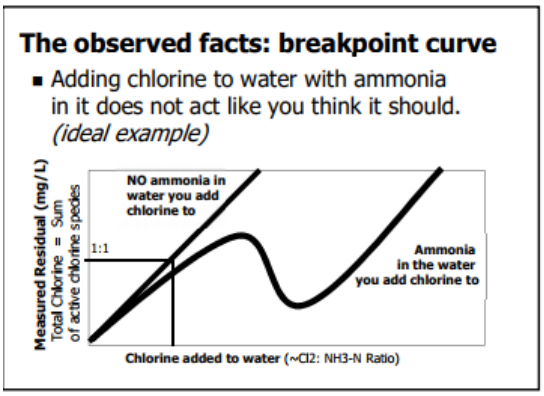
Normally, if you add a chemical to water, you get a straight-line response. For example, if you add sugar to tea, it keeps getting sweeter (till you reach saturation). Or, if you add salt to stew, it just gets saltier.

That is not how adding chlorine to ammonia-containing water works.

To show this, we graph the concentration of total chlorine on the Y-axis, and the chlorine-to-ammonia-nitrogen ratio on the X axis. That basically says

> ***"Here is what happens to the total chlorine when we add free chlorine to water that has some free ammonia in it."***

Instead of going up in a one-to-one fashion, the total chlorine goes up at first, but then it goes DOWN before going up again.



The wastewater operators that discovered this just thought of this as extra 'demand.' They wanted a free chlorine residual, and to get that they had to go past the 'dip' (which they named the 'breakpoint).

WE want something else entirely—to never get to the dip!

Using chemistry to explain the breakpoint curve

Chlorine LOVEs to react with ammonia.
The reaction is quick and complete.

However, it really matters what the number of chlorine atoms is compared with the number of nitrogen atoms is. That is why the X axis on the breakpoint curve is the mass ratio of chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N).

If chlorine + ammonia acted normal, we would just be able to graph total chlorine on the Y axis and chlorine added on the X axis—but we would never do that because it would be a boring straight line going up at a slope of 1 to 1.

But remember—total chlorine measures the sum of all active chlorine species.

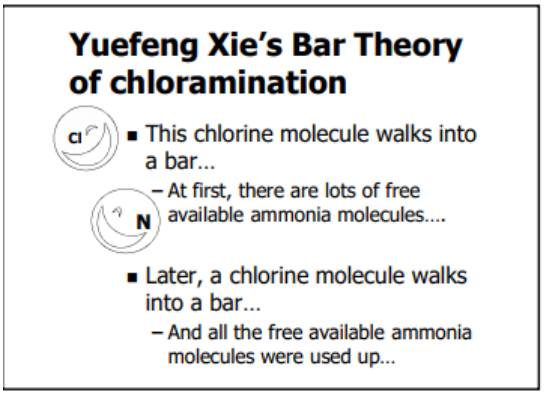
Total chlorine = $HOCl + OCl^- + NH_2Cl + NHCl_2 + NCl_3$

That is a clue to what is going on!

What happens when you add chlorine to water with ammonia in it is, at first there is one ammonia atom available for every single chlorine atom that you add. And, when there is only one chlorine for every ammonia, you get monochloramine, which is great:

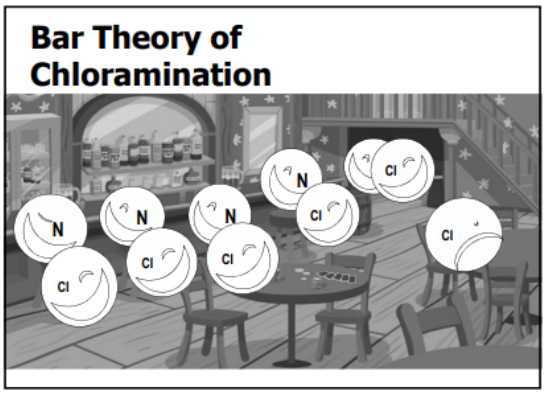
$HOCl + NH_3 \leftrightarrow NH_2Cl$ (monochloramine)

So here is one way to visualize that—Yuefeng Xie's "Bar Theory of Chloramination."



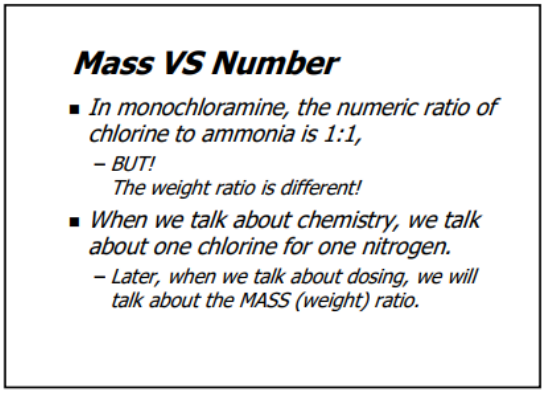
Imagine that there are ammonia molecules lined up on every bar stool early in the night. As the chlorine molecules come into the bar, each one sees an ammonia molecule it likes, and interacts.

That is great until a little later in the night when every single ammonia has found a chlorine molecule. Then, when another chlorine comes in, and there is no ammonia available, the fights break out!



Now, before we move on to talk about how those 'fights' generate dichloramine and trichloramine, lets step back and review the difference between mass and number. That way, when we start talking about MASS ratios, we won't get confused with the NUMBER ratio we want—which is One-To-One chlorine-to-ammonia-nitrogen MOLECULES.

When we draw the breakpoint curve and do the dosing chemistry, we are going to want to use MASS ratios, because that is how we measure chemicals.



This slide is just a reminder for later as we start talking about chlorine-to-ammonia-nitrogen (Cl2:NH3-N) axis on the breakpoint curve. The relative weights are 71 for Cl2, and 14 for N, so a 1:1 number ratio is equivalent to a 5.1:1 mass ratio.

Now, let's do the chemistry to figure out how the breakpoint curve is made.

Chloramine chemistry details

Chloramines are a family of three main chemicals:

- Monochloramine,
- Dichloramine, and
- Trichloramine.

Monochloramine

When free chlorine is first added to water that has ammonia in it, monochloramine is formed—which is great, because monochloramine is the disinfectant. It is what we want and need for keeping the distribution system protected from pathogens.

The chemical equation for monochloramine formation is:

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

In English this says

> *"Free chlorine in contact with ammonia forms monochloramine and water, in equilibrium, but mostly in the form of monochloramine."*

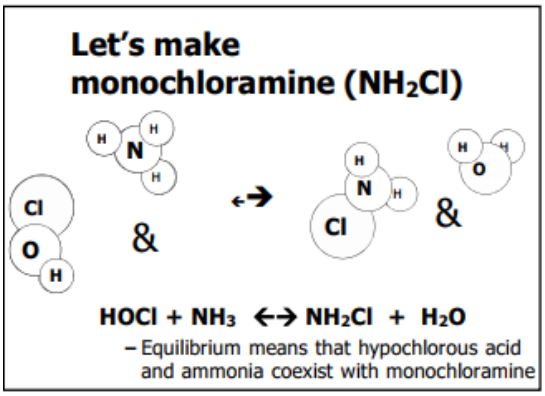
Monochloramine formation

- $HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$
  - Free chlorine in contact with ammonia forms monochloramine and water, in equilibrium
  - Monochloramine is the desired species for chloramination in drinking water treatment
    - It is the disinfectant
  - Forms fastest at pH 8.3
  - Dominates when Cl:N mass ratio is 0 to ~5:1
  - The breakpoint curve rises at about 1:1 during monochloramine formation

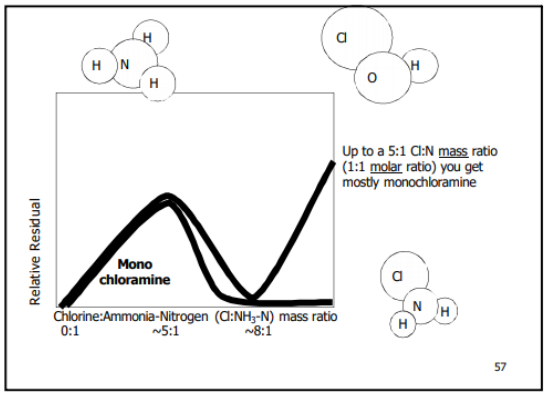
In terms of the 'Bar Theory', it is still early in the evening.

This is an extremely rapid reaction, it only taking seconds. It is fastest at pH 8.3, but it is very fast at all normal drinking water pH levels. As a side note, when chlorine and ammonia are mixed at much, much higher concentrations, the reaction is explosive—that is a demonstration of just how quick the reaction is.

Monochloramine is the chemical that dominates when Cl_2:NH_3-N mass ratio is 0 to about 5:1. This corresponds to the number ratio of one Cl_2 at 71 grams per mole, to one N, at 14 grams per mole. The weight ratio of 71:14 = 5.06:1.



Remember, on this breakpoint curve, we plot the total chlorine mass-based residual (mg/L) on the vertical axis, and plot the chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio on the horizontal axis. This represents the amount of chlorine added to water that contains a fixed amount of nitrogen (from free ammonia).



Then, above the 'peak point' at a Cl_2:NH_3-N ratio of 5:1, monochloramine decays as it starts getting used up making di- and trichloramine. The dip in the breakpoint curve occurs at a Cl_2:NH_3-N ratio of about 8:1.

The breakpoint curve rises at a slope of about one-to-one during monochloramine formation.

> ***In terms of the 'Bar Theory,' it is early in the evening when you have monochloramine, and everything is okay.***

Dichloramine

If a little too much chlorine is added to water with ammonia in it, the chlorine atoms are going to want to react—but there won't be enough free ammonia for every chlorine—so some chlorines are going to have to double up and form dichloramine.

Dichloramine has some disinfecting power, but it decays rapidly, and is hard to measure so it is not useful. Plus, it smells a little too chlorine-y and unpleasant.

Dichloramine forms two ways. One way is when free chlorine reacts with monochloramine to stick two chlorines onto the monochloramine's nitrogen.

The other way is called auto-decomposition, which means that one monochloramine attacks another monochloramine to form dichloramine.

Dichloramine formation

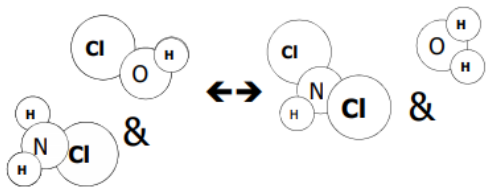
- Two reactions
  - $HOCl + NH_2Cl \rightarrow \mathbf{NHCl_2} + H_2O$
    - Monochloramine reacts further with chlorine to give dichloramine and water, essentially 1-way
    - Occurs at pH <8
  - $2\ NH_2Cl \leftrightarrow \mathbf{NHCl_2} + NH_3$
    - Autodecomposition of monochloramine into dichloramine – equilibrium
  - When you are getting significant dichloramine, the breakpoint curve will start dropping

In terms of the 'Bar Theory,' it is later in the evening, and some fights are starting!

The first reaction that makes dichloramine—free chlorine attacking monochloramine—is shown below.

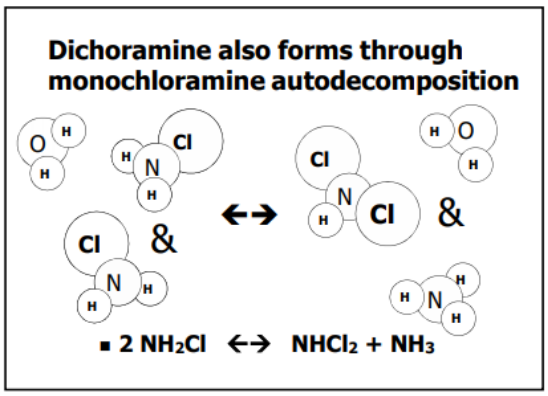
Making dichloramine ($NHCl_2$)

from monochloramine and hypochlorous acid



$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$

The second reaction—monochloramine attacking itself—is shown below.

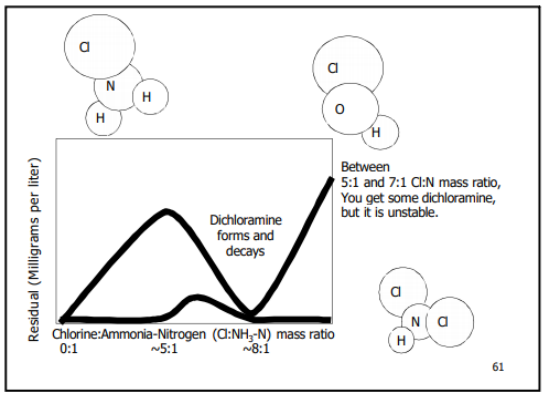


Below a Cl_2:NH_3-N mass ratio of 5:1 there is no dichloramine because all the chlorines can find their own nitrogen to react with.

Above a Cl_2:NH_3-N mass ratio of 5:1, there is a little extra chlorine that can form dichloramine.

But as the Cl_2:NH_3-N mass ratio gets closer to 10:1, the dichloramine gets involved in other reactions and decays rabidly.

In summary, dichloramine is most likely to occur when the Cl_2:NH_3-N mass ratio is higher than 5:1, but lower than ~10:1.



In that same range of ratios, another reaction can happen… formation of trichloramine.

Trichloramine

In the dichloramine molecule, two chlorines are attached to the nitrogen, and there is one hydrogen. If there is a little bit more free chlorine around that needs to react with something, it can stick one last chlorine on that nitrogen to form trichloramine.

Trichloramine just happens to smell terrible. It has been called ‘medicine-y’, ‘sharp’, or ‘chlorine-y.’

Also, it is very unstable, generally lasting for nanoseconds. (However, at low pH it can persist through the free chlorine zone, causing stinky headaches for swimming pool operators.) It is not a good disinfectant.

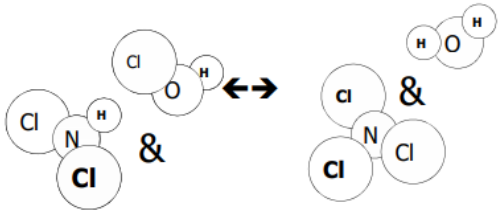
Trichloramine formation

- Trichloramine, AKA Nitrogen trichloride (NCl_3)
  - $HOCl + NHCl_2 \rightarrow \mathbf{NCl_3} + H_2O$
    - Dichloramine reacts with chlorine to form nitrogen trichloride
    - Favored at low pH, only detectable at pH < 4
    - Trichloramine is not soluble in water, it off-gasses
    - Present at Cl:N ratios ~ 7:1 – 8:1
    - It smells terrible
  - Present at the breakpoint – the dip of the breakpoint curve

In terms of the 'Bar Theory,'
it is closing time!
Everyone is leaving!

Trichloramine starts with dichloramine. Free chlorine, present because of the various equilibria, attacks a dichloramine molecule and kicks off the last hydrogen. After which, it degrades rapidly.

Let's make trichloramine (nitrogen trichloride) NCl_3



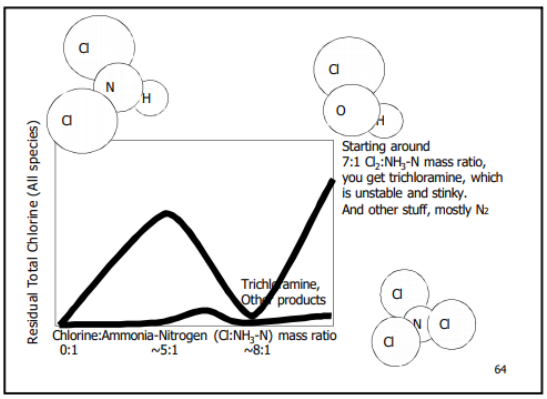
- $NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$

Looking at where this happens on the breakpoint curve, there is no trichloramine when the Cl_2:NH_3-N ratio is below 5:1 because every chlorine atom can find a nitrogen atom from ammonia to react with to form monochloramine.

As soon as there is some dichloramine to attack—just above a Cl_2:NH_3-N ratio of ~5, trichloramine can start to form.

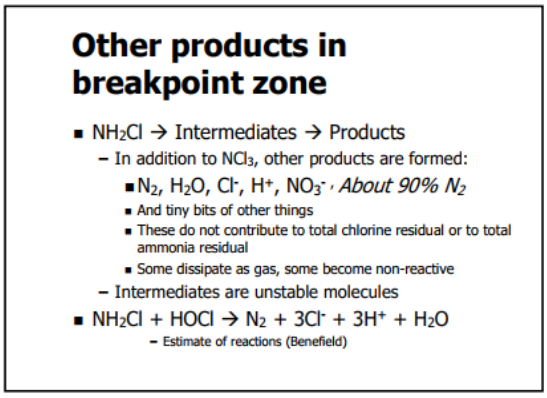
Between a ratio of 5:1 and ~10:1 trichloramine forms and decays.

Above a ratio of ~10:1, a little trichloramine can be present, especially at low pH. This does not concern us because we are trying to chloraminate, not chlorinate.

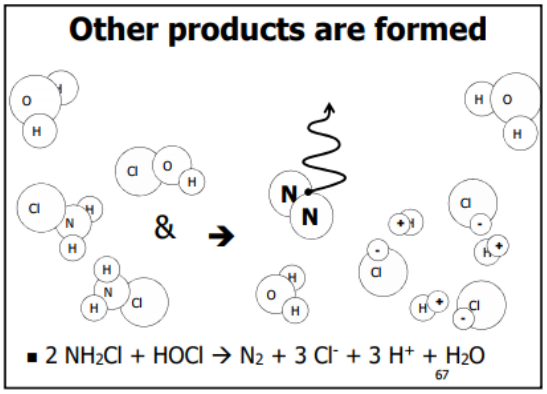


Other products in the 'dip'

In the 'dip' or 'breakpoint' of the breakpoint curve, there is a lot going on, but it is hard to figure out exactly what, because it is pretty chaotic. Other products in the breakpoint 'dip' DON'T include any useful disinfectants, and DO include mostly nitrogen gas, which leaves the water very quickly, taking away the nitrogen.



In addition to nitrogen gas, some of the other useless chemicals formed in the 'dip' include chloride ion, hydrogen ion, and water.

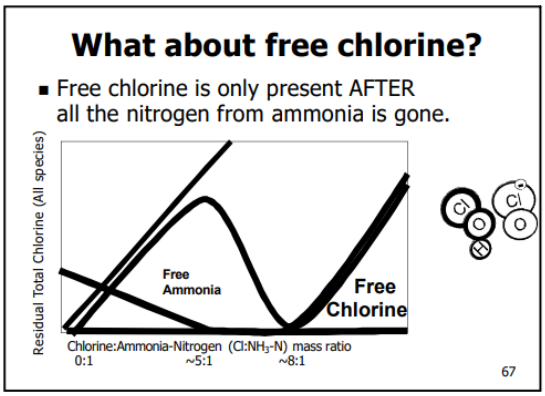


In terms of the breakpoint, these are some of the reactions that cause a dip in total chlorine at a Cl2:NH3-N ratio around 10:1—The Breakpoint, or 'dip'!

Free chlorine and ammonia

We have looked at our chloramine family—but we are also interested in free chlorine and ammonia, which are mutually exclusive. After the ammonia has been used up to form amines and other chemicals, any additional chlorine added is all free chlorine.

Wastewater operators (who figured out chloramination) wanted to operate in the free chlorine zone, past the breakpoint. We don't. We want to stay safely in the monochloramine zone. There is some reason the system uses chloramines—usually to control disinfection byproducts. Operating in the free chlorine range would be going backwards.



Ammonia is not really part of the breakpoint curve, because it is not part of total chlorine. However, it is useful to look at the ammonia curve along with total chlorine. The most notable thing is the observation that free chlorine CAN'T exist when there is free ammonia in the water.

False positives in the free chlorine method sometimes lead people to think that free ammonia and free chlorine exist at the same time…

This cannot happen, because… chemistry!

Organic amines

One thing that can complicate matters is when source water has organic molecules that have an amine (ammonia) chunk attached to them. This is one reason we use the FREE ammonia test instead of the TOTAL ammonia test. If you used the total ammonia test, you would measure some organic amines and think you had more ammonia than you actually do. Only free ammonia can form monochloramine, not organic amines.

Organic amines

- *In drinking water treatment, chlorine and chloramines react with naturally occurring organic molecules*
  - *This reaction can form stable organoamines*
    - *Commonly expressed as R-NH_x*
  - *Normal field tests may detect organoamines as total ammonia.*

Putting it all together: Drawing the breakpoint curve

Now that we have looked at each chemical individually, we can put them all together on one graph that we call the 'breakpoint curve.'

In this section we show several different versions of the breakpoint curve to demonstrate that there is not just ONE breakpoint curve. First—the same information can be presented differently, and second—the curve varies depending on pH, demand, etc. so it will look different when developed for different waters.

All of the curves that we looked at for monochloramine, dichloramine, trichloramine, and free chlorine add up to form total chlorine,

which we graph and call the breakpoint curve.

Putting it all together

- The total chlorine breakpoint curve is the sum of all those curves: Mono, Di, and Trichloramine, plus Free chlorine.

70

Remember, the breakpoint curve shows the total chlorine residual on the vertical axis, and the chlorine-to-nitrogen ratio on the horizontal axis—here represented as the amount of chlorine added to water than contains a fixed amount of nitrogen.

The X and Y axes of the breakpoint curve are:

- Y-axis—mass concentration of total chlorine in milligrams per liter, and
- X-axis—chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio.

Breakpoint curve Y-axis—Total chlorine

The Y-axis of the breakpoint curve is total chlorine.

Total chlorine measures the sum of all active chlorine species.

Total chlorine = $HOCl + OCl^- + NH_2Cl + NHCl_2 + NCl_3$

Breakpoint curve X-axis—Chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio

The X-axis of the breakpoint curve is the Cl_2:NH_3-N ratio. We will talk more about this ratio in later chapters—for now we just need to understand this X axis.

For dosing chloramines, we target the optimum 5:1 chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio to maximize monochloramine formation and minimize leftover ammonia. It is acceptable to dose at lower ratios, but not higher ones.

Most instruments measure total chlorine and monochloramine "as Cl_2." It is specified that free available ammonia must be measured "as N."

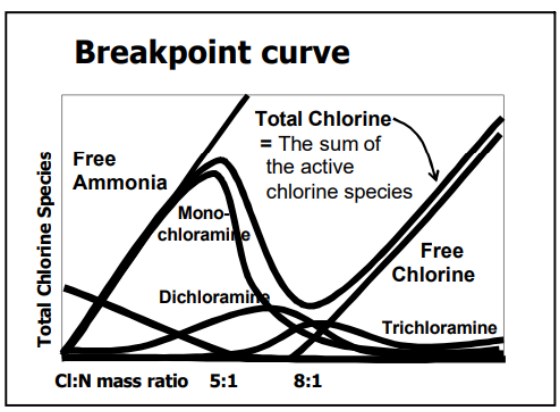
1 mole HOCl (as CL_2) + 1 mole NH_3 (as N) →
1 mole of NH_2Cl + 1 mole of H_2O

A single chlorine molecule (Cl) weighs 35.5 grams per mole. Since monochloramine is measured as Cl_2, the total weight is two times 35.5 = 71 grams per mole. Ammonia is measured as N (nitrogen), which weighs 14 grams per mole.

The weight ratio of chlorine (Cl_2) to nitrogen (N) in monochloramine is:

71 / 14 = 5.06

Therefore, the peak of the breakpoint curve (at normal pH) happens at a Cl2:NH3-N ratio of about 5:1.



In the slides that go with this presentation, an example of how to interpret results using the breakpoint curve is provided.

In this manual, several different examples of the breakpoint curve are provided, with different information on them. The purpose of this is to allow the student to become familiar with the breakpoint curve and understanding it, no matter how it is shown.

Simple breakpoint curve illustration

A simple version of the breakpoint curve is shown here (and is shown on the accompanying slide).

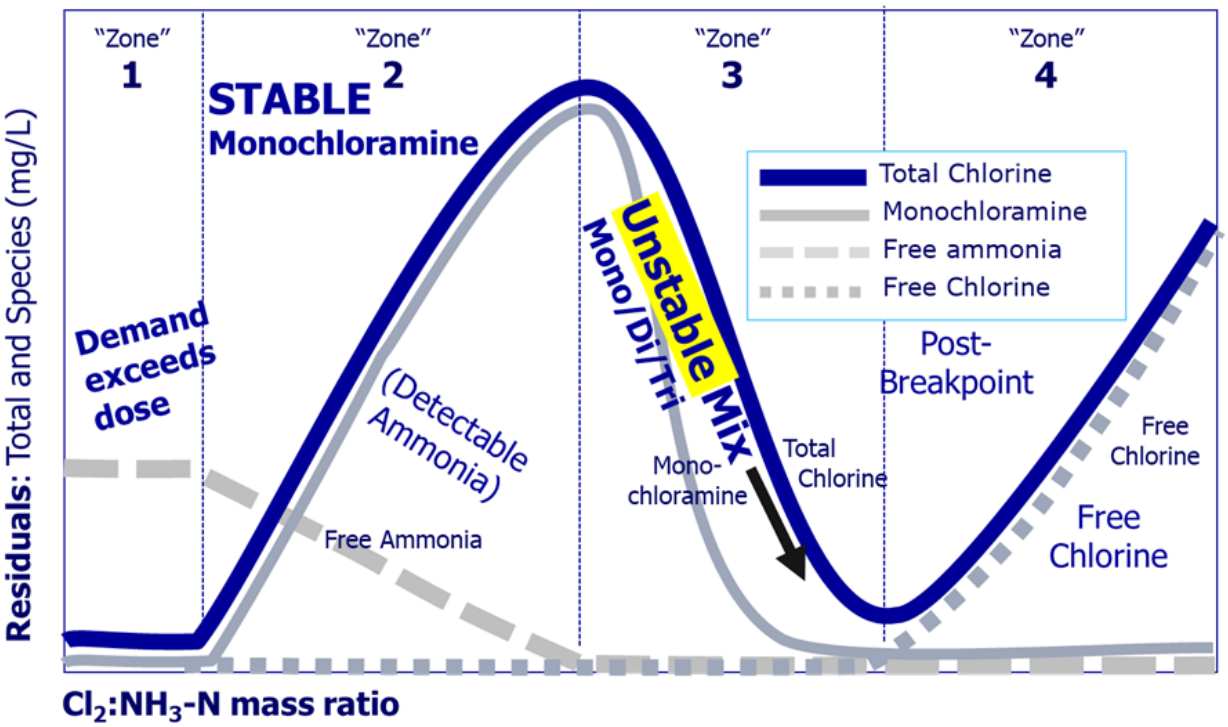
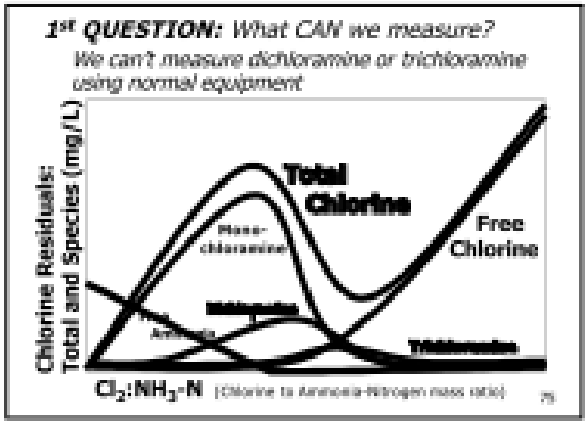


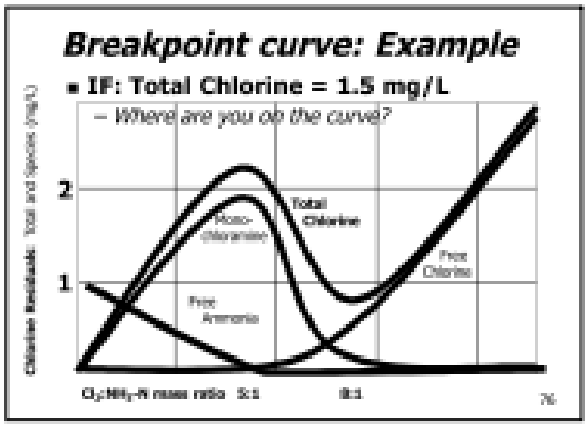
Figure 3. Breakpoint curve, showing the major 'zones'

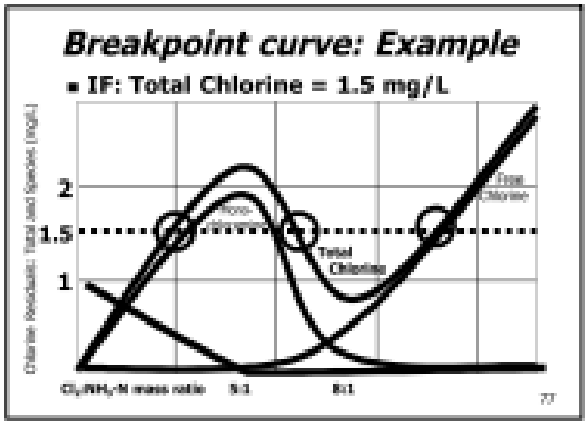
This simple curve (Figure 3) can be used to figure out which 'zone' your water is in—whether you have a stable monochloramine residual, whether you are starting to form di- and trichloramine, whether you are on the 'peak,' or whether you have passed the breakpoint dip and are in the free chlorine zone.

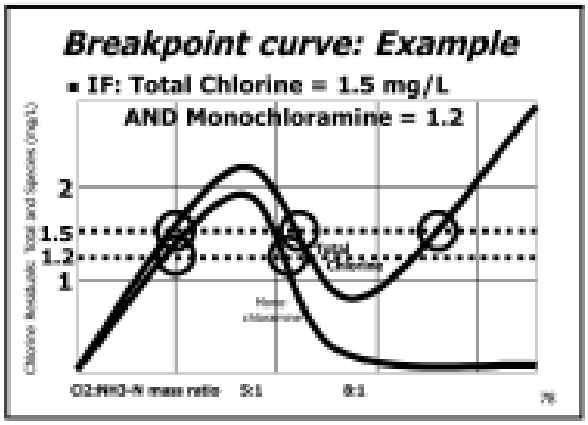
Breakpoint examples: What 'zone' are you in?

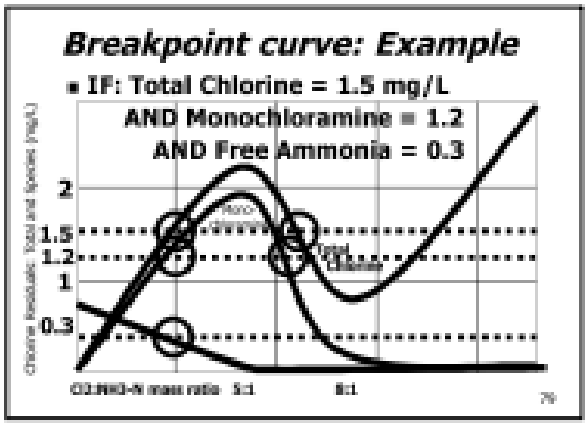
This example is also provided in the accompanying slides:


1st QUESTION: What CAN we measure?
We can't measure dichloramine or trichloramine using normal equipment
Chlorine Residuals: Total and Species (mg/L)
Total Chlorine
Mono-chloramine
Free Chlorine
Ammonia
Cl2:NH3-N (Chlorine to Ammonia-Nitrogen mass ratio)
75


Breakpoint curve: Example
IF: Total Chlorine = 1.5 mg/L
– Where are you on the curve?
Chlorine Residuals: Total and Species (mg/L)
2
1
Total Chlorine
Mono-chloramine
Free Chlorine
Free Ammonia
Cl2:NH3-N mass ratio 5:1
8:1
76


Breakpoint curve: Example
IF: Total Chlorine = 1.5 mg/L
Chlorine Residuals: Total and Species (mg/L)
2
1.5
1
Mono-chloramine
Total Chlorine
Free Chlorine
Cl2:NH3-N mass ratio 5:1
8:1
77



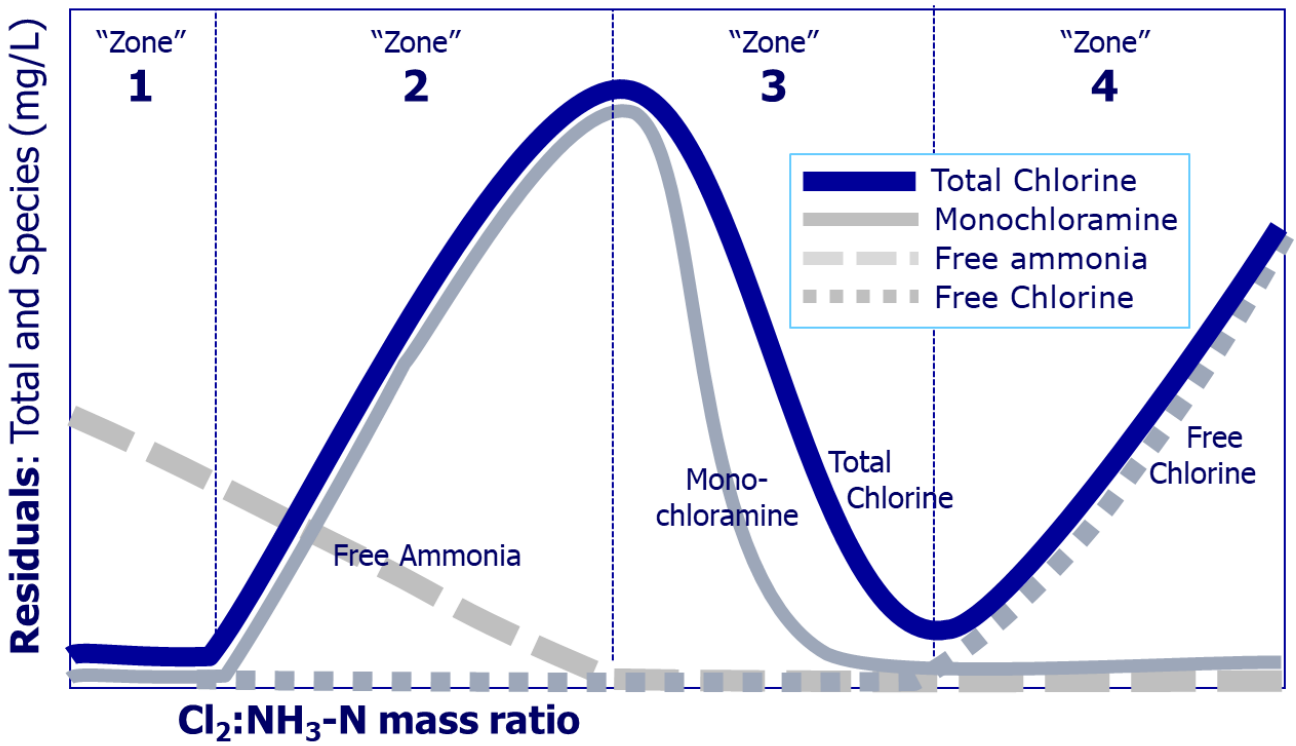


What do you need to monitor to know whether you are in the monochloramine zone?✓

A. Total chlorine ○
B. Monochloramine ○
C. Free ammonia ○
D. Free chlorine ○
E. A, B, and C ○
F. All of the above ○

Next: Do examples on page 49 and 50 of Student Guide 80

The following examples ask us to look at the data provided, and figure out what 'zone' of the breakpoint curve the water is in, using this graph:



Example 1.1: Monday

Your PWS is purchasing and redistributing treated potable water.
On Monday, you analyze the water and find:

Total chlorine	=	0 mg/L
Monochloramine	=	0 mg/L
Free ammonia	=	1.1 mg/L
Free chlorine	=	0 mg/L

Which 'zone' of the breakpoint curve (above) are you in?

Example 1.2: Tuesday

On Tuesday, at the same purchased water PWS, you analyze the water and find:

Total chlorine	=	2.0 mg/L
Monochloramine	=	1.9 mg/L
Free ammonia	=	0.49 mg/L
Free chlorine	=	0 mg/L

Which 'zone' of the breakpoint curve (above) are you in?

Bonus question: Did you really need to measure free chlorine to find that out?

Example 1.3: Wednesday

On Wednesday, at the same purchased water PWS, you analyze the water again, and find:

Total chlorine	= 2.0 mg/L
Monochloramine	= 2.0 mg/L
Free ammonia	= 0 mg/L
Free chlorine	= 0 mg/L

Where on the breakpoint curve (above) are you?

Example 1.4: Thursday

On Thursday, at the same purchased water PWS, you analyze the water again, and find:

Total chlorine	= 2.0 mg/L
Monochloramine	= 0.7 mg/L
Free ammonia	= 0 mg/L
Free chlorine	= 0 mg/L

Which 'zone' of the breakpoint curve (above) are you in?

Example 1.5: Friday

On Friday, at the same purchased water PWS, you analyze the water again, and find:

Total chlorine	= 0.2 mg/L
Monochloramine	= 0.1 mg/L
Free ammonia	= 0 mg/L
Free chlorine	= 0.1 mg/L

Where on the breakpoint curve (above) are you?

Example 1.6: Saturday

On Saturday, at the same purchased water PWS, you analyze the water again, and find:

Total chlorine	= 1.0 mg/L
Monochloramine	= 0 mg/L
Free ammonia	= 0 mg/L
Free chlorine	= 1.0 mg/L

Which 'zone' of the breakpoint curve (above) are you in?

Other breakpoint curve examples

The breakpoint curve can be drawn in different ways to emphasize different points. Some more examples are provided here for the adventurous student.

The 'stages' or 'zones' may be labeled differently, but the information on each example represent the same concepts.

'Schulze' breakpoint curve

A more detailed discussion and illustration are developed by Jack C. Schulze, PE is shown below in Figure 4.

Chloramination is a complex process that involves a variety competing chemical reactions that are occurring simultaneously. Although all of the reactions begin the moment that chlorine is added to the water (that has ammonia in it), some of these reactions occur rapidly while others occur slowly.

Consequently, the reactions that dominate in Stage 2 of the breakpoint curve actually begin in Stage 1. Similarly, some of the reactions that dominate in Stage 1 might continue well into Stage 2 or maybe even Stages 3 or 4.

Nevertheless, the following is a reasonable (but admittedly grossly oversimplified, ***though less grossly oversimplified than the previous figure***) description of what happens during each stage on the breakpoint curve.

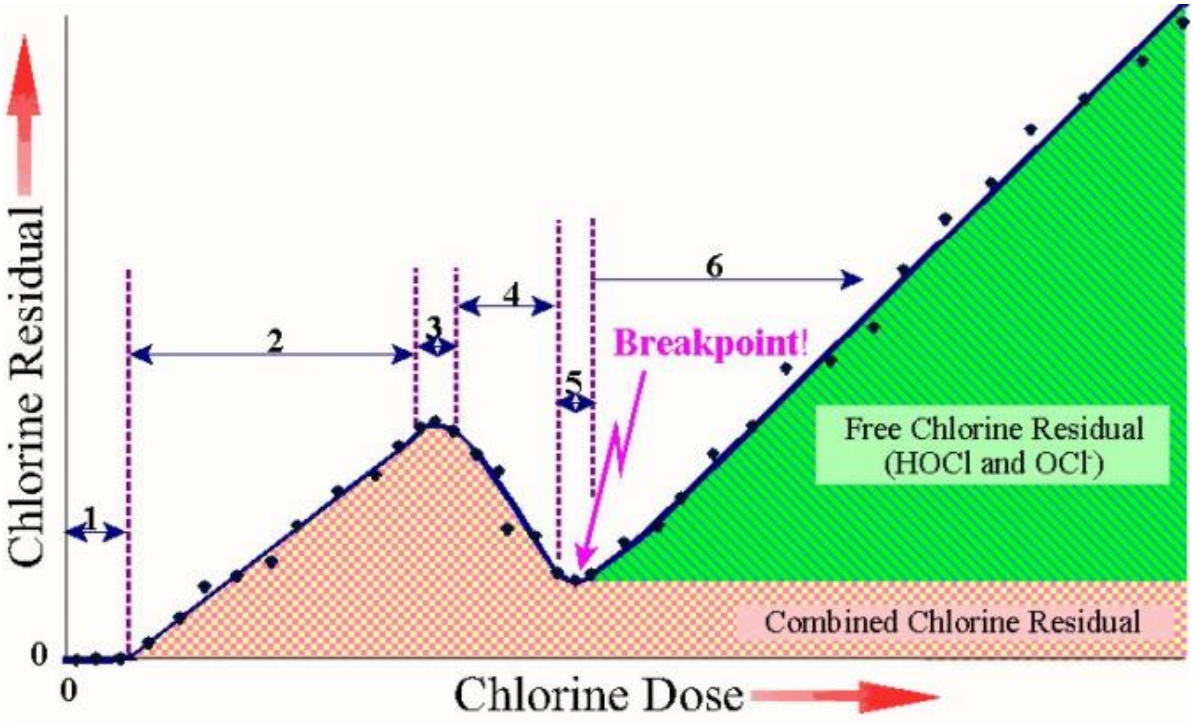


Figure 4. The Schulze breakpoint curve.

Stage 1. Using up (non-ammonia) demand

Chlorine is consumed by readily oxidizable, simple components (soluble iron, soluble manganese, nitrite, hydrogen sulfide, etc.) in the source water. Total chlorine residual is 0.0 mg/L (or close to it).

Stage 2. Monochloramine formation

Chlorine reacts with ammonia-nitrogen forming chloramines, mainly monochloramine.
Total chlorine residual rises. False-positive free chlorine residuals might be detected.
A 1.0 mg/L increase in the chlorine dose may produce less than a 1.0 mg/L increase in the total chlorine residual because some of the chlorine is reacting with organic nitrogen from source water.

Stage 3. Transition zone—The mountain peak point

Transition zone—total chlorine residual is created and destroyed at the same rate; monochloramine (NH_2Cl) starts turning into dichloramine ($NHCl_2$).

Stage 4. Di- and trichloramine formation

Total chlorine residual is being destroyed faster than it is forming; dichloramine ($NHCl_2$) is being formed and destroyed and trichloramine (NCl_3) begins to form.

Stage 5. The breakpoint—The 'dip'

Breakpoint! Almost all of the available nitrogen has been oxidized, and most of it turned into nitrogen gas (N_2) and other compounds that don't have any disinfecting power.
A free chlorine residual begins to persist.

Stage 6. Free chlorine formation

The ammonia-nitrogen (NH_3-N) is gone, so the free chlorine residual increases; trichloramine (NCl_3), and organic chloramines may also be present but the monochloramine is gone. A 1.0 mg/L increase in the chlorine dose will probably produce close to a 1.0 mg/L rise in both the free and total chlorine residuals. At low pH, trichloramine (NCl_3) may persist.

AWWA breakpoint curve with reactions

The American Water Works Association magazine "OpFlow" published an article called "DO YOU REALLY HAVE A FREE CHLORINE RESIDUAL" in the June 2008 edition. The article included a useful example of the breakpoint curve amended with the reactions in each zone and the total ammonia curve, shown in Figure 5.

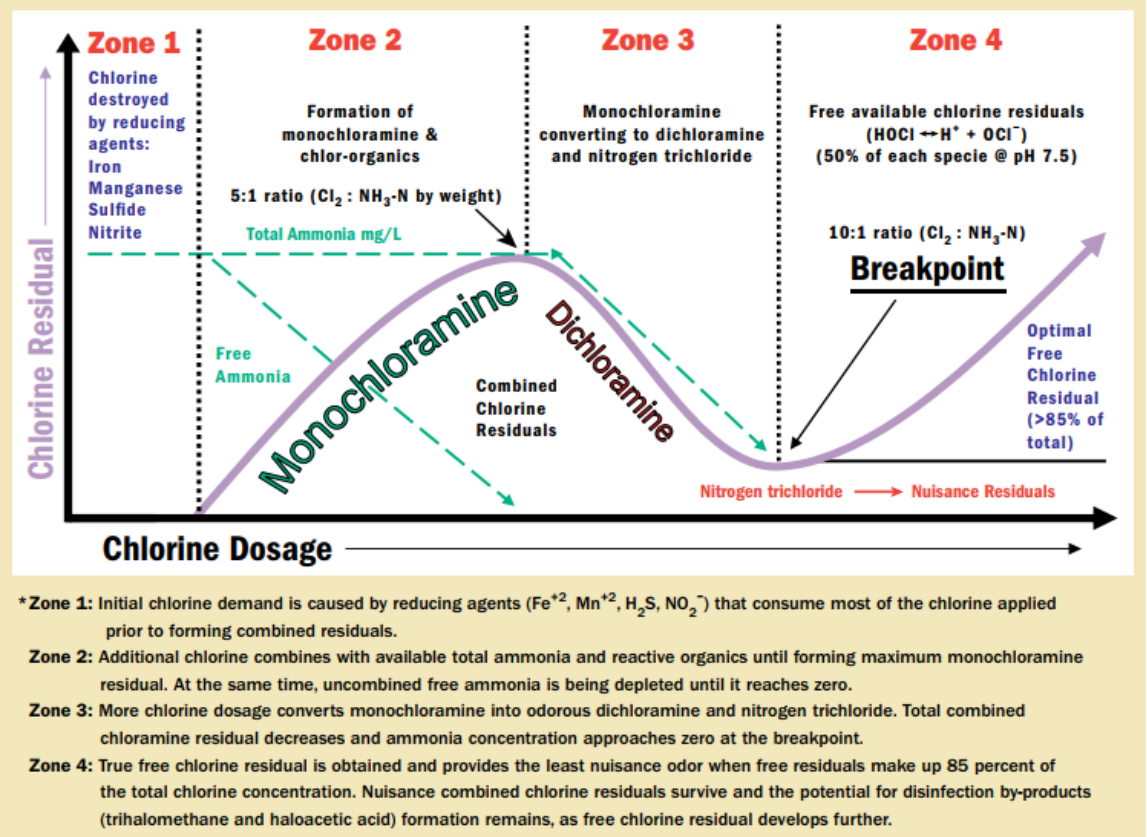


Figure 5. AWWA breakpoint curve showing reactions.

Breakpoint curve as a function of pH

In the real world, the chemical reaction is not only affected by the chlorine-to-ammonia ratio but also a variety of other factors that include pH, temperature, chlorine demand, and competing reactions. Although we will address some of these issues again later, let's look at how pH can affect the rates of the chemical reactions shown in Figures 3 and 4.

Figure 6 shows that low pH conditions encourage the formation of dichloramine and trichloramine, even if we have the correct Cl_2:NH_3, (or Cl_2:NH_3-N) ratio.

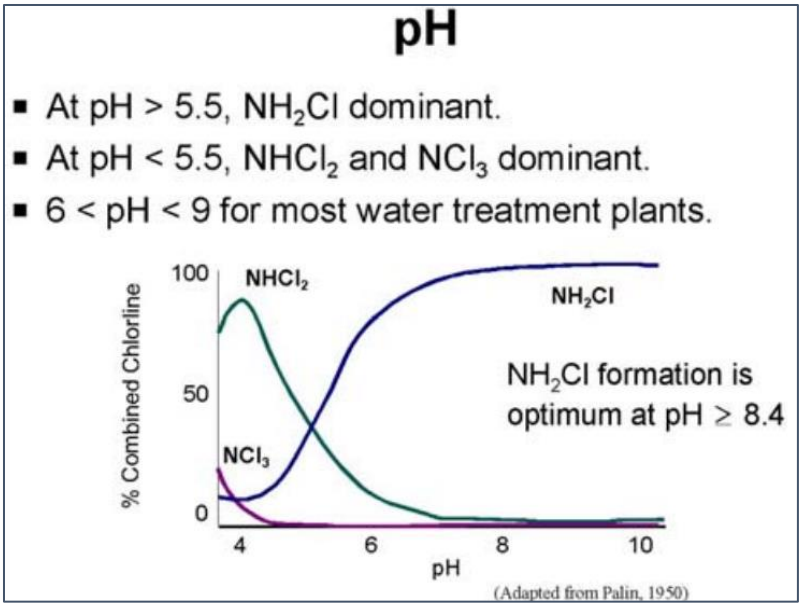


Figure 6. Impact of pH on monochloramine (NH2Cl) formation (Adapted from Palin, 1950)

The EPA Office of Research and Development has an application on the internet you can use to estimate the ideal decay of chloramines for your water. It is online at:

usepaord.shinyapps.io/Breakpoint-Curve/

To use the model, just input the levels of chemicals for your water. If you don't know certain values, try the defaults in the application.

Examples of the output of this model is shown in Figure 7. These show the impact of pH on the chloramine system.

When you look at these graphs, it shows how we simplified the earlier discussion to show normal pH situations, like at about a pH of 7.5 and higher. When the pH drops, it is easier for dichloramine and trichloramine to form and persist, which changes the shape of the breakpoint curve.

That does not mean the simplified discussion is wrong, it just reminds us that there is another good reason not to have a low pH, besides corrosivity.

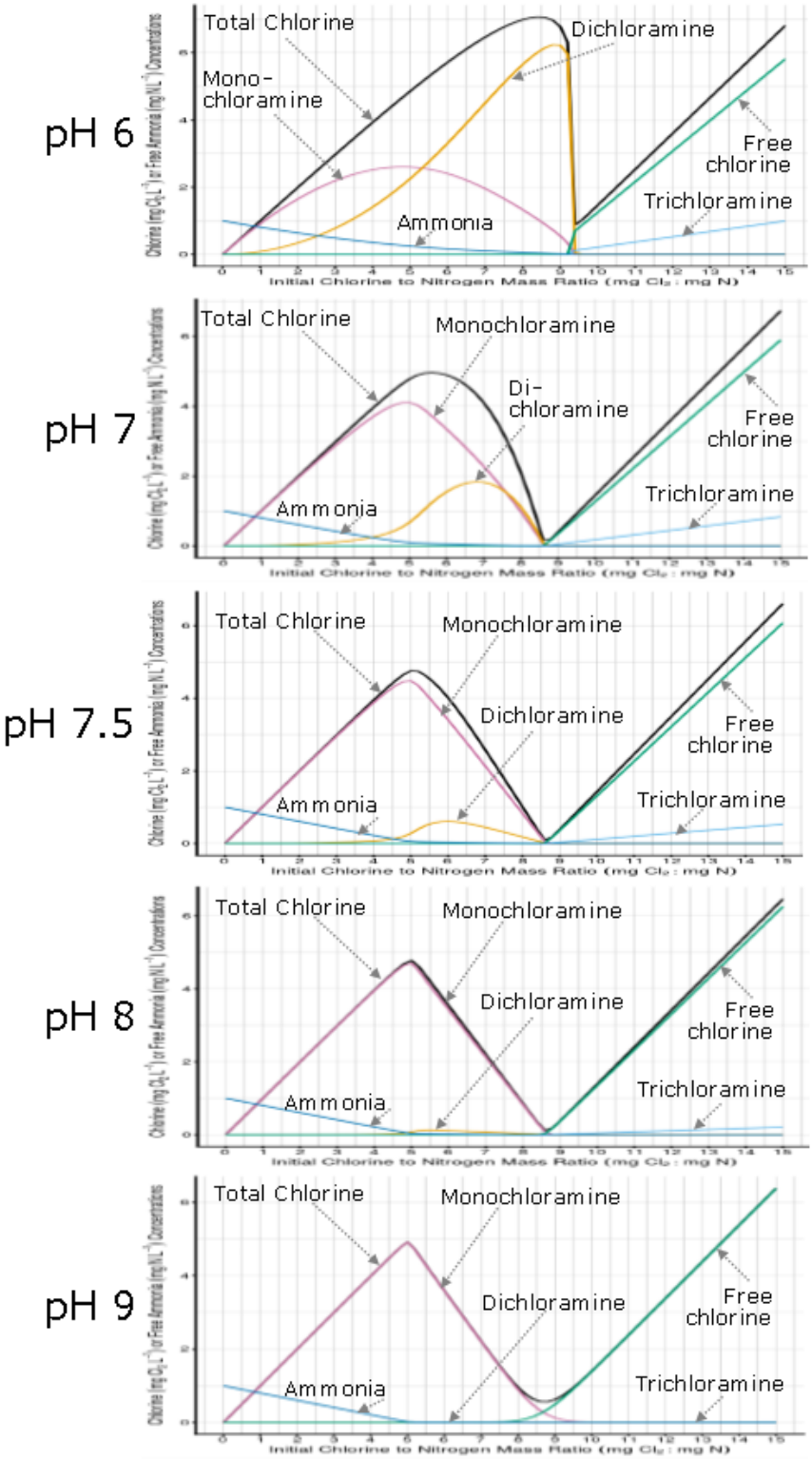


Figure 7. Ideal breakpoint curves as a function of pH.
(X-axis is initial Cl_2:NH_3-N ratio, Y-axis is chemical concentration in mg/L—as Cl_2 for chlorine constituents and —as N for free ammonia.)

The breakpoint bottom line

1. **The number of molecules is not the same as the weight of molecules.**
   We have to convert our molecular-based system of measurement to a weight-based system of measurement when we discuss test results, dosage calculations, and feed rate measurement.

2. **One unit of free chlorine will produce one unit of monochloramine.**
   If you add 1 mg/L of free chlorine with enough ammonia for each chlorine atom to attach to a nitrogen atom, you will get 1 mg/L of total chlorine as monochloramine.

3. **Free chlorine and monochloramine cannot exist in the same sample for very long (except at super low pH).**
   If ammonia is present, you don't have free chlorine,
   and if it looks like you do—you have an analytical error.
   Free chlorine false positives are very common.
   In the real world, we might get a trace of free chlorine in a sample containing mostly monochloramine or a trace of monochloramine in a sample containing mostly free chlorine.
   The DPD test is likely to give a false positive of ~0.01-0.2 mg/L.
   This problem is bigger the lower the pH.

4. **Use the right ratio of chlorine and ammonia.**
   If a plant does not mix chlorine and ammonia in the right ratios, there can be excess leftover ammonia or we can wind up slipping into the breakpoint dip and destroying monochloramine.
   The calculations to make sure we have the right ratios are described in the following Chapters of this manual.
   Be careful! Are you using Cl_2:NH_3 or Cl_2:NH_3-N?
   In theory, the optimum weight-based Cl_2:NH_3-N (chlorine-to-ammonia-nitrogen) ratio is ~5:1.
   (Instruments report levels as mg/L Cl_2 and as N.)
   Elsewhere (Chapter 5) we refer to the CL_2:NH_3 (chlorine-to-ammonia)-ratio (Cl_2:NH_3) of 4.2:1. The former (Cl_2:NH_3-N ratio) is more frequently used nowadays.

5. **Reality can be tricky! Seek help when needed.**
   There may be interference or other complicating factors.
   In reality, a number of environmental conditions can influence our chemical reaction rates and the stability of our disinfectant. We need to consider these factors when we design and operate our chloramination facilities.
   If you are getting data that does not make sense to you, seek additional assistance from the TCEQ, your association, the vendor, or other operators.

Example:
'Breakpoint Hold Study' to create a breakpoint curve for your water

By starting with raw water, you can also create a breakpoint curve specific to your water. This might be useful to:

- Understand the exact ratios associated with unstable chloramines in your water.
- Compare the results at different pH to choose possible operating conditions.
- Compare the results from different sources to evaluate compatibility.
- Demonstrate the breakpoint curve concept to students.

First, gather equipment

To do the Hold Study to develop a breakpoint curve for your water, you will need to:

- Collect enough **raw source water** for all the measurements.
- Mix chlorine and ammonia standards for dosing. Make enough.
    - You can get help mixing standards from the TCEQ's FMT assistance program—call 512-239-4691 or email FMT@tceq.texas.gov.
- Figure 8, below, shows what you need for a breakpoint curve special study.

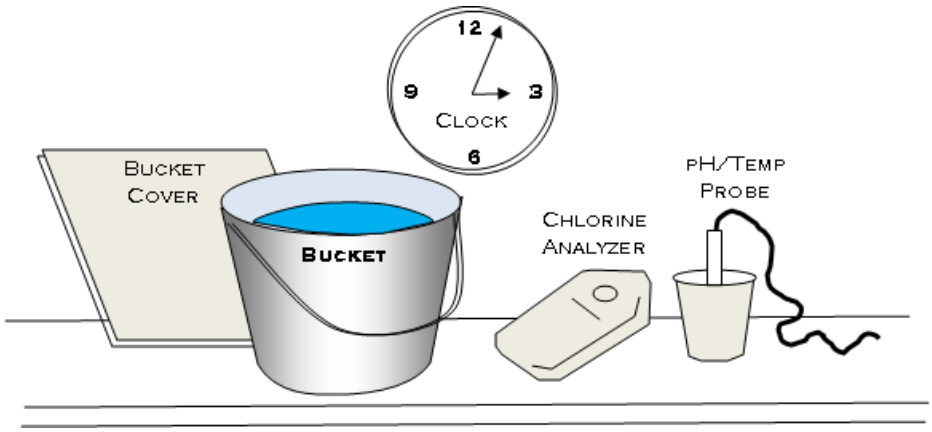


Figure 8. Equipment for a breakpoint curve special study (the same as for a 'Water Age Hold Study).

Procedure

- Add a predetermined amount of ammonia to the bulk water, mix it, and verify the free ammonia (as N) concentration.

- Make sure the bulk water is at a pH and temperature typical of the conditions for the system.

- From the ammonia-dosed bulk water, collect 10 500-mL samples in clean sample containers, being careful to measure volume accurately.
- Calculate the chlorine dose for each sample in progressive amounts, from chlorine-to-ammonia-nitrogen ratios of zero to ten, based on the concentration of ammonia in the bulk water and the chlorine dosing solution concentration. Gather the needed volumetric glassware to dose each sample correctly.
- Dose each sample using a stir bar at medium speed. (Don't do them all at once. Dose, mix, and measure each sample sequentially)
- After mixing briefly (5 seconds) measure and record free chlorine, total chlorine, monochloramine, and free ammonia (as N).
  - You can also measure total ammonia and pH if you want.
  - If the system performs heterotrophic plate count (HPC) monitoring as part of their process management, enough sample can be collected to see if there is any difference in the effect on HPC.
  - If your laboratory has the capability, you can measure dichloramine.

Graph the results. Consider using an expanded second Y-axis for graphing the free ammonia. Your results might look similar to (but not exactly the same as) Figure 9.

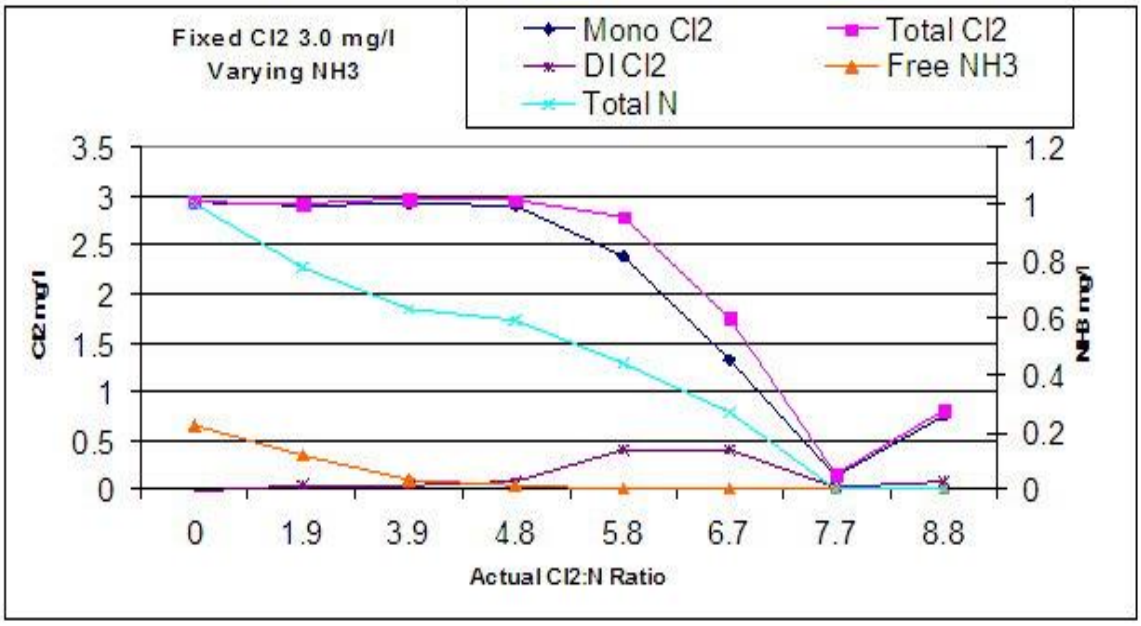


Figure 9. Example results for a site-specific breakpoint curve, using the system's source water, typical pH and water temperature.

Breakpoint ratio

Note that in this graph, the researchers were using a ratio of chlorine-to-ammonia so they don't pass the break point till a ratio of about 8:1. If they had been calculating using the chlorine to ammonia nitrogen ratio (Cl2:NH3-N), they would have had to exceed a ratio of about 10:1 to get to free chlorine.

Chapter 1 Review Questions

(Questions may have MULTIPLE correct answers.)

Which species provide disinfecting power?

1. Dichloramine
2. Trichloramine
3. Ammonia
4. Chlorpheneramine maleate
5. Monochloramine

What does the breakpoint curve represent?

1. What happens when you add sugar to tea
2. What happens when your points break
3. What happens when you add chlorine to water with ammonia in it
4. What happens when you add ammonia to water with chlorine in it

What is the purpose of monitoring ammonia?

1. Determine where on the breakpoint curve you are
2. Determine whether there is enough ammonia present
3. Determine whether monochloramine is present

If you want to produce water with 2 mg/L of total chlorine, how much free chlorine and free ammonia should you add (assume no non-ammonia demand)

- 2 mg/L : 2 mg/L
- 2 mg/L : 10 mg/L
- 1 mg/L : 2 mg/L
- 2 mg/L : 1 mg/L
- 2 mg/L : .0.4 mg/L

If you want to produce free-chlorinated water from water that has ammonia in it, what chlorine to ammonia nitrogen ratio (Cl2:NH3-N) do you need to exceed?

- 3:1
- 5:1
- 7.7:1
- 10:1

Chapter 1 Checklist

Hopefully, after this chapter, you are more comfortable with the chemistry needed to understand chloramines.

Make sure by going through this checklist. If there is something you need to work on, note that on your recommended action plan.

Chapter 1 checklist:

Part 1: Basic (and acidic) chemistry

- Do you feel comfortable with the concept of pH?
- Do you understand the idea of moles as a number, and how that relates to the mass (weight) of chemicals?
- Do you understand how pH can impact chemical equilibria?

Part 2: Breakpoint curve

- Do you know the chemicals in the chloramine family?
- Do you understand the 'Bar Theory' of chloramination?
- Do you know which member of the chloramine family is your friend and which ones are undesirable?

Next steps:

If you understand the breakpoint curve, you are doing great. This understanding will help you learn more about how to analyze samples and dose chemicals.

Recommended actions?

If you feel like you did not 'get' it as well as you would like, you may want to schedule follow-up training, or re-read the manual in your own time.

If so, note this on your Plan of Action.

Notes

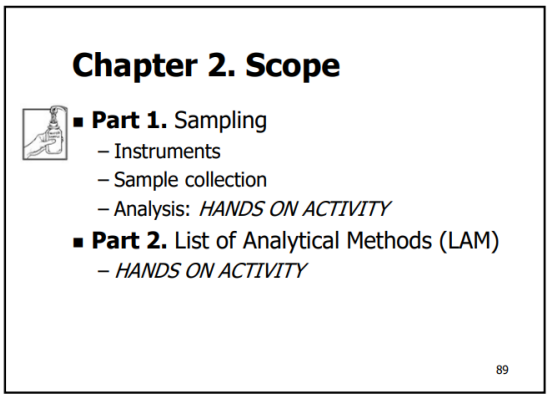
Chapter 2. Sample collection and analysis

To effectively evaluate and control our chloramination process, we need to be able to accurately measure total chlorine, free chlorine, monochloramine, and free ammonia. Good data leads to smart decisions—bad data leads to bad decisions. This chapter is intended to help you make sure that you are getting good data. This section (like this whole DAM) ties in with the NAP because the sampling methods described here are required in order to comply with NAP requirements.

Scope

First, we will talk about various instruments and do the hands-on workshop of analyzing samples from a potable water tap at the training location. This will give us a chance to review good analytical technique before going out into the field. There are two parts to this chapter:

- **Part 1:**
  - **Instruments**
  - **Sample collection procedure**
  - **Analysis**—including the hands-on activity of analyzing samples,
- **Part 2:**
  - Filling out **the List of Analytical Methods** (LAM) form.



Materials

For this section, the student should look at:

- ✓ The PWS's instruments and instrument manuals;
- ✓ The analytical method documentation;
- ✓ Their SOPs for sample collection and analysis,
- ✓ Data sheets and/or log books for recording results, and
- ✓ This Student Guide.

Learning goals

The learning goals for this workshop are:

- Be able to identify instruments that can be used for analysis;
- Know how to collect samples correctly;
- Be able to analyze samples correctly—and demonstrate proficiency; and
- Know how to document methods on the LAM—and complete that form.

Chapter 2. Learning Goals

- **Part 1.** Be able to collect and analyze samples to get good data
- **Part 2.** Be able to complete your List of Analytical Methods (LAM) to comply with TCEQ rules

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Remember: Good data supports good decisionmaking.

Good data supports **good decisions**

- Decisions like…
  - How good is my disinfection?
    - Do I need to make a change?
      - Total chlorine
      - Monochloramine and ammonia
  - Is it nitrification or something else?
      - Nitrite and nitrate

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Part 1: Sampling: Instruments, collection, and analysis

Instruments

The reason for monitoring is to be aware of any problems. If instruments are not accurate, operators may not find out about problems, or may think problems are happening when they are not. Having reliable, accurate instruments is a first step to compliance and success at holding residuals.

IMPORTANT!

Does the PWS have an instrument to measure total chlorine?

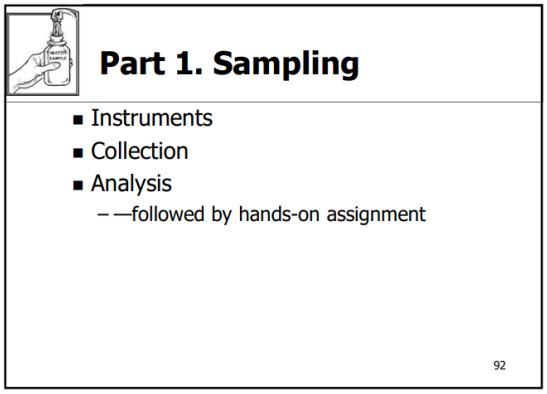
Does the PWS have an instrument to measure monochloramine and free ammonia?

If not, the PWS may need to reschedule this DAM till after the PWS has gotten the required instruments.

If the operators can borrow instruments from a neighboring system or from a vendor; or if the instructor can provide instruments for the day, it may be possible to complete the DAM, but the operators will probably benefit from follow-up assistance after they have purchased their own instruments.

We will assume that the PWS has instruments, instrument manuals, and written methods before proceeding.

Note: The mention of any manufacturer names is not a recommendation for their use.



Common instruments

How they work

The most common supplier of instruments is Hach, but Hanna, Great Lakes, and other manufacturers also supply analytical instruments. These instruments all use a colorimetric analysis method.

Instruments

- What have you got?
- What is available?
- What are some pros and cons?
- Calibration/verification requirements.

A list of available instruments for mono, ammonia, nitrite, and nitrate is in the Student Guide on page _____

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Terminology note: Spectrophotometer vs. Colorimeter

A 'spectrophotometer' is an instrument that uses a variable wavelength of light that can be adjusted to measure different chemicals.

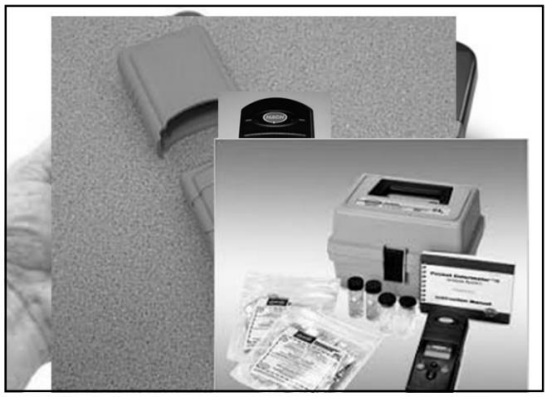
A 'colorimeter' is an instrument that uses a single wavelength of light, so it can only be used for the chemical(s) listed in its name.

The way that these methods work is that some special reagent chemicals mix with the chemical being tested to make a colored compound. Then, a special light is shone through the colored sample to see how intense the color is. The stronger the color is, the more of the chemical being tested is present.

Popular instruments

Field instruments are available to measure

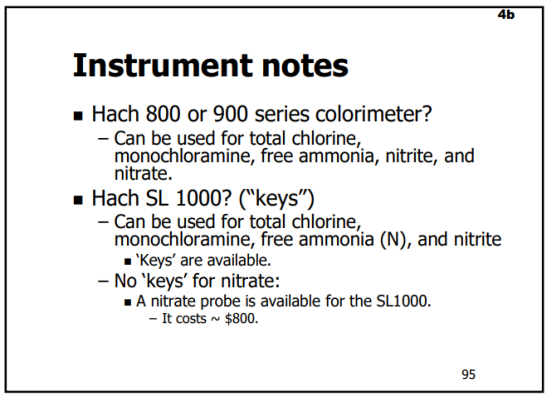
- Total chlorine,
- Monochloramine and free ammonia,
- Nitrite/nitrate.



Total chlorine: The most commonly used instruments is the Hach Pocket Colorimeter 2 (PC2)—for Free/Total Chlorine. The Hach 890/900 series of spectrophotometers can also be used. The Hach SL1000 also does total chlorine. It uses ChemKeys, so it is easier to use, but the ChemKeys cost more than powder packets.

There are Hanna, National Instrument, and other brands of total chlorine instruments. Total chlorine has to be measured in the field.

Monochloramine/Free Ammonia: With normal (indophenol) methods, you have to measure monochloramine at the same time. The most commonly used instrument is the Hach PC2 for Monochloramine/Free ammonia, followed by the Hach 900 spec, and the SL1000. Monochloramine and free ammonia should be measured in the field.



Nitrite/Nitrate: Most systems send their samples to a lab. However, the lab needs to meet the accuracy levels, so you need to double check and make sure they are doing that. A bench top method is the Hach TNT instrument, which uses a diazotization method. The SL1000 has chemkeys for nitrite. For nitrate, the SL1000 has a probe, which does not work very well in drinking water testing.

Calibration/verification

All instruments that are used to measure chemicals must be calibrated or verified every 90 days as required by 30 TAC §290.46(s), shown below:

Specifically:

§290.46(s)(2)(C) Chemical disinfectant residual analyzers shall be properly calibrated.

§290.46(s)(2)(C)(i) The accuracy of manual disinfectant residual analyzers shall be verified at least once every 90 days using chlorine solutions of known concentrations.

NOTE: <u>At this time</u>, TCEQ investigators routinely accept verification using gel standards purchased from the instrument manufacturer.

§290.46(s)(2)(C)(ii) The accuracy of continuous disinfectant residual analyzers shall be checked at least once every seven days with a chlorine solution of known concentration or by comparing the results from the on-line analyzer with the result of approved benchtop method in accordance with §290.119 of this title (relating to Analytical Procedures).

§290.46(s)(2)(C)(iii) If a disinfectant residual analyzer produces a result which is not within 15% of the expected value, the cause of the discrepancy must be determined and corrected and, if necessary, the instrument must be recalibrated.

§290.46(s)(2)(D) Analyzers used to determine the effectiveness of chloramination in §290.110(c)(5) of this title shall be properly verified in accordance with the manufacturer's recommendations every 90 days. These analyzers include monochloramine, ammonia, nitrite, and nitrate equipment used by the public water system.

If analyzers are not maintained, that data is suspect. Bad data leads to bad decisions. Records of calibration and verification must be retained by the PWS.

If the PWS does not have a calibration/verification process, it is a good idea to schedule follow up assistance to get that happening.

Methods

You must document your methods, instruments, and laboratories on your List of Analytical Methods (LAM). **In Part 2 of this Chapter we will fill out the LAM form.**

Methods are NOT JUST manuals. The manual does not cover the sample collection portion of the process. The manual does not say what to do if your results are not in the range expected. You need a system-specific SOP. It can be simple, but it is needed.

Manuals: The instruments should come with the manufacturer's instructions for how to do the analysis. Those are called 'methods.' The operators should have these at their fingertips.

SOPs: A PWS should have their own instructions to operators that explain any system-specific needs or requirements—for example, the CFTs for various sample sites. For example, if operators are not in the habit of checking the expiration date of chemicals, there may need to be an SOP to remind them. Or, when a new operator starts, the SOP will make sure that they follow the right procedures.

We need be aware of some issues that can influence our tests results. For example:

Reagents

All chemicals decay over time—some slower than others. The reagents—like powder packets and pH buffers—have a stamped expiration date. These chemicals should not be used after that expiration date.

Free chlorine DPD test interferences

We don't talk about free chlorine a lot in this manual. You don't need to monitor routinely for free chlorine if you are using chloramines.

However, if you are performing a temporary conversion to chloramines, be aware that monochloramine can falsely elevate the free chlorine reading when using the DPD test. Because of this interference, we should not use the DPD free chlorine method when we know that the monochloramine residual is above 0.5-mg/L or so. We should be especially suspicious of any free chlorine reading we get when the free ammonia level is 0.1 mg/L or higher because free chlorine and free ammonia cannot coexist.

Hardness interference

If the water's hardness is over 120 ppm, it may be necessary to work with the instrument supplier to use their method to eliminate hardness interference.

Total chlorine method

Total chlorine is the regulatory measurement for disinfectant residual. Therefore, total chlorine must be analyzed using a method approved by EPA. The methods for the other four chemicals must be approved by TCEQ.

Total chlorine must be analyzed in the field.

DPD colorimetric, DPD ferrous titration, or amperometric titration are acceptable methods. DPD colorimetric is the most common method—the one that turns pink in the presence of active chlorine species.

The instrument manufacture tells what the instrument is capable of doing in terms of accuracy in the method documentation. Check the range of your kit. If a sample is outside range, reanalyze. The most common colorimeter used for measuring total chlorine has different methods for measuring up to 2.0 mg/L and measuring up to 4.0 mg/L.

Total chlorine is measured "as Cl_2."

Monochloramine and free ammonia method

Monochloramine and ammonia must be analyzed in the field. They have to be measured together. The methods for must be TCEQ approved. Any method approved for the drinking water matrix is acceptable.

Indophenol is the most common method for analyzing monochloramine and ammonia—the water turns green in the presence of monochloramine.

Monochloramine and ammonia must be measured at the same time because in this method, the ammonia is analyzed by turning it into monochloramine first, using a drop of 'free ammonia reagent' (which is just very special bleach). The ammonia cell should be a darker green than the monochloramine cell, and the amount of ammonia present is the difference in that color intensity.

Free ammonia—NOT Total ammonia

We have seen in the field where a PWS tries to use a wastewater method for free ammonia—that is usually a bad idea. Free ammonia just measures the useful portion. Double check that your instrument is measuring free—not total—ammonia.

Although many nitrogen-containing compounds can react with free chlorine, only free ammonia reacts to form our target disinfectant, monochloramine. Therefore, we must be able to distinguish between free and total ammonia just as we must be able to distinguish between free and total chlorine. Consequently, we need to use a free ammonia method that will only detect free ammonia and not all forms of nitrogen (e.g., nitrate, nitrite, or urea and organic molecules containing amine groups).

Note: Instrument settings: Cl_2 and N

We need to be aware of and understand how our instruments are reporting our results so that we can interpret our data. Since we refer to Cl_2:NH_3-N ratios, instruments should be set to measure in those units. Instruments should be set to:

a) report total chlorine and monochloramine results as "mg/L as Cl_2", and
b) report free ammonia levels as "mg/L as N" (NOT mg/L as NH3).

Nitrite and nitrate methods

Nitrite and nitrate may be analyzed in the field and/or in an accredited or approved lab.

Field methods are available. Most of them use the 'cadmium reduction' method. A color-wheel method is about $150; more accurate methods are available for more money. If you have a Hach 900 you can get powder packets to run nitrite/nitrate. The Hach SL1000 has ChemKeys for nitrite, but not nitrate.

We will talk more about the importance of nitrite and nitrate sampling in "**DAM 8: DEVELOPING A NITRIFICATION ACTION PLAN (NAP) FOR A PUBLIC WATER SYSTEM (PWS)**."

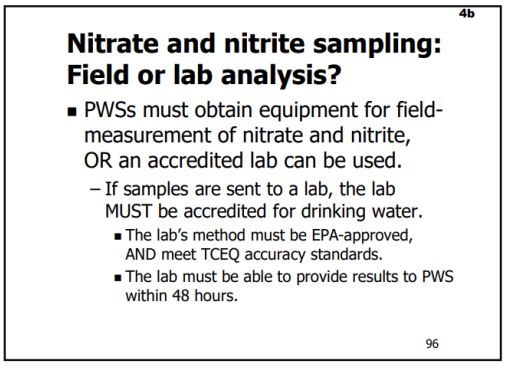
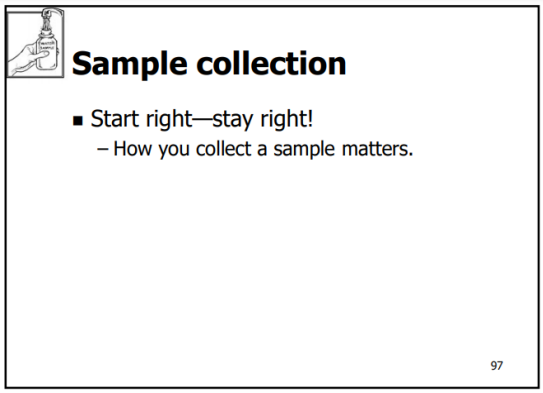


Table 3. List of available instruments for free ammonia, monochloramine, nitrate, and nitrite.

Instrument: **Manufacturer and Instrument #**	**Free Ammonia ±0.1 mg/L**	**Mono-chloramine ±0.15 mg/L**	**Nitrate ±0.1 mg/L**	**Nitrite ±0.01 mg/L**
Hach Pocket Colorimeter II w/ Hach MTD 10200	x	x		
Hach Pocket Colorimeter II w/ Hach MTD 8039 (*Total* Nitrate)			x	
Hach DR 800 Series, DR900 w/ Hach MTD 8192			x	
Hach DR 800 Series, DR900 w/ Hach MTD 8507 *				x
Hach DR 1900, 2800, 3800, 3900, 5000, 6000 w/ Hach MTD 10206			x	
Hach DR 1900, 2800, 3800, 3900, 5000, 6000 w/ Hach MTD 10207				x
Orion ISE meter and probe			x	
Orion Aquafast AQ4000 w/ Orion MTD AC2046 **				x
Orion AQ3700		x		
Orion AQ3700**				x
LaMotte 7-2000-UV	x		x	x
LaMotte Smart 3			x	x
LaMotte Smart Spectro			x	x
Hanna HI 96707				x
Hanna HI 96786 (*Total* Nitrate)			x	

Sample collection

In this part of Chapter 2, we will talk about collecting samples, now that we know we have instruments that can analyze them correctly. We will focus primarily on distribution system monitoring, and rely on the student to apply these concepts to other sites as appropriate.



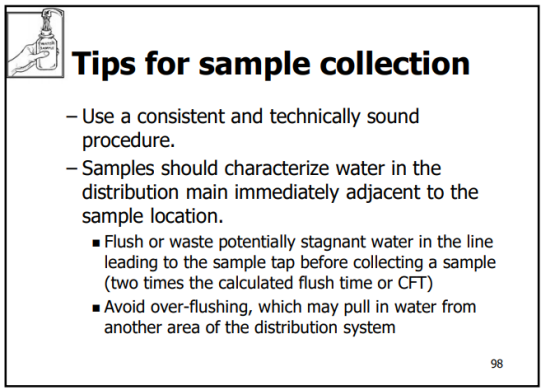
A big part of sample collection success is knowing exactly where the water is coming from:

- Does it truly characterize the water in the main at this location?
  - Is it actually stagnant water from the sample line?
  - Or is it water from so far away that you can't draw any conclusions about the water in this vicinity?

In order to evaluate that, we will discuss calculated flush times (CFT). First, we will briefly review the types of sample locations that are likely to be used in the distribution system.

Sample taps

Sample taps come in a variety from small to large.



Customer taps as sample: locations

A customer tap is a possible sample location. These taps can be less reliable than fire hydrants, because there are often many unknowns about the length and diameter of the lines leading to the taps.

The flushing flow is assumed to be two gallons per minute (2 gpm). The actual flow rate can be found by discharging water from the tap into a five-gallon bucket and timing it.

Only houses (or buildings) that use water on a normal frequency should be used—an unoccupied house can have excessive water age.

Fire hydrants as sample locations:

Fire hydrants—1,000 gpm

Usually, fire hydrants can be problematic for sampling because:

- The flow is not a 'pencil-thin' stream (which is inconvenient);
- It can waste a lot of water, which is undesirable during drought;
- In locations with sediment, particles may get into sample water; and
- If you turn the hydrant too quickly, it can cause water hammer.

Hydrant sampler—20 gpm

Using a hydrant sampler with flow control—like the one shown—can solve some of the issues with sampling hydrants. These are described in Attachment 3.

Fire hydrants have good qualities for collecting distribution system samples because they conform to generally consistent construction and operational parameters.

By using a hydrant sampler

- The flow rate from the hydrant is limited to 20 gpm,
- The water velocity is too low to pick up sediment,
- A pencil-thin stream is available for sampling, and
- Water is not wasted.

Typical hydrants

Figure 10 shows some typical construction guidelines for fire hydrants. From these, or from site specific construction information we can estimate the volume of the pipe.

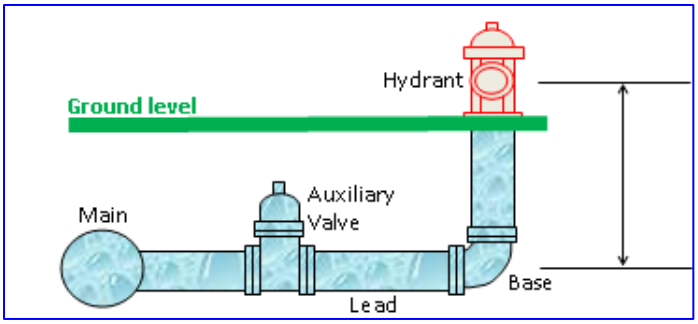


Figure 10. Hydrant location relative to distribution main.

Tips for estimating hydrant size
for determining calculated flush time:

(These assumptions may differ from actual sizes—verify if possible.)

Typical leads:

- Diameter: AWWA Manual M17 suggests a 6" diameter lead.
  Assume a hydrant lead diameter of 6"
- Length: Assume the pipe length to be the horizontal distance from the auxiliary valve to the hydrant plus 1' to be conservative.

Typical hydrant diameter:

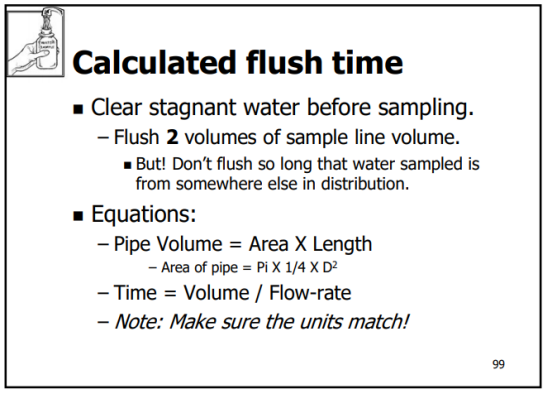
The majority of hydrants are 5 1/4" or 4 1/2" (main valve opening).
Assume a 6" diameter hydrant.

Typical vertical distance:

AWWA standards suggest a minimum of 60" from the hydrant nozzle to hydrant lead pipe.
Assume 6' length to be conservative.

Calculated flush time:
How long should you flush before taking the sample?

The first step in figuring out what is going on with disinfectant residual is to collect samples correctly. This is mainly about making sure that you know what part of the piping network the water you are analyzing represents—Is it water from inside a customer's house? Or is it water from the main?



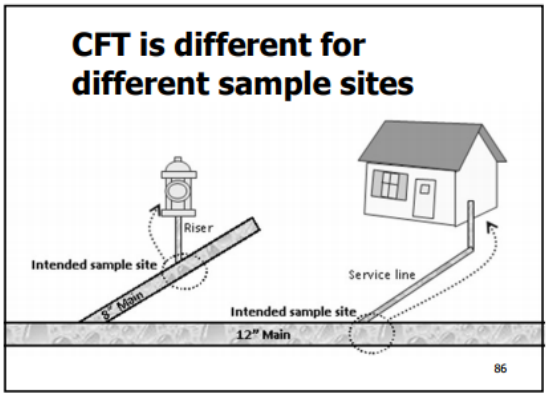
Consider what water the sample represents

Think about where the water you collect in your bottle or cell comes from.

Is it stagnant water from the sample line?

Is it bulk water from the closest main?

Or is it from far away?



Water may sit in fire hydrants and service lines for a long time, but that water does not characterize or represent the water that is in the main lines, and it is not the water that we should be sampling (Figure 11).

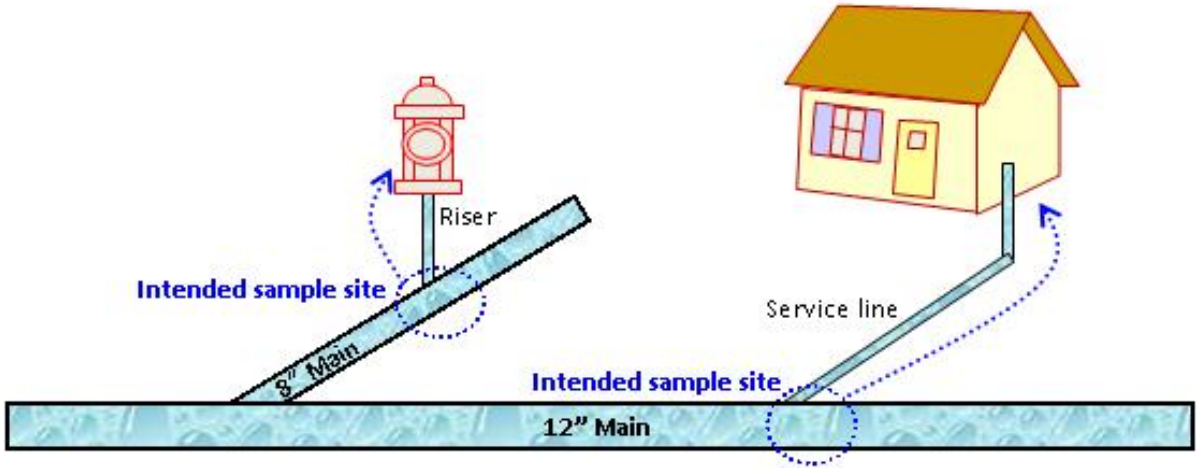


Figure 11. showing the intended sample site that characterizes bulk water in the main (See slide)

Ideally, water should be flowing through your mains constantly to reach distant areas and to meet customer demands. Continually flowing water is normally of better quality than the water sitting stagnant in customer's service line.

Flushing versus sampling

Flushing a line to clear out older water for quality control purposes is different from flushing a line to collect a representative sample. When we are performing

routine flushing, we want to scour sediment and debris from the line. However, when we are collecting a sample, we want to find out the condition of the water—picking up debris does not help us collect good samples.

Often, PWSs use a rule-of-thumb, like "flush for five minutes." Five minutes may or may not be a good amount of time depending on the length and diameter of the pipes.

Calculating flush time

The calculated flush time is the time it takes for water to travel from the intended sample location to the sample tap.

We use a safety factor of two (2) and flush for two times the calculated flush time in order to fully clear the line of standing water, but not bring in water from too far away.

Site specific calculations

When we do know the pipe diameter and length serving the hydrant, we can calculate the flush time much more accurately.

Safety factor of 2

Often, the line diameter will be based on the operator's best judgement, but sometimes the customer can provide the information. Measure the distance from the meter to building and estimate the pipe length to the outside tap you are using.

When we can do this we can normally accept a safety factor of two by flushing two of the calculated volumes from the line.

If the total line length is 10 feet and the diameter is 6 inches, then the volume of the pipe is 14.7 gallons. If we flush at 20 gpm, we only need to flush for 0.7 minutes. However, we also want to have a safety factor. Because we are making assumptions about the length of the pipe from the main to the valve, we will add a larger than normal safety factor and just establish a flush time of 3 minutes for rarely used flush valves with unknown pipe length and pipe diameter.

Calculations

In general, the amount of time for water to get through a pipe is calculated as:

$$\text{Time} = \text{Volume} / \text{Flow}$$

In this case, we have a safety factor (2, unitless) so we amend the equation to be:

$$\text{Time} = (\text{Safety Factor} \times \text{Volume}) / \text{Flow} = (2 \times \text{Volume}) / \text{Flow}$$

We will need to do some conversions to make the units work out. The units we start with are:

Calculated Flush Time (in minutes) (with safety factor)

= 2 × Volume (in gallons) / Flow (in gallons per minute)

That won't work! Gallons don't match inches cubed (in^3) or feet cubed (ft^3)! Luckily, we remember that the conversion factor between ft^3 and gallons is:

7.48 gallons = 1 ft^3

Also luckily, we remember how to get the volume of a pipe:

Volume = Area × Length

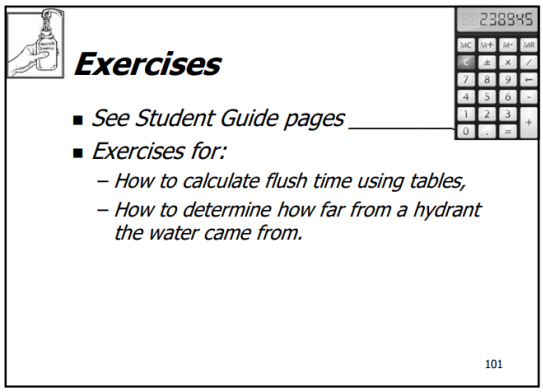
And, for a round pipe, the area is:

Area = Pi × Diameter squared (D^2) /4 = 3.14 X D^2 / 4

(We remembered that Pi is 3.14, unitless)

If we are careful, and use matching units, we can get to the right answer. The units that we need to make match are those for volume.

Let's do an example:



Example of calculating CFT at a flow of 20 gpm, through 100' of 6"pipe

Let's calculate the CFT (with a safety factor of 2) for water flowing at a rate of 20 gallons per minute through 100 feet of 6 inch pipe.

First, let's calculate the volume of the pipe (=Area X Volume). We need to use the area in feet squared to match the length in feet.

Area = Pi X D^2 / 4 = 3.14 X D ft^2 X 0.25 (because 0.25 = ¼)

= 3.14 X [6 inches/(12 inches per foot)]^2 X 0.25

= 3.14 X 0.5^2 ft^2 X 0.25 = **0.19625 ft^2**

Volume = Area X Length

= 0.19625 ft^2 X 100 ft = **19.625 ft^3**

That is great—but we need the volume in gallons to match the flow rate in gpm. Let's convert it using the conversion of 7.48 gallons = 1 ft3

Volume (gallons) = Volume (ft^3) X 7.48 (gallons per ft^3)

Volume (gallons) = 19.625 ft^3 X 7.48 gallons per ft^3 = **147 gallons**

Now we are ready to plug the volume into the CFT equation:

Calculated Flush Time (in minutes)

= 2 X Volume (in gallons) / Flow (in gallons per minute)

= 2 X 147 gallons / 20 gallons per minute = **14.7 minutes**

So, when we take a sample at this location, the CFT (with a safety factor of 2) is **15 minutes**, so we should flush 15 minutes before collecting the sample.
That water will represent the water near the sample location.
Longer flushing would make the sample not represent the location as well.

(NOTE: A table for CFT at 20 gallons per minute, for a range of pipe sizes (with a safety factor of 2) is shown below. Does this calculation match the table?)

Let's do another example, this time at a lower flow rate, like a lower flow that might be experienced at a customer's tap or hose bibb.

Exercise: Calculate CFT
at a flow of 2 gpm, 100', 1" pipe

Let's calculate the CFT for water flowing at a rate of 2 gallons per minute through 100 feet of 1-inch pipe.

First, we calculate the volume of the pipe (=Area X Volume). We need to use the area in feet squared to match the length in feet.

Area = Pi X D^2 / 4 = _____

Volume = Area X Length = _____

Volume (gallons) = _____

Now we are ready to plug the volume into the CFT equation:

CFT (in minutes) = 2 X Volume (in gallons) / Flow (in gpm)

= _____

<u>Questions for consideration:</u>

Is it okay if we set the CFT for this tap at the standard of 5 minutes?

How would you determine how far upstream the water is taken from?

(NOTE: A table for CFT at 2 gallons per minute, for a range of pipe sizes and diameters (with a safety factor of 2) is shown below. Does the result you got correspond to that table?)

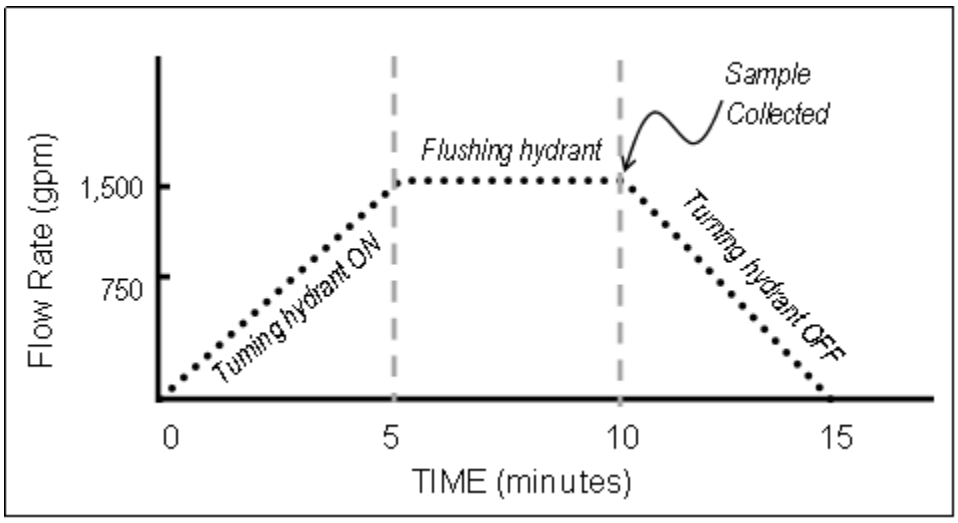
Let's do another example, this time at fire hydrant.

Example of calculating CFT at a flow of 1500 gpm, in a 6" pipe, turning the valve on and off slowly, and flushing for 5 minutes

Let's consider how far the water is drawn from when we flush a dead-end hydrant.

The process will be a little different. We know the volume of water that we flush… but we need to find the volume of pipe that it filled in order to figure out how far away it comes from.

To do that, we need to think about how much water is used as the hydrant is turned on, then flushed, as shown in the figure below



First, we estimate the volume of water that is flushed. For the period when the hydrant is being turned on, we can estimate that about ½ the flow rate occurs for that time period.

Volume of water flushed while being turned on
= ½ _____gpm X _____ min. = _____ gallons

Next, we need the volume of water used during the flushing period:

Volume of water during 5 minutes of flushing = _____ gallons

We need to add those two volumes to get the total volume of water flushed:

Volume during turn on + Volume during flushing = _____

Now that we know the volume of water flushed before sample collection, we can figure out the linear feet of pipe that represents where that water came from.

The linear distance that the water came from is the Length from the Volume calculation, only in this example, we already know the Volume.

Volume = Area X Length, so Length = Volume / Area

The pipe is 6” in diameter, so we need to calculate its Area first:

Area = Pi X D^2 / 4 = _____

Before we go farther, we need to convert the gallons of water that we flushed into cubic feet so that the units will work out.

_____ gallons / 7.48 gallons per cubic foot = _____cubic feet

Now we are ready to plug in the Volume and Area to calculate Length

Length = Volume / Area

= _____ cubic feet / _____ square feet

= _____ feet

That distance is how far the water that we are sampling came from.

Questions for consideration:

Is that a long distance?

Could the flushing this much water hide problems that are occurring at the hydrant location itself?

If you wanted to get a sample of water closer to the location of the hydrant, what could you do?

If the hydrant was located in the middle of distribution instead of at a dead end, how would that impact where the sample water came from?

Tables of Calculated Flush Time (CFT)

The Calculated Flush Time (CFT) Matrix is provided below. This matrix was created by the EPA Technical Support Center (TSC) in Cincinnati, Ohio. The times shown in the matrix (in minutes) assume that:

- The sampler wishes to flush **two** volumes from the line to ensure that a sample representative of the water in the main is collected.
- The sampler has a means to flush at 20 gallons per minute (gpm) in the first table, a flushing rate chosen to:
  - Prevent scouring debris from the main line, and
  - Minimize the necessary flush time to as low a number as practical.
  - The flow rate can be assured by a flow control device or by capturing water in a five-gallon bucket to confirm and/or adjust the flow rate.

Table 4a. Flush Time in Minutes at 20 gpm (with Safety Factor of 2)
(Time shown in minutes for flushing two (2) pipe volumes)

Length of Pipe (ft)	Inside Diameter (Nominal) of the Fire Hydrant or Pipe (inches)					
	2	4	6	8	12	16*
1	**0.0****	**0.1**	**0.1**	**0.3**	**0.6**	**1.0**
5	**0.1**	**0.3**	**0.7**	**1.3**	**2.9**	5.2
10	**0.2**	**0.7**	**1.5**	**2.6**	5.9	10.4
15	**0.2**	**1.0**	**2.2**	**3.9**	8.8	**15.7**
20	**0.3**	**1.3**	**2.9**	5.2	**11.8**	**20.9**
25	**0.4**	**1.6**	**3.7**	6.5	**14.7**	**26.1**
30	**0.5**	**2.0**	**4.4**	7.8	**17.6**	**31.3**
35	**0.6**	**2.3**	5.1	9.1	**20.6**	**36.6**
40	**0.7**	**2.6**	5.9	10.4	**23.5**	**41.8**
45	**0.7**	**2.9**	6.6	**11.8**	**26.4**	**47.0**
50	**0.8**	**3.3**	7.3	**13.1**	**29.4**	**52.2**
55	**0.9**	**3.6**	8.1	**14.4**	**32.3**	**57.4**
60	**1.0**	**3.9**	8.8	**15.7**	**35.3**	**62.7**
65	**1.1**	**4.2**	9.5	**17.0**	**38.2**	**67.9**
70	**1.1**	**4.6**	10.3	**18.3**	**41.1**	**73.1**
75	**1.2**	**4.9**	**11.0**	**19.6**	**44.1**	**78.3**
80	**1.3**	5.2	**11.8**	**20.9**	**47.0**	**83.6**
85	**1.4**	5.5	**12.5**	**22.2**	**49.9**	**88.8**
90	**1.5**	5.9	**13.2**	**23.5**	**52.9**	**94.0**
95	**1.6**	6.2	**14.0**	**24.8**	**55.8**	**99.2**
100	**1.6**	6.5	**14.7**	**26.1**	**58.8**	**104.4**

* This would normally flow at over 20 gpm

** Although less than 5 minutes flushing is needed for the values shown in bold blue, it will be a normal practice for samplers to flush for 5 minutes.

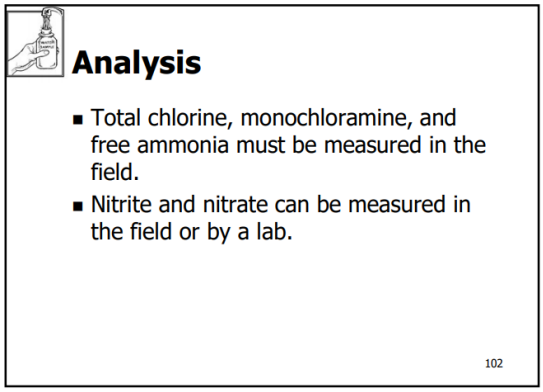
The Calculated Flush Time Matrix for premises (also developed by the TSC) is shown below. Notice that the same safety factor is used as with the fire hydrants: two (2).

Table 4b. Flush Time in Minutes at 2 gpm (with Safety Factor of 2)(Time shown in minutes for flushing two (2) pipe volumes)

Length of Pipe (ft)	Inside (Nominal) Diameter of the Pipe (inches)									
	3/4	1/2	5/8	3/4	1	1 1/2	2	2 1/2	3	4
1	0.02	0.01	0.02	0.02	0.04	0.09	0.2	0.3	0.4	0.7
5	0.11	0.05	0.08	0.1	0.2	0.5	0.8	1.3	1.8	3.3
10	0.23	0.10	0.16	0.2	0.4	0.9	1.6	2.5	3.7	6.5
15	0.34	0.15	0.24	0.3	0.6	1.4	2.4	3.8	5.5	9.8
20	0.5	0.2	0.3	0.5	0.8	1.8	3.3	5.1	7.3	13.1
25	0.6	0.3	0.4	0.6	1.0	2.3	4.1	6.4	9.2	16.3
30	0.7	0.3	0.5	0.7	1.2	2.8	4.9	7.6	11.0	19.6
35	0.8	0.4	0.6	0.8	1.4	3.2	5.7	8.9	12.9	22.8
40	0.9	0.4	0.6	0.9	1.6	3.7	6.5	10.2	14.7	26.1
45	1.0	0.5	0.7	1.0	1.8	4.1	7.3	11.5	16.5	29.4
50	1.1	0.5	0.8	1.1	2.0	4.6	8.2	12.7	18.4	32.6
55	1.3	0.6	0.9	1.3	2.2	5.0	9.0	14.0	20.2	35.9
60	1.4	0.6	1.0	1.4	2.4	5.5	9.8	15.3	22.0	39.2
65	1.5	0.7	1.0	1.5	2.7	6.0	10.6	16.6	23.9	42.4
70	1.6	0.7	1.1	1.6	2.9	6.4	11.4	17.8	25.7	45.7
75	1.7	0.8	1.2	1.7	3.1	6.9	12.2	19.1	27.5	49.0
80	1.8	0.8	1.3	1.8	3.3	7.3	13.1	20.4	29.4	52.2
85	2.0	0.9	1.4	2.0	3.5	7.8	13.9	21.7	31.2	55.5
90	2.1	0.9	1.4	2.1	3.7	8.3	14.7	22.9	33.0	58.8
95	2.2	1.0	1.5	2.2	3.9	8.7	15.5	24.2	34.9	62.0
100	2.3	1.0	1.6	2.3	4.1	9.2	16.3	25.5	36.7	65.3

Analysis

Now that we have verified that our instruments are appropriate, and our sample collection method is good, we can talk about the actual sample analysis.



After we discuss this in the classroom, we will actually analyze some samples.

IMPORTANT

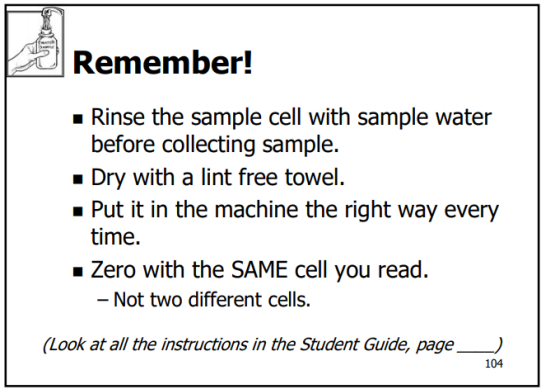
Note: Use the correct method
—don't use the high-range method for a low-range sample.

System specific SOPs

It is helpful to have SOPs in addition to the methods from the instrument manufacturer. SOPs can document important things that the instrument manual does not always say, for example:

- ✓ Flush for the calculated flush time before collecting the sample.
- ✓ Rinse the sample cell 3 times with the ***sample water*** before analysis.

- ✓ Zero the instrument with sample water. Zero with the SAME CELL that you are going to use for analysis—different cells have different scratches so zeroing with a different cell can cause error.
- ✓ Place the cell in the SAME ROTATION every time. If there is an assigned rotation in the instrument method—use that.
- ✓ Make sure the sample cell is clean.
- ✓ Dry the outside of the spectrophotometer or colorimeter cell before hitting 'zero' or 'read'. Use Lab Wipes—not paper towels or toilet paper—to dry the cells. Do not scratch the cells.
- ✓ Use the right powder pillows (or ChemKeys for the Hach SL1000). (For example, using the low or high range depending on concentration)
- ✓ Don't use expired reagents. Check the date before using.
- ✓ Don't use un-calibrated/verified instruments. Check the date.
- ✓ Shake the sample as directed by the method. Then, check for bubbles on the cell wall before analysis. Gently invert the cell to remove bubbles.
- ✓ Wait for the right amount of time between steps. The chemicals need this time to react. In cold temperatures, look at the table in the method and extend the wait time as needed.
- ✓ Do a dilution if ammonia is flashing out-of-range at 0.55 mg/L.



After sampling:

- ✓ After you put cells away, rinse with distilled or deionized water, and allow to air dry, if possible.

Important: Instrument settings: "As Cl_2 and N"

We need to be aware of and understand how our instruments are reporting our results so that we can interpret our data.

Since we refer to **Cl_2:NH_3-N** ratios, instruments should be set to measure in those units.

Instruments should be set to:

a) report total chlorine and monochloramine results as "mg/L as Cl_2", and

b) report free ammonia levels as "mg/L as N" (NOT mg/L as NH_3).

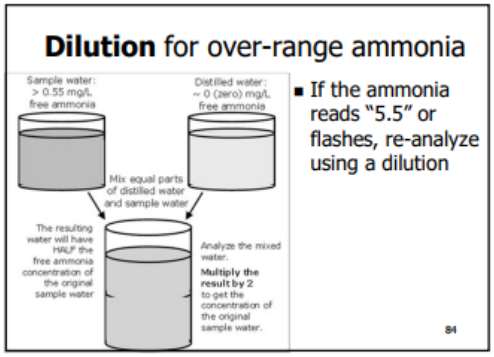
Diluting free ammonia samples

The ammonia method pegs out at 0.55 mg/L. If you analyze a sample and get 0.55, you need to:

- Dilute the sample water one-to-one with deionized (or distilled) water,
- Re-analyze that sample, and
- Multiply the result by 2.

You need deionized (DI) (or distilled) water to dilute samples. Keep some in the truck. DI water has zero ammonia and zero monochloramine in it.

The simplest way to dilute is to make a half-and-half solution, and multiply the result by 2 as shown in Figure 12, and on the accompanying slide.



If the result found when measuring the 1:1 dilution water is still over range, subsequent 1:1 dilutions can be done.

Note: You have to dilute and analyze BOTH monochloramine and ammonia because the monochloramine is used to zero the instrument for the ammonia analysis.

Watch out—doing the dilution on the previously analyzed cells

You may be tempted to dilute the sample that you analyzed and found the over range ammonia in. That sample is 10 mL, in the sample cell. If you do this, you

need to dilute both the monochloramine and free ammonia cells, and re-zero using the monochloramine cell.

However, this method is NOT recommended. The accuracy will be poor because the sample cells are small, the wait-times are exceeded, and drops on the side of the sample cells will cause there to not be exactly 1:1 sample-water-to-deionized water—and the result will be incorrect.

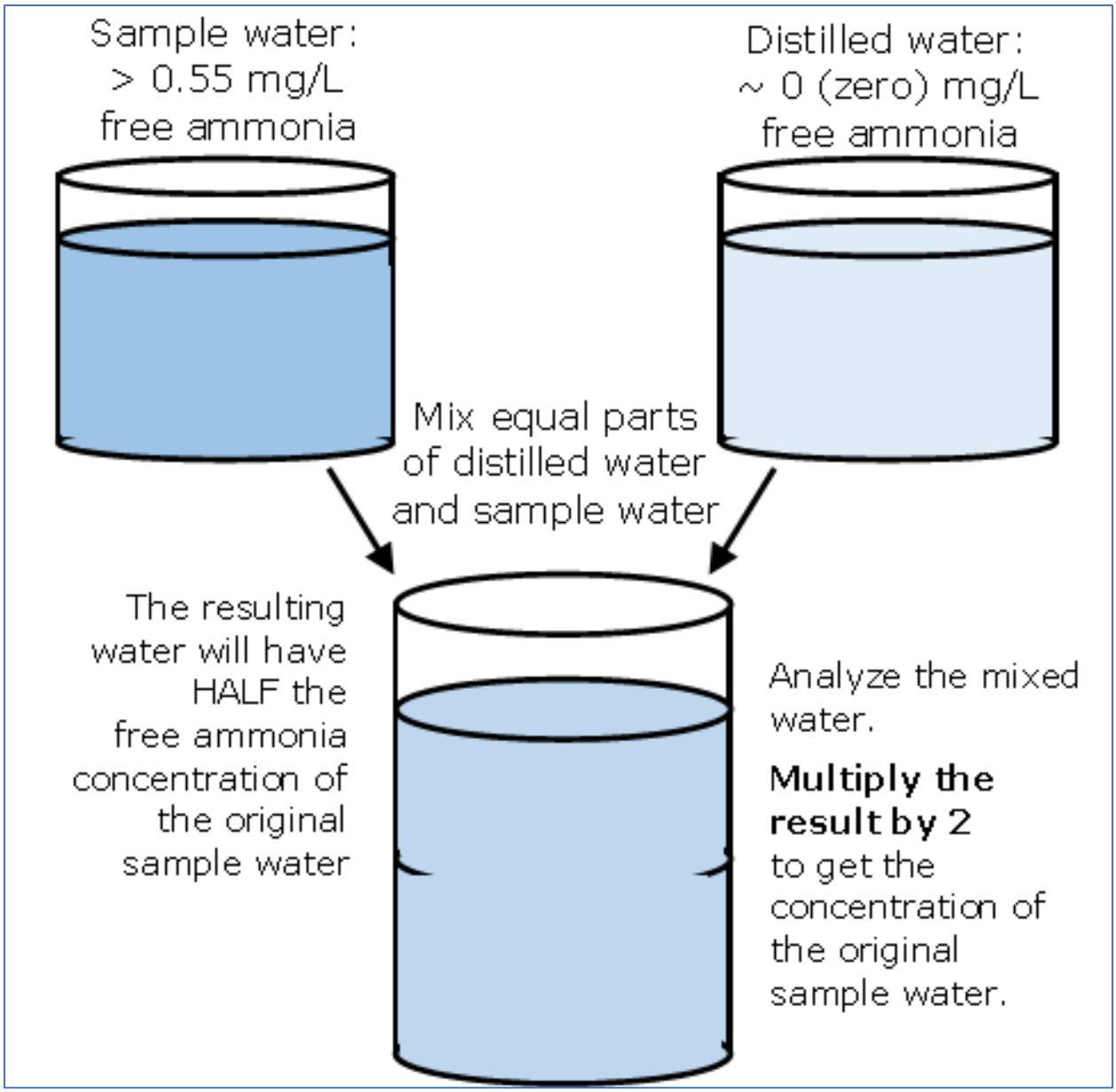
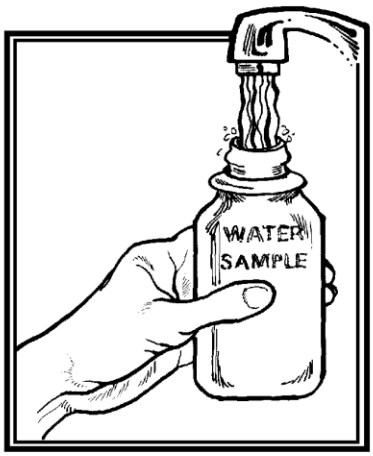


Figure 12. How to do a 1:1 dilution to figure out ammonia when the original result is over-range (> 0.55 mg/L)



Assignment: Analysis Hands-On Workshop

Get ready!

- Take out the PWS's (and instructor's) instruments, sample cells, reagents;
- Get 'Kim-Wipes',
- distilled or deionized water
- Get the instrument manuals—with the analytical methods;
- Get your SOP;
- Take out reagents, etc.

Using a clean container, gather some sample water from the nearest potable water tap that has chloramines.

Analyze samples

In this activity, the Instructor will watch as the trainee(s) perform sample analysis for chloramine-effectiveness parameters. If the instructor has brought analytical instruments, comparisons will be made between the two.

Select a sample tap near (or in) the office where the DAM is being held.

Measure:

- Total chlorine, monochloramine and free ammonia.
- pH and temperature (optional).

And, if the PWS has the ability to measure them:

- Nitrite, and
- Nitrate.

Good sampling (and a good sampling SOP) will include:

- Flush for the calculated flush time before collecting the sample.
- Look at the SOP or method during analysis.
- Have a good, clean sample cell—no chips, no smudges, no 'fog'.
- Rinse the sample cell with the sample water before analysis (3x).
- Dry the outside of the spectrophotometer or colorimeter cell with a clean, lint-free towel before hitting 'zero' or 'read'.
- Use the right powder pillows (or ChemKeys for the Hach SL1000). (For example, using the low or high range depending on concentration)
- Use un-expired reagents.
- Use calibrated/verified instruments.

- Shake the sample as directed by the method.
- Wait for the right amount of time between steps.
- Use the SAME CELL to zero the instrument.
- Put the cell in the instrument at the SAME rotation every time. If the manual says what rotation to use, use that.

If ammonia is flashing out-of-range at 0.55 mg/L—doing a 1:1 dilution (etc.) to be able to read the free ammonia.

If the instructor has brought another instrument, both the instructor and operators should take samples and compare the results.

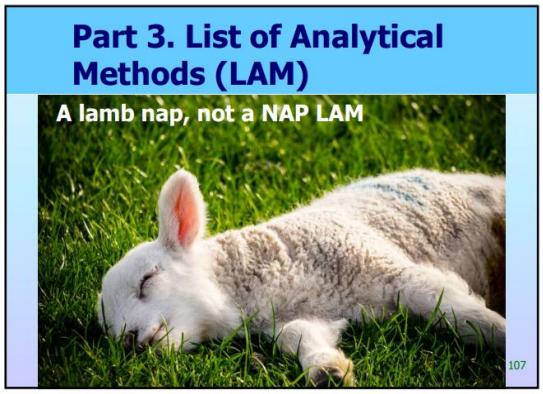
Here is a data table to record that data.

Sample Site	**Instrument/ Method**	**Analyst**	**Result**	**Comments**
Example: "Lab Tap"	*Hach PC2 Total Chlorine*	*Ann A. Litical*	*2.05 mg/L*	*11:15 am*

<u>Discuss your results.</u>

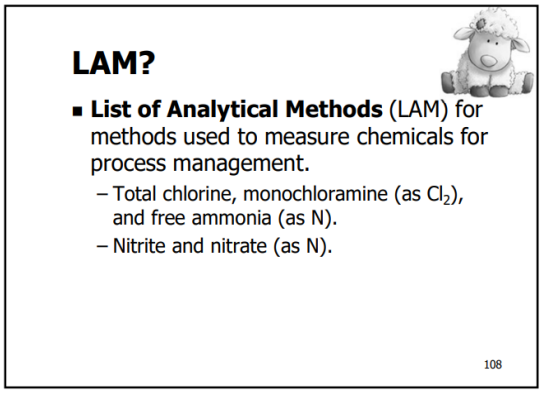
Did you find anything that you need to change?

Part 2: List of Analytical Methods (LAM)



In this part, we will update your List of Analytical Methods to include all current sampling instruments and methods.

- Document all analyses that are performed by the PWS for total chlorine, monochloramine, ammonia, nitrite, and nitrate. If you measure pH and temperature, document those as well.
- Check the manuals and record the accuracy for each field instrument.
- If you use a commercial laboratory, document that and attach a copy of their List of Analytical Methods. (Make sure that their contact information is listed.)

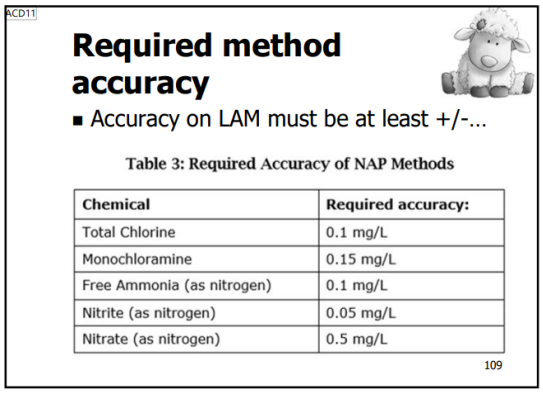


Required accuracy

You must use methods that are accurate enough when doing NAP sampling. The methods used must be accurate enough to measure changes that can indicate nitrification. The rules require that analytical methods meet the accuracy given in Table 5.

Table 5: Required Accuracy of NAP Methods (see slide)

Chemical	Required accuracy:
Total Chlorine	0.1 mg/L
Monochloramine	0.15 mg/L
Free Ammonia (as nitrogen)	0.1 mg/L
Nitrite (as nitrogen)	0.05 mg/L
Nitrate (as nitrogen)	0.5 mg/L



For example, if you analyze the same water sample ten times in a row, all of the results should be within the 'required accuracy.'

Ideally, you would use a sample of known concentration and compare your performance. For example, if you had a total chlorine sample with a known concentration of 2.0 mg/L, you would only get results ranging from 1.9 to 2.1 mg/L. The instrument manufacturers evaluate the instruments this way and publish their results in the instrument manual so we can look them up.

Table 6. Explanation of fields in the List of Analytical Methods (LAM)

Analyte:	The chemical or value that you are analyzing.
Analytical Method:	Fill in the method that you use to measure for each analyte. For example, you can insert a standard method—for example, 'Standard Method Cl-4500D', or the make and model of the analyzer—for example 'Hach SL 1000'.
Instrument Name:	Document the make and model of the instrument you are using to measure the analyte.
Accuracy:	Report the number of decimal places to which you can accurately report the value for each analyte. For a list of analytical requirements, please see §290.110(d).
Calibration Frequency and Method:	Report the frequency and method with which you calibrate or verify the accuracy of your equipment.

List of Analytical Methods (LAM) instructions

List of Analytical Methods (LAM) for Monitoring Chloramines	
You must document the methods and laboratories on this List of Analytical Methods (LAM).	
Analyte:	The chemical or value that you are analyzing.
Analytical Method:	Fill in the method that you use to measure for each analyte. For example, you can insert a standard method—for example, 'Standard Method Cl-4500D', or the make and model of the analyzer—for example 'Hach SL 1000'.
Instrument Name:	Document the make and model of the instrument you are using to measure the analyte.
Accuracy:	Report the number of decimal places to which you can accurately report the value for each analyte. For a list of analytical requirements, please see §290.110(d).
Calibration Frequency and Method:	Report the frequency and method with which you calibrate or verify the accuracy of your equipment.

Form for LAM

Table 7 shows the LAM with embedded instructions.

Another copy is provided with the exercise following this section for the system to remove from the book and use for their own NAP/Monitoring Plan.

Table 7: LAM form, with embedded instructions

Analyte	**Method (& Analyzer Type)**	**Accuracy[5]**	**Calibration Frequency[6]**	**Calibration Method**
pH	*(if used, otherwise "N/A")*	± pH unit	*(OR Verification)*	*(OR Verification)*
Temperature	*(if used, otherwise "N/A")*	± C		
Disinfectant				
Total Chlorine	(Also on LAF)	± mg/L		
Free Chlorine	(Also on LAF)	± mg/L		
Monochloramine		± mg/L		
Free Ammonia (as nitrogen)	*(as Nitrogen)*	± mg/L		
Chlorine Dioxide	*(if used, otherwise "N/A")*	± mg/L		
Chlorite	*(If chlorine dioxide is used)*	± mg/L		
Ozone	*(if used, otherwise "N/A")*	± mg/L		
Nitrification				
Nitrite	*(Use the lab's information if an outside lab is used)*	± mg/L		
Nitrate	*(Use the lab's information if an outside lab is used)*	± mg/L		
Other-Microbial				
HPC (Heterotrophic plate count bacteria)	*(if used, otherwise "N/A")*	± CFU/100 mL		
DNA (Microbial DNA)	*(If ATP analysis is used, modify form to include that here)*	± mg/L		
Other		±		
Hardness	*(if used, otherwise "N/A")*	± mg/L		
Alkalinity	*(if used, otherwise "N/A")*	± mg/L		
Total dissolved solids	*(if used, otherwise "N/A")*	± mg/L		
Dissolved oxygen (DO)	*(if used, otherwise "N/A")*	± mg/L		

Example of completed LAM

Table 8 shows an example of a completed LAM for a variety of instruments. This is just an example—it probably lists things you don't need to measure. Just delete those rows or put 'N/A.'

Table 8. Example of a Completed LAM form

Analyte	Method (& Analyzer Type)	Accuracy5	Calibration	
			Frequency6	Method
pH	Oakton General-Purpose pH Probe	±_____0.1_____pH unit	daily	pH 4, 7 buffer
Temperature	Frey Scientific Thermometer	±_____0.5_____C* *per Frey manual	N/A	N/A
Disinfectant				
Total Chlorine	Hanna chlorine meter Total/Free 0-2.5 mg/L	±_____0.1_____mg/L	90 days	CAL Check™
Free Chlorine	Hanna chlorine meter Total/Free 0-2.5 mg/L	±_____0.1_____mg/L	90 days	CAL Check™
Monochloramine	Hach Pocket Colorimeter II-Mono/Ammonia	±_____0.1_____mg/L	90 days	SpecCheck Gel Standards
Free Ammonia (as nitrogen)	Hach PC II-Mono/Ammonia	±_____0.1_____mg/L	90 days	SpecCheck Gel Stds
Chlorine Dioxide	N/A	±_____N/A_____mg/L	N/A	N/A
Chlorite	N/A	±_____N/A_____mg/L	N/A	N/A
Ozone	N/A	±_____N/A_____mg/L	N/A	N/A
Nitrification				
Nitrite	Ada-lab-see attached Lab Approval Form	±___0.001_____mg/L* * per Ada-lab	N/A	N/A
Nitrate	Ada-lab-see attached Lab Approval Form	±___0.01_____mg/L* * per Ada-lab	N/A	N/A
Other-Microbial				
HPC (Heterotrophic plate count bacteria)	N/A	±_____N/A_____mg/L	N/A	N/A
DNA (Microbial DNA)	N/A	±_____N/A_____mg/L	N/A	N/A
Other				
Hardness	N/A	±_____N/A_____mg/L	N/A	N/A
Alkalinity	N/A	±_____N/A_____mg/L	N/A	N/A
Total dissolved solids	N/A	±_____N/A_____mg/L	N/A	N/A
Dissolved oxygen (DO)	Omega DOH-247-KIT Probe	±_____0.5_____mg/L	90 days	Manufacturer

---

Schedule flexibility for LAM (and LAF):

If there is not enough time to complete the LAM during this DAM, note that as an action item for follow up.

If additional time is available, double-check the system's LAF

Laboratory Approval Form (LAF)

The LAM is an attachment to the required Laboratory Approval Form (LAF). A copy of the LAF is shown below, for completeness (Figure 13).

To remove this form click here

Drinking Water Lab Approval Form

Laboratory or Plant Name		Contact Name	
PWS ID (TCEQ issued)		E-mail	
Lab ID No		Phone	
Address		Date form completed	
City/State		Does this lab perform analyses for other Public Water Systems?	☐ Yes ☐ No
Zip			

Analytes and Methods

Analyte	Analytical Method [2]	Instrument Name [3]		Accuracy [4]		Calibration Frequency [5]	Calibration Method [6]	NELAP Accredited [7]	PT Study [8]
Turbidity	EPA 180.1	hjghjhgjhj	±	ghjghj	NTU	ghj	ghj		
pH			±		pH unit				
Temperature			±		°C				
TOC			±		mg/L				
UV_{254}			±		cm^{-1}				
Alkalinity			±		mg/L				
Free Chlorine[9]			±		mg/L				
Total Chlorine[9]			±		mg/L				
Chlorine Dioxide[10]			±		mg/L				
POE Chlorite[10]			±		mg/L				
Calcium [1]			±		mg/L				
Phosphate [1]			±		mg/L				
Conductivity [1]			±		µmho/cm				
Silica [1]			±		mg/L				

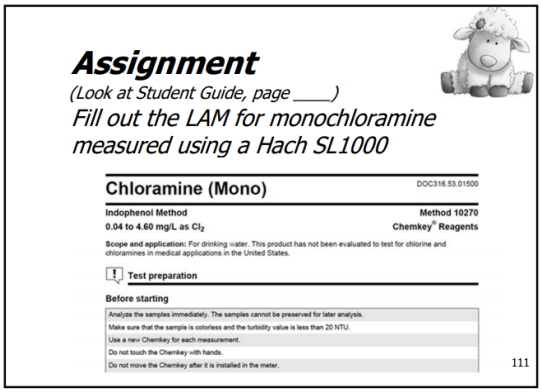
Lab Analyst or Operator Validation

I certify that I am familiar with the information contained in this report and that, to the best of my knowledge, this information is true, complete and accurate.

Lab Analyst or Operator's Name and Title

Lab Analyst or Operator's Signature

Figure 13. Laboratory Approval Form (LAF)



Assignment

(Look at Student Guide, page ____)

Fill out the LAM for monochloramine measured using a Hach SL1000

Chloramine (Mono) DOC316.53.01500

Indophenol Method **Method 10270**

0.04 to 4.60 mg/L as Cl_2 **Chemkey® Reagents**

Scope and application: For drinking water. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

Test preparation

Before starting

Analyze the samples immediately. The samples cannot be preserved for later analysis.
Make sure that the sample is colorless and the turbidity value is less than 20 NTU.
Use a new Chemkey for each measurement.
Do not touch the Chemkey with hands.
Do not move the Chemkey after it is installed in the meter.

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Exercise: Finding data for the LAM

Let's consider the case where a system uses a Hach SL1000 to measure monochloramine. We will go through the process of filling in that line.

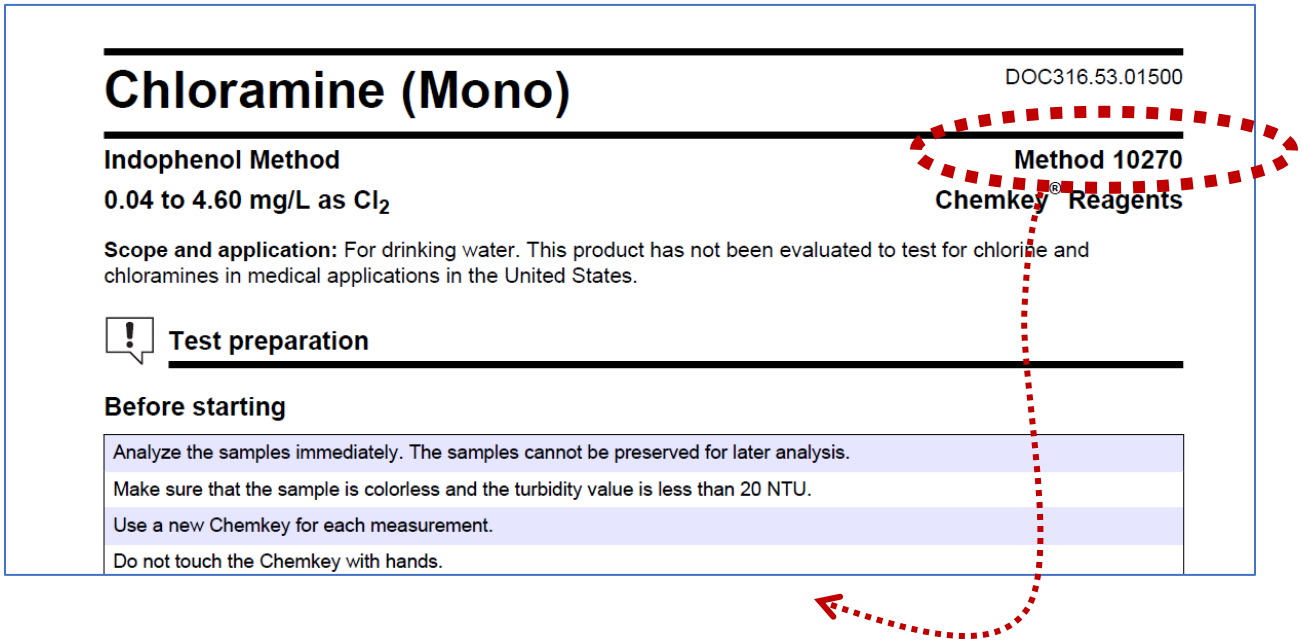
Here is a picture of the line on the LAM form:

NAP Required Parameters					
Analyte	Analytical Method	Instrument Name	Accuracy	Calibration Frequency	Calibration Method
Monochloramine			*mg/L*		
Free Ammonia (as nitrogen)			*mg/L*		
Nitrite (as nitrogen)			*mg/L*		
Nitrate (as nitrogen)			*mg/L*		

The things we need to fill in are:

1. Analytical Method,
2. Instrument Name,
3. Accuracy (+/- mg/L),
4. Calibration Frequency, and
5. Calibration Method.

Here is a picture of the manual for the Hach SL 1000. If you don't have a manual for your instrument, you can download one from the internet.



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Test preparation

Before starting

Analyze the samples immediately. The samples cannot be preserved for later analysis.
Make sure that the sample is colorless and the turbidity value is less than 20 NTU.
Use a new Chemkey for each measurement.
Do not touch the Chemkey with hands.

1. Analytical Method: **From the Manual, page 1**
2. Instrument Name: **We know it is a SL1000**

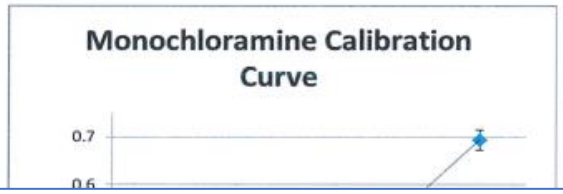
Correlation Coefficient (r^2)	>0.999
Method Version	27-11
Date	1 November 2016

The detection and the quantitation limits were determined in conformity with USEPA method 40 CFR Appendix B to Part 136, Revision 1.11.

Detection limit	<0.03 mg/L
Quantitation limit	<0.09 mg/L

Results are certified for 12 months after manufacture date when stored at 25C or below.

Result	Precision Confidence Interval (95%)
2.00 mg/l	± 0.08 mg/L
4.00 mg/l	± 0.12 mg/L



3. Accuracy (+/- mg/L): **We need to look in the Manual**

Finally, we need to consider the system's own **standard operating procedures (SOPs)** for the next two columns:

4. Calibration Frequency, and
5. Calibration Method.

Record retention

The LAM does not need to be submitted to the TCEQ for approval.

Keep your LAM with the system's NAP, attached to your Monitoring Plan.

Make it available to the TCEQ upon request.

Change your NAP LAM as needed to reflect your procedures.

Any changes to your LAM do not need TCEQ approval.

Keep LAM on site for review

- The LAM does not need to be submitted to the TCEQ for approval.
  - Keep your LAM with the system's NAP, attached to your Monitoring Plan.
  - Make it available to the TCEQ upon request.
- Change your NAP LAM as needed to reflect your procedures.
  - Any changes to your LAM do not need TCEQ approval.

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Assignment: List of Analytical Methods (LAM)

This assignment is to complete the LAM for the system where the DAM is held.

Name of PWS: _____: LAM

Analyte	**Method (& Analyzer Type)**	**Accuracy[5]**	**Calibration Frequency[6]**	**Calibration Method**
pH		± pH unit		
Temperature		± C		
Disinfectant				
Total Chlorine		± mg/L		
Free Chlorine		± mg/L		
Monochloramine		± mg/L		
Free Ammonia (as nitrogen)		± mg/L		
Chlorine Dioxide		± mg/L		
Chlorite		± mg/L		
Ozone		± mg/L		
Nitrification				
Nitrite		± mg/L		
Nitrate		± mg/L		
Other-Microbial				
HPC (Heterotrophic plate count bacteria)		± FU/100 mL		
DNA (Microbial DNA)		± mg/L		
Other		± _____		
Hardness		± mg/L		
Alkalinity		± mg/L		
Total dissolved solids		± mg/L		
Dissolved oxygen (DO)		± mg/L		

After completion, attach a copy to the system's Monitoring Plan

Chapter 2. Review questions

(Questions may have MULTIPLE correct answers.)

Chlorine should be measured:

1. "As ClO_2"
2. "As Cl"
3. "As Cl_2"

Ammonia should be measured:

1. "As NH_4"
2. "As NH_3"
3. "As N_2"
4. "As N"

Methods for analysis of monochloramine and ammonia in distribution must be:

1. EPA approved
2. NELAC approved
3. TCEQ accredited
4. TCEQ approved

The TCEQ process for approving the methods that a system uses is:

1. The TCEQ sends the LAF and LAM to the EPA for review
2. The TCEQ reviews the LAF and LAM during regularly scheduled (or special) investigations
3. The TCEQ reviews the LAF and LAM after the system sends them to TCEQ's Central Office in Austin

Chapter 2 Checklist

Hopefully, after this chapter, you are comfortable with the sampling needed to use chloramines and ready to do a great job. Make sure by going through this checklist.

Part 1: Sampling: Instruments, Collection, and Analysis

Instruments

- Do you have instruments, manuals, and reagents for all the field methods?
- IF NOT, do you have funds to purchase needed supplies or equipment?

Sample collection methods

- Do you have an idea of how long to flush before collecting a sample at each site?
    - Are all sample collectors clear on the difference between flushing long enough to collect a sample versus flushing long enough to move fresh water into the area?
- If you want to make a hydrant sampler and/or tap sampler, do you know how? And how to request funding for the parts?

Analysis

- Do you have an SOP or instructions for analyzing samples?
- Are all operators comfortable with the analytical methods and sample analysis SOP? (especially new operators and new methods)?
- Are all operators comfortable with diluting monochloramine/ammonia samples if needed? and calculating the concentration?
- Do you have a way to get nitrite and nitrate analyzed?
    - If you use a commercial lab, can you get these samples analyzed quickly in an emergency? Are they accredited for drinking water? Are they accurate enough.

Part 2: LAM

- Is your LAM up-to-date?
- If you need to send nitrite/nitrate samples to a lab, have you got a copy of that lab's Laboratory Approval Form?

Follow up:

If you have the necessary field instruments, know how to collect and analyze samples accurately, and have a completed LAM, you are on the road to success.

Notes

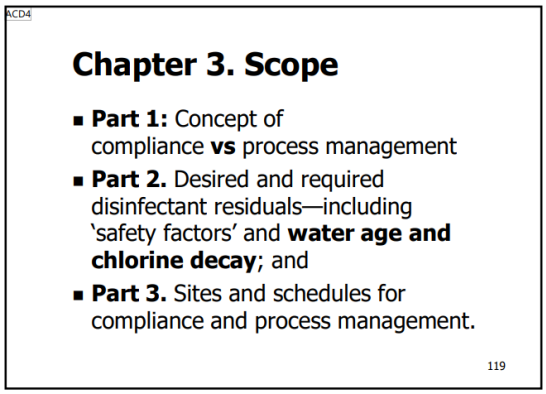
Chapter 3. Monitoring and reporting

Every PWS that uses chloramines must comply with the TCEQ rules for monitoring and reporting described in this Chapter.

Scope

There are three technical parts to this chapter, plus the follow up:

- **Part 1**: Concept of compliance vs process management
- **Part 2**. Desired and required disinfectant residuals —including 'safety factors' and water age; and
- **Part 3**: Sites and schedules for compliance and process management.



Hands-on Activity

The activity for this workshop is to go over the system's actual map of sites and sample schedules. This ties into the NAP, because this is the sampling that needs to be documented in the NAP portion of the Monitoring Plan.

Materials

For this section, we will look at:

- ✓ The Student Guide;
- ✓ Monitoring Plan with (Nitrification Action Plan)
  - Distribution Map,
  - Schedule,
  - List of sample sites,
- ✓ Daily sheets, log books, or whatever paperwork exists for tracking residuals.

Learning goals

The learning goals for this workshop are:

- **Part 1:** Understand the difference between compliance and process management sampling,

- **Part 2:** Know what residual levels you are aiming for (desired and required),
    - Know your system's 'safety factors';
    - Be familiar with water age and chloramine decay;
    - Understand how total chlorine, monochloramine, and free ammonia levels change as water ages; and
- **Part 3:** Be able to select sites—sources, treatment plants, entry points, and representing distribution, and be able to set and implement schedules.

ACD7

Chapter 3. Learning Goals

- **Part 1.** Understand and apply the concept of process management vs. compliance
- **Part 2.** Know the required residual levels, and the ones desired in your system.
  - Understand safety factors, monochloramine decay, and water age
- **Part 3.** Be able to select sample sites and schedules
  - Sources, treatment plants, entry points, and representing the entire distribution system

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Part 1. Compliance and process management sampling

It is important to know what your purpose in sampling is so you know how to document and report the results.

ACD6

Part 1. Compliance vs. Process Management

- Since 7/30/15, the monitoring requirements are in the rule—
  - 30 TAC 290.110(c)(5)
- Some results ARE used for calculating compliance—Others are NOT.

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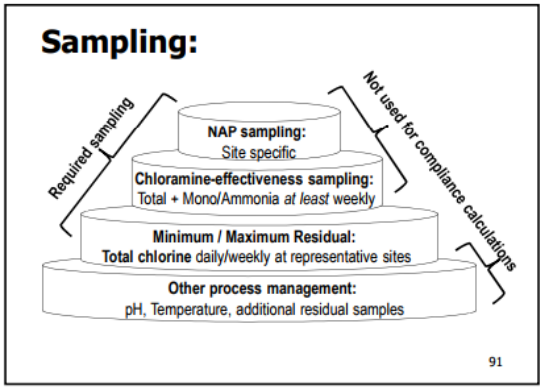
There are two kinds of sampling:

- **Compliance:** Total chlorine monitoring for compliance with maximum and minimum residual levels, and
- **Process management:** Monochloramine and free ammonia monitoring to determine the effectiveness of your chloramines, (and nitrite/nitrate monitoring to determine if nitrification is happening).



You will take the most samples for process management, not compliance. The rules are minimum standards. Table 9 shows the table of required sampling, which includes BOTH compliance and process management samples.

(This table appears 2 more times in this Chapter and once in Attachment 2.)

Table 9. Required Sample Frequency of 290.110(c)(5) (See Slides)

	At or after all Entry Point(s)	**In the distribution system**	**Before and after any chlorine or ammonia injection points**
Total Chlorine	At least weekly.	Daily at large PWSs Weekly at small PWSs. [b]	At least weekly and before and after adjusting the chlorine or ammonia feed rate.
Mono-chloramine	At least weekly.	At least weekly. [a]	
Free Ammonia	At least weekly.	At least weekly.	
Nitrite and Nitrate	Monthly for the first six (6) months to set baselines, then quarterly.	In response to action triggers; and at least quarterly	Routine sampling not required.

[a.] When collecting a routine sample such as a bacteriological or routine disinfectant residual sample.

[b.] Total chlorine must be collected weekly for systems serving fewer than 250 connections and fewer than 750 people, or weekly for systems serving at least 250 connections or at least 750 people, in accordance with §290.110.

Note: Additional sampling may be needed to follow up on results that are not as expected.

See series of slides:

ACD8
ACD9

Minimum Sampling Requirements

We will discuss this in more depth later.

Process Management **Compliance**

Constituent	At the Treatment Plant	At the Entry Point	In the Distribution System
Total Chlorine	Weekly and prior to and after adjusting the chlorine or ammonia feed rate	Weekly	Daily or Weekly * Used to calculate compliance with min/max
Free Ammonia / Mono-chloramine	Weekly and prior to and after adjusting the chlorine or ammonia feed rate	Weekly	Weekly

* Under 250 cnx/750 pop = Weekly, Over 250/750 = Daily

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ACD10

Minimum Sampling Requirements

Process Management

Chemical	At All Plants	At All Entry Points	In the Distribution System
Nitrite / Nitrate	Not required	Monthly for six months, *(to find NAP baselines)* then **Quarterly**	**Quarterly**, at representative sites, ***(and also in response to NAP triggers)***

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This concept is important because often, fear of having a 'bad' sample makes people flush longer than they should because they want to see 'good' results—or even fail to take samples at all. But in the context of process management, the only 'BAD sample is an INACCURATE sample. If the sample does not represent and characterize the water quality in a way that is accurate, it is a 'bad' sample even if the residual is high. 'Good' process management samples lead to good decision making; inaccurate and 'bad' (or nonexistent) process management samples lead to bad decision making.

Reason for process management monitoring

- Regulatory total chlorine monitoring **may not identify issues** early enough to avoid problems.
- **You** are the expert on your system:
  - Your process-management sampling can identify problems before they start.
  - Specifically, a "Nitrification Action Plan" (NAP)
    - (A topic for another presentation).

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It is recommended that a PWS make a clear distinction between compliance and process management sites. For example, an active service connection may be used for both coliform and disinfectant residual for compliance, but a nearby hydrant may be used for process-management chloramine-effectiveness monitoring.

Sites: Compliance sites versus process management sites

For both of these kinds of monitoring, you must sample at sites representing the entire distribution system. Otherwise, you could have problems and not find them till it is too late.

It is important to distinguish between compliance samples and process management samples.

- ***Compliance sites*** are just that—they are collected to report to the state and to base compliance decisions on.
    - Compliance sites must be listed in the NAP which is attached to the Monitoring Plan.
- ***Process management sites*** are all other sites.
    - Process management sites should be listed in the NAP, but they should be distinguished from compliance sites.
        - For example, the list of dead-end mains is not in the Monitoring Plan, but samples are collected there, and the results are NOT used for compliance (except if collected by a TCEQ Regional Investigator under special circumstances.)

For total chlorine, compliance samples are those collected at the disinfectant residual sites shown in the Monitoring Plan. ***All total chlorine samples collected at those compliance locations must be used for compliance calculations.***

For example—systems must report routine distribution coliform results monthly. But PWSs also take special or construction coliform samples, for example, to verify the results of their post-construction disinfection. The microbial results of those special or construction coliform samples are not included in the TCEQ's compliance calculations. However, if the coliform sites are also the disinfectant residual sites—the total chlorine collected with the special coliform MUST be considered as a compliance result.

The monochloramine and ammonia samples are ***always*** process management samples. They are not used for compliance determination (just for implementing the NAP). A low monochloramine or ammonia result has no compliance impact—it is just to help manage water quality.

Likewise, much of the nitrite and nitrate data is for process management not compliance. The exception is the entry point results collected by the TCEQ's contractor, which WOULD be considered for compliance (if collected according to TCEQ procedures and policies—check with WSD at 512-239-4691 if needed).

Communication

Results at compliance sites must be noted on the system's 'daily logs' and transferred to the correct form to send to TCEQ. Results at process management sites don't have to be sent to TCEQ. However! Lead operators need to look at both compliance and process management results.

One common issue is that miscommunication or lack of communication occurs, especially for process management sampling. For example, an operator flushing a main may find very low residuals during process management sampling. Then, the person flushing may fail to tell their supervisor about that. Or, the flusher may tell the supervisor, but the supervisor may not listen. Either way, it is a fail.

Poor communication is the quickest way to get in trouble.

Document compliance results

- No surface water treatment plant (SWTP):
  - Community/Nontransient noncommunity
    - Submit on DLQOR
      - Disinfectant Level Quarterly Operating Report
  - Transient noncommunity
    - Retain DLQOR for review by TCEQ
- SWTP: Submit on SWMOR
    - Surface Water Monthly Operating Report

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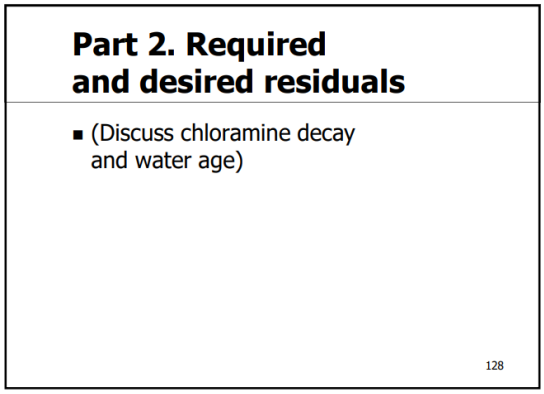
Part 2: Residual levels: Required and desired

As every water operator knows, disinfection provides protection of pathogen regrowth and intrusion in the distribution system. However, as the water age increases, the residual goes away.



Before we talk about where and when to measure, let's go over what levels we have to—or WANT to—achieve.

Required residuals

Process management versus compliance:

- There is a regulatory minimum for total chlorine at the entry point and in distribution.
- There is a regulatory maximum for total chlorine in ***distribution*** (not entry points—except if the first customer's tap is used).
- ***There are no regulatory requirements for monochloramine or ammonia levels at any site.***

Minimum total chlorine

The minimum allowable total chlorine residual is 0.5 mg/L at the entry point and in distribution. As we will discuss further, generally we need to hold a residual much higher than 0.5 mg/L at the entry point. Compliance with the minimum total chlorine level is based on 95% of all samples being over the minimum. If 5% or more samples are less than the minimum in two consecutive months, the PWS is in violation.

Slid

ACD1

Required minimums

- Residual throughout distribution system must not be below the minimum:
  - Either **0.2 mg/L** free chlorine,
  - Or **0.5 mg/L** total chlorine
    - If monochloramine is the disinfectant.

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Desired residuals and safety factors

If you aim for the minimum, any deviation will cause unacceptably low results. Therefore, PWSs use a safety factor to keep them on the right side of the line. Desired residuals are set based on the required residual at the maximum water age locations, plus a safety factor.

Safety factor

- Minimum residual for chloramines at every point in the system is 0.5 mg/L.
- Is your disinfectant goal = 0.5 mg/L?
  - WHY NOT?
- Your goal at the far reaches should include a Safety Factor.
  - For example, good goals are: 1, 0.8, etc.
    - So that when something goes wrong, it does not instantly cause levels too low in distribution.

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For example, if a system has one location where they have trouble keeping a 0.5 mg/L residual, they may turn up the dose of monochloramine and add a safety factor so that their goal at this location is a 1.0 mg/L.

Desired residuals will vary depending on location. The desired residual at the entry point has to be high enough at the entry point that they monochloramine won't all go away before it gets to the last customer.

Maximum total chlorine

The maximum residual disinfectant level (MRDL) for total chlorine is 4.0 mg/L. Compliance is based on the running annual average of all distribution system samples.

Entry points are NOT distribution sites, so entry point results should not be included in calculating the average unless the entry point sample site is at the first customer's tap. If a PWS has a running annual average over 4.0 mg/L, the PWS is in violation.

ACD2

(Required maximum)

- *Maximum residual disinfectant level:*
  - *Either free or total chlorine:*
  - *4.0 mg/L based on*
    - *The running annual average of quarterly averages of all sites in **distribution**.*
      - *At compliance sites listed in Monitoring Plan.*
  - *Take home: Water can be over 4.0 mg/L at the entry point without violating rules.*
    - *The entry point, by definition, is not in the distribution system.*

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The point of this is that it is possible to have total chlorine levels greater than 4.0 mg/L at the entry point without violating TCEQ rules. Some PWSs need to run this hot to get chloramines through the whole system!

Water age and monochloramine decay

As water travels through the distribution pipes and tanks, it gets older. More importantly, the disinfectant gets older and disappears.

WATER AGE

- Monochloramine decays over time.
  - Older water has less monochloramine.
  - Called 'stagnation'.

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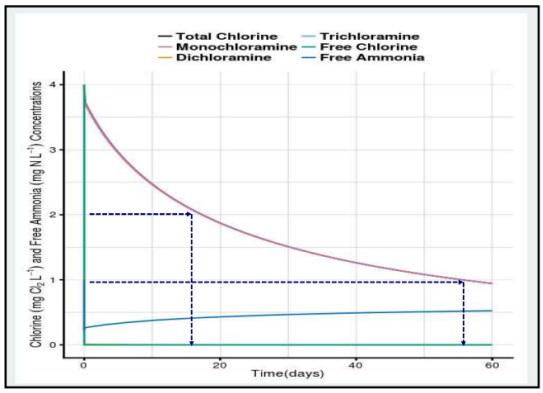
For example, you could say that the water age is zero at the point we inject disinfectant. Then, as it spends time in the pipe, water age increases.



Water age changes depending on system operation. When there is more usage, the water moves out of the pipes quicker. When usage is low, it sits in the pipes longer, aging. Summer and winter water-age can be very different.

Monochloramine decay

Monochloramine goes away as water ages, but not as quickly as free chlorine. (The ratio of total chlorine and monochloramine stays the same during decay if the disinfectant residual is stable.)

Software to estimate chloramine decay

The EPA Office of Research and Development has an application on the internet you can use to estimate the decay of chloramines under ideal conditions.

It is online at:

usepaord.shinyapps.io/Unified-Combo/

To use the model, just input the levels of chemicals for your water. If you don't know certain values, try the defaults in the application.

An example of the output of this model is shown in Figure 14.

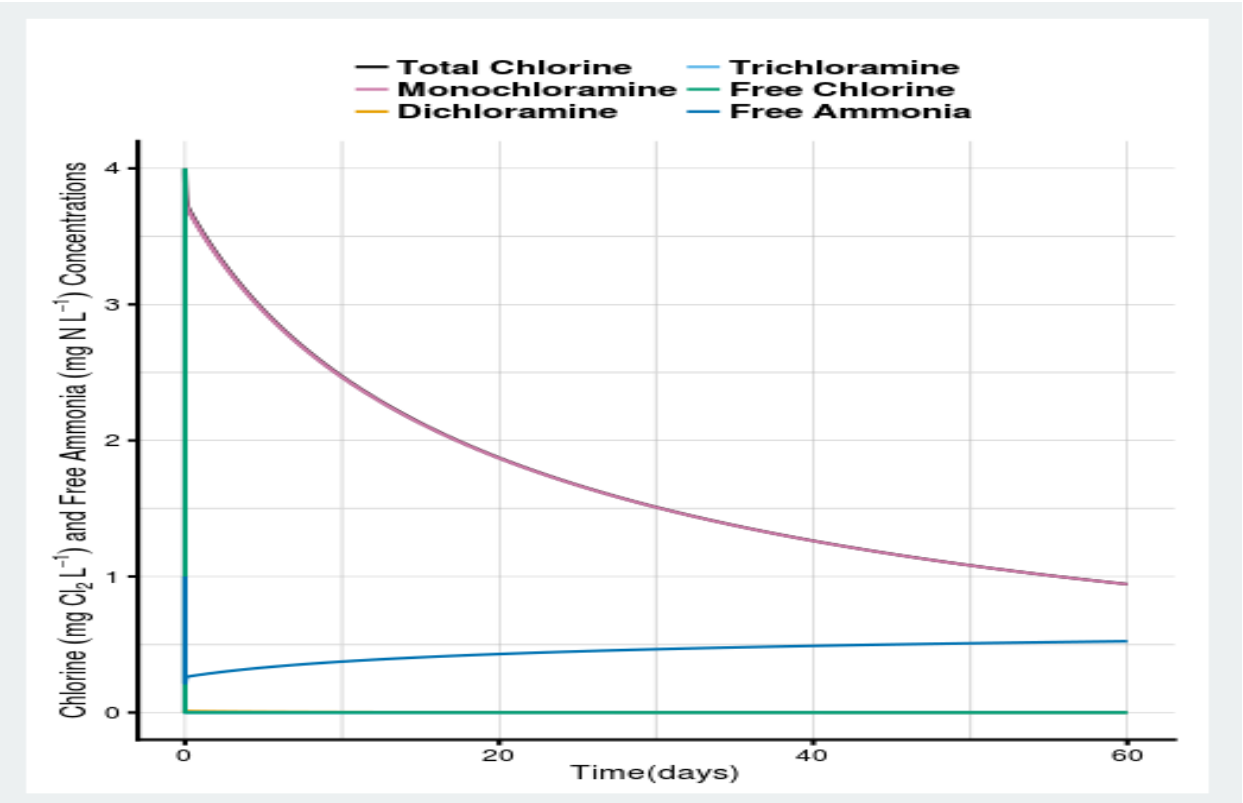


Figure 14: Example of decay curve generated for water with an initial total/monochloramine concentration of 4 mg/L. (See slide) (Top line is mono/total decaying, lower line is ammonia increasing)

In Figure 14, note that there is still a good residual—well over 0.5 mg/L—even after two months! This graph is for an ideal simulation, but experience shows that there are real PWSs in Texas that really can hold a residual for that long.

When you see the monochloramine residual disappearing in areas with less than about two weeks water age, it is a concern!

Figure 15a and 15b shows a decay curve for free chlorine and a decay curve for monochloramine.

As shown in Figure 15a, free chlorine decays significantly over the course of 60 hours—about 2 ½ days. For example, the middle curve (round open circles) starts at about 2 mg/L and drops to 1 mg/L in about 10 hours. Then, after another 10 hours, the level is about 0.6 mg/L.

If you did a similar test on your water, the exact numbers would be different but you would see the same shape of the curve.

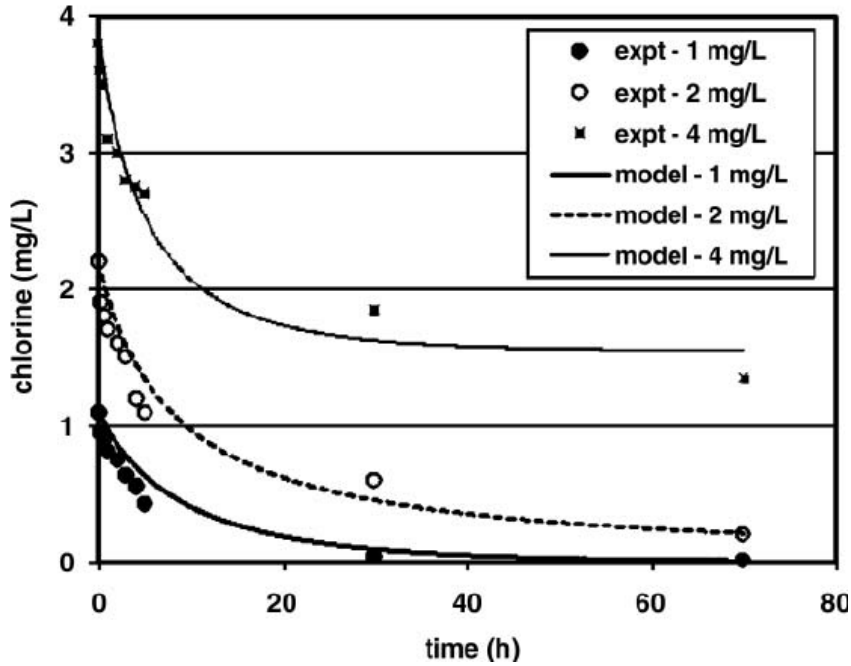


Figure 15a. Decay curve for free chlorine at different initial concentrations (From Fisher, Kastl , Sathasivan & Jegatheesan (2011) "Suitability of Chlorine Bulk Decay Models for Planning and Management of Water Distribution Systems", Critical Reviews in Environmental Science and Technology, 41:20, 1843-1882)

Figure 15b shows the decay rate for monochloramine (measured in millimoles, mM). Notice that the x-axis is also in hours, but the monochloramine decays much more slowly than free chlorine.

For monochloramine, it takes about 70 hours for the water at pH = 6.55 to lose half of its initial monochloramine concentration. The monochloramine lasts about 7 times longer than the free chlorine.

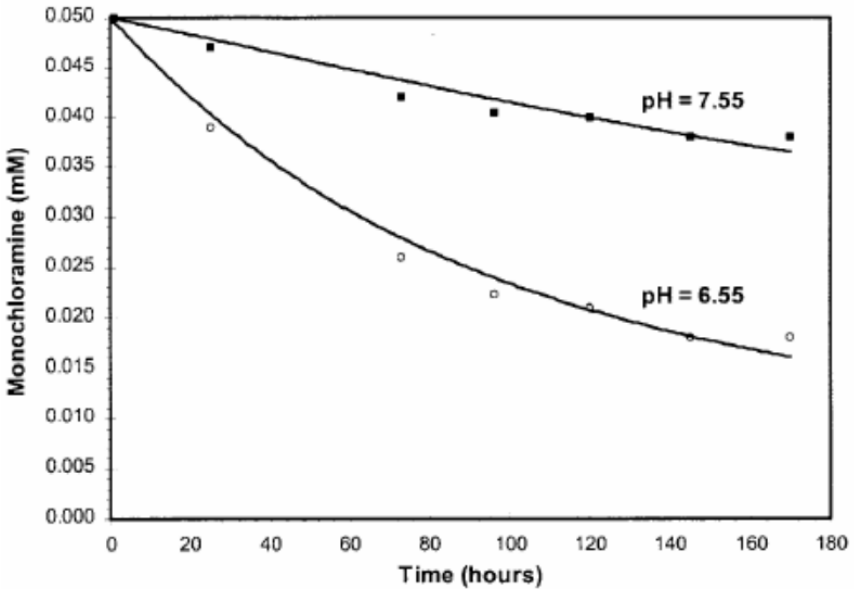


Figure 15b. Decay curve for monochloramine at pH 7.55 and pH 6.55. (From McVay "Production of Chloramines and Chloramine Monitoring in Water Supply Systems" Florida Rural Water Association)

Note that this graph also shows the impact of pH. For water at pH = 7.55, half of the residual has not been lost even at the end of the experiment, at about 150 hours—over 6 days.

Knowing that monochloramine decays, we need to set goals that ensure compliance with the 0.5 mg/L total chlorine residual at the connections farthest from the source. *To do so, let's talk about what causes monochloramine to decay.*

Why does the residual decay?

As the water ages, the disinfectant residual decays by reacting with organic matter in the source water—including killing pathogens. Every time it reacts with dirt or pathogens, it is lost.

Monochloramine is an extremely stable molecule. It will last a really long time—much longer than free chlorine—but not forever. Monochloramine lasts weeks to months, and free chlorine only lasts days up to maybe week or so.

Some of the things that can cause monochloramine decay are

- Oxidation with organic matter,
- Auto-decomposition,
- Oxidation by iron
- Consumption by bacteria.

Oxidation with organic matter

Monochloramine's job is to oxidize organic matter—for example the organic matter in pathogens. The more 'stuff' in the water, the more the chloramine will decay, just like with free chlorine.

Auto-decomposition

Even in a perfect environment, monochloramine can react with itself to decay, (producing ammonia). That is called 'auto-decomposition'. It happens faster at low pH.

Oxidation by iron, etc.

Some pipe systems have a lot of inorganic demand—like iron and manganese. The more corrosion, the more decay of residual.

Consumption by nitrifying organisms

If nitrifying organisms start growing in your system, they will eat up the residual. You will learn more about this in DAM 8: Nitrification Action Plans.

Estimating water age in the lab

Operators who have worked at a system for a long time often have a good idea what the water age is in their system. However, even if you are unfamiliar with a system, you can figure out the how monochloramine decays in your water system by using software generated by EPA or by running a simple lab experiment, called a 'Hold Test'

Note

Although there is not time to do a software or lab experiment during this DAM, these are described so that you can try this later.

How to do a 'Hold Study' for chloramine decay in your water

When looking at the results of distribution system testing, the question may arise: "What SHOULD it be?" One way to evaluate what the ideal residual would be is to do a simple 'bucket test' or 'Hold Test.'

More detailed instructions on performing simple Hold Study for chloramine decay or to generate a breakpoint curve follow.

The Hold Study concept can also be used to look at disinfection byproduct formation. The TCEQ's DAM 4a is a two-day course designed to help SWTPs with performing the Hold Study for that purpose.

The principle is that chlorine decays in a very predictable way when there are not confusing elements like biofilm, rotting pipes, etc. The chlorine decay test is straightforward.

> ***Consider the PWS details:***
>
> If the PWS has multiple sources feeding the distributions system at different places, it might be good to do a separate Hold Study on each source, treatment plant, and/or pressure plane.

The simplest Hold Study is described first. There are much more controlled ways to do a Hold Study. An excellent article using a more sophisticated set up is in the AWWA Op-Flow magazine, Issue May 2019. The Simulated Distribution System and Uniform Formation Control methods are types of hold study in Standard Methods.

The "Hold Study" procedure is as follows:

Gather equipment:

You will need:

- Enough treated water from the entry point to run a series of samples, for example—4 gallons in a clean 5-gallon bucket.
- A place to hold that water at constant temperature, in the dark, where dust can't fall in it, for example, a cabinet.
- Analytical instruments to measure total chlorine, monochloramine, and free ammonia.
- Thermometer or probe to measure temperature.
- If desired, a pH probe. (Not entirely necessary)

Figure 16, below, shows what you need for a chloramine decay bucket test.

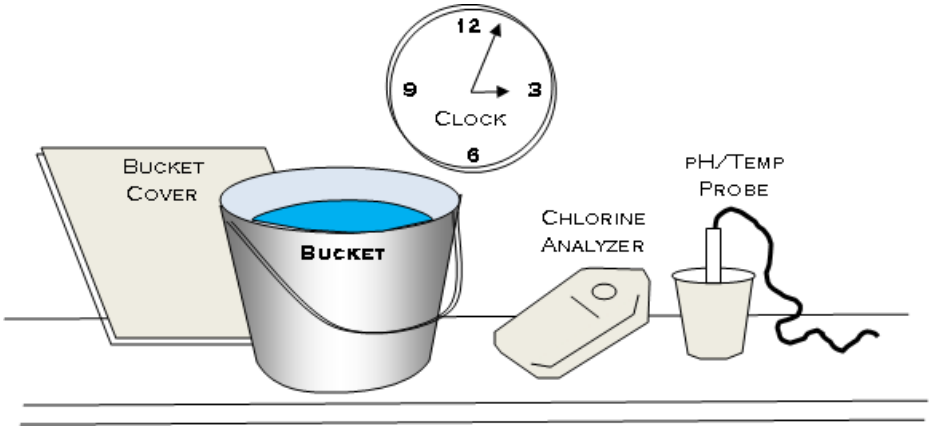


Figure 16. Equipment for a chloramine residual decay hold study (see slide)

Hold Test procedure

- Get a **bucket of water** from the PWS entry point of interest.
  - Use a clean bucket.
  - Rinse it out with entry point water several times (3x) to wash out any contamination.
  - Then, fill it up with entry point water.
- Measure the **chlorine, pH, and temperature** at the time of collection.
  - Note the **time**—the time of collection is **t=0 (zero)** for the test
- Set the bucket somewhere you can generally **control temperature** and contamination.
  - For example, in a closet or cupboard.
  - **Cover the bucket** so that stuff does not fall in, and to keep it dark.
- **Measure and record chlorine, pH, and temperature over time**, till the chlorine is gone.
  - Chloramines will last for weeks. If it doesn't—more research is needed!
  - Free chlorine will last a few days, if you do the test on water with free chlorine in it.
- **Graph** the results.

The results might look something like Figure 17.

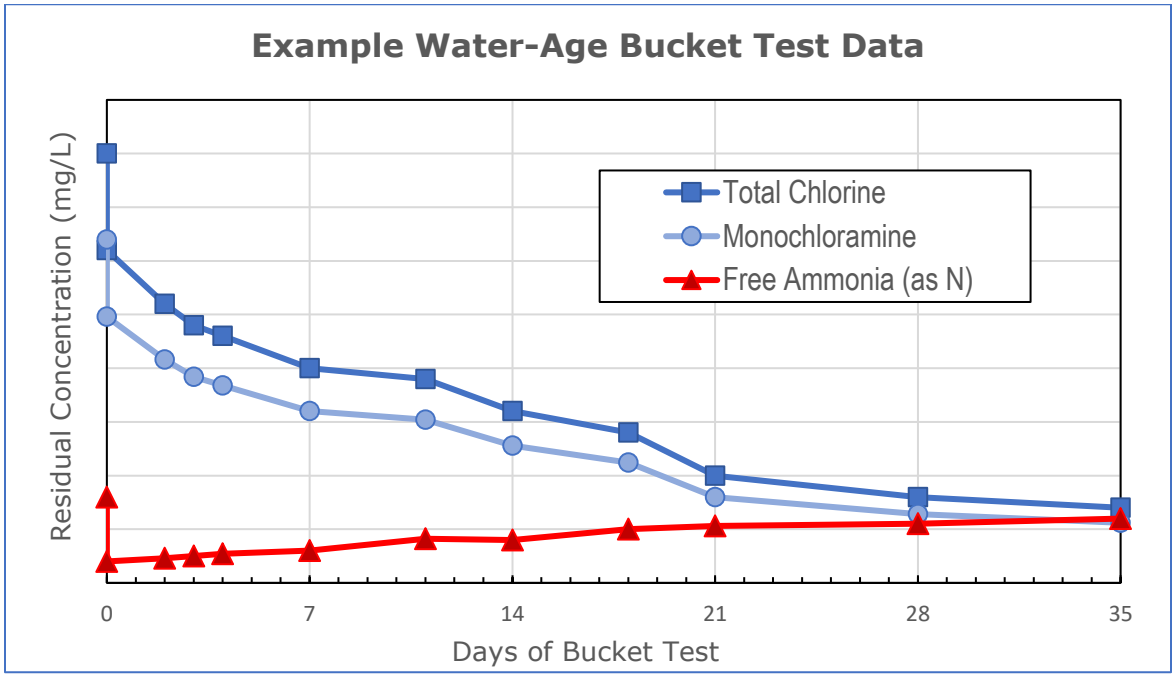
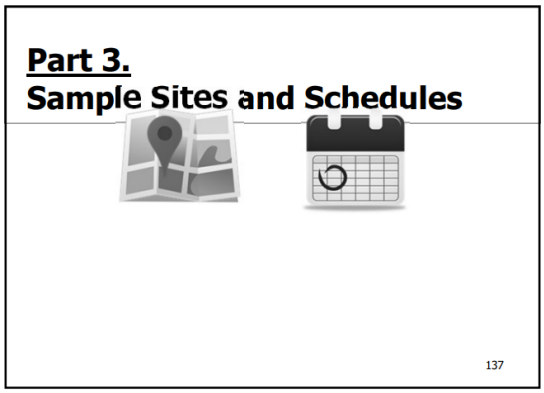


Figure 17. Example results for a site-specific water age bucket test. (see slide)

Part 3. Sample sites and schedules

In this part of Chapter 3, we discuss the frequency and location of chloramine-effectiveness monitoring.



Sites

The locations where samples are needed are:

- Sources,
- Treatment plants,
- Entry points, and
- Distribution.

Each of these has its own special issues.

Sample sites can be different depending on what type of water you have:

- Surface water,
- Groundwater, and/or
- Purchased water.

In a system that treats raw water to produce drinking water, sites should be available to characterize:

- Raw surface water,
- Dosing in the SWTP,
- Entry point(s), and
- The whole distribution system, including at-risk sites.

All of those sites are needed for purchased water except the SWTP sites.

Sample Sites

- Sources
- Plants
- Entry points
- Sites representative of entire distribution system, for example:
  - All high-risk (high water age) areas,
  - All pressure planes

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Sample Sites

- Required sites are listed on the table in the rules.

Required Sample Frequency of 290.110(C)(5)

	At or after all Entry Point(s)	In the distribution system	Before and after any chlorine or ammonia injection points
Total Chlorine	At least weekly.	Daily at large PWSs Weekly at small PWSs. [b]	At least weekly and before and after adjusting the chlorine or ammonia feed rate.
Mono-chloramine	At least weekly.	At least weekly. [a]	
Free Ammonia	At least weekly.	At least weekly.	
Nitrite and Nitrate	Monthly for the first six (6) months to set baselines, then quarterly.	In response to action triggers; and at least quarterly	Routine sampling not required.

[a] When collecting a routine sample such as a bacteriological or routine disinfectant residual sample.

[b] Total chlorine must be collected weekly for systems serving fewer than 250 connections and fewer than 750 people, or weekly for systems serving at least 250 connections or at least 750 people, in accordance with §290.110.

Note: Additional sampling may be needed to follow up on results that are not as expected.

Figure is on Pages _____ of Student Guide

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ACD9

Sample Sites

- Plants, entry points, and distribution

Constituent	At the Treatment Plant	At the Entry Point	In the Distribution System
Total Chlorine **Compliance**	**Weekly** and prior to and after adjusting the chlorine or ammonia feed rate	**Weekly**	**Daily** or **Weekly** * Used to calculate compliance with min/max
Free Ammonia Mono-	**Weekly** and prior to and after adjusting the	**Weekly**	**Weekly**

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Sample Sites, cont'd.

- Plants, entry points, and distribution

Chemical	At All Plants	At All Entry Points	In the Distribution System
Nitrite Nrate	Not required	**Monthly** for six months, *(to find NAP baselines)* then **Quarterly**	*At least* **Quarterly**, at representative sites

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Sources

The most important thing we need to know about raw water is whether it contains free ammonia. The second most important thing we need to know is how much 'demand' it has.

Surface water sources

Surface water treatment plants (SWTPs) do daily source water monitoring. Therefore, every plant has a handy sample tap for raw water (hopefully).

Raw surface water sample taps inside of SWTP labs may have verrry long sample lines. Some SWTPs run the raw sample tap continuously, so that the water does not sit in the sample line for long. Others flushes

Groundwater sources

There is a rule requirement that every well have a raw sample tap. You can collect water from that well tap to see how much free ammonia it has.

If multiple wells are manifolded together before treatment, each well still needs a tap. Different wells may contribute different levels of ammonia to the blended water. Then, depending on which well is in operation, you will have an idea how much ammonia and demand is present.

Purchased water sources

It is highly recommended that a PWS which purchases and redistributes treated water be aware of the quality of the water it is purchasing, especially its variability. The only way to know whether upstream source changes might impact it is to maintain good communication with the seller.

Entry points

Entry point sample sites are where the TCEQ's contract samplers pick up samples for things like minerals and metals—arsenic, nitrite, nitrate, etc.

An entry point is defined as any point where treated water enters the distribution system. The concept is that water should be safe before it reaches any customer.

Surface water entry points

A PWS that owns and operates a SWTP usually has one main entry point, and TCEQ picks up samples quarterly there.

However, a large system may pipe water from their SWTP into different areas of the distribution system—for example, into two separate pressure planes. In that case, there are multiple entry points—each one needs a tap.

Groundwater entry points

The most common type of water system in Texas is one well/one entry point. For these systems, just make sure the sample site is after chlorination.

Often, water from more than one well comes together in a manifold or tank before chlorination. In that case, there are multiple sources with a single entry point.

Purchased water entry points/source

Basically—the purchased water source EQUALS the purchased water entry point to the system.

Since July 30, 2015 when the chloramine rules started, it is a requirement to monitor sources. For a purchased water system, the purchased water is the source, so it is now a requirement to have a place to sample it.

Of the three source types, purchased water is the most likely to have ammonia in it. In order to successfully make and maintain stable chloramines, we need to know how much ammonia is in the water. DAM 8 explains how the amount of ammonia can be related to nitrification.

As previously noted, a system that purchases and redistributes potable water has challenges, so it is really important to know the water quality coming in.

Treatment plants

In-plant sampling for chloramines is critical to make stable monochloramine, without too much ammonia.

The rules require that plants have sample sites that allow them to dose correctly to make stable monochloramine.

Surface water treatment plant

Getting the dose right in a SWTP is a daily—even hourly—job, depending on variable surface water conditions. Chapter 5 of this DAM talks in detail about how monitoring fits into SWTP disinfection processes.

Groundwater treatment plant

Most groundwater treatment plants consist of chlorine and ammonia dosing. Usually, the raw water tap is assumed to be the pre-treatment tap, and the entry point tap is assumed to be the post-treatment tap. That may be ok. However, if there is a large tank between those two sites, that is not so great. The tank adds water age, so you can't tell what the result of a dose change till hours after you make it.

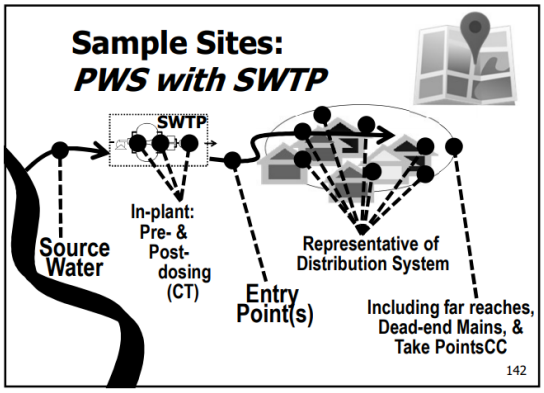
Booster disinfection in distribution

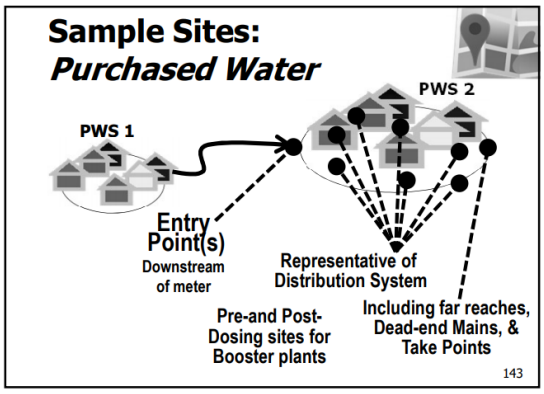
Most groundwater treatment plants consist of chlorine and ammonia dosing.

Some older plants may have been constructed with limited sample taps. That may be a challenge that needs to be solved long-term.

Distribution

Every system must have sites that represent the distribution system.





Compliance note: Total chlorine compliance monitoring

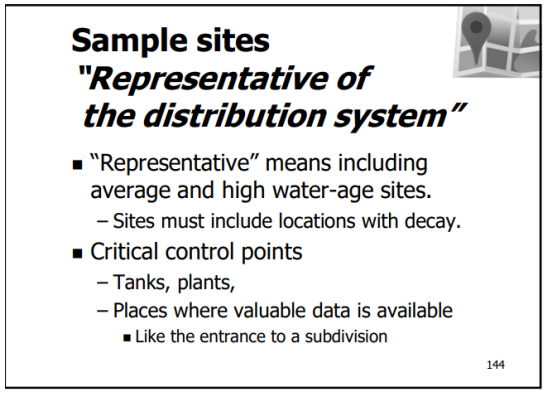
Note: Total chlorine compliance monitoring ONLY occurs in distribution—samples collected inside of a plant or at an entry point are NOT used for compliance calculations for distribution minimum or maximum required residuals. (The entry points are not in distribution, they are before it, unless the first customer's tap is used as the entry point sample site.)

Representative sample sites—the concept

Representative sample sites for disinfectant residual must:

- Include high water age (most important), and also medium and low water age;
- Include every pressure plane;
- Include water from every source.

The fundamental question answered by this part of Chapter 3 is **"What does representative mean"**?



Representative means that sampling should:

- **Represent the entire system:**
  - Sample sites should represent water throughout the entire distribution, impacted by pressure planes, hydraulic features, and facilities—*not* just a few small areas.

The PWS's monitoring must be representative of the entire distribution system including the range of water age, treatment, and sources in your system.

What does "Representative" mean?

In general, representative means representative sites, schedule, and water. Sampling must represent:

Disinfectant sample sites must represent the entire system: Water throughout the entire distribution, impacted by major hydraulic features and facilities.

The first two items—sites and schedules—are covered in this Appendix.

Representative sites

Sample sites must be representative of the entire distribution system including the range of water age, treatment, and sources in your system.

Distribution sample sites must represent:

- The entire distribution system;
- Every pressure plane;
- Critical control points like tanks and booster plants;
- Low, medium, and high water age;
- Including various high water age locations as needed; and
- Critical infrastructure, recommended.

Sites should reflect current conditions

Distribution sample sites must be current. The site locations should be reviewed and changed if the system changes.

If the system has grown, additional sites should be identified for the newly developed areas.

If the system has shrunk, sites should be reallocated to areas with a remaining population.

For example, if the population changes from 749 to 750, a PWS must go from collecting samples weekly to daily.

Number of sites

Table 10. Minimum required schedule and number of sites for distribution total chlorine residual compliance samples.

Population	Minimum Number of Disinfectant residual sites	Schedule
1-750	5	Weekly (every 7 days)
750 to 4, 900	5	Daily
4,901 to 50,000	Same # as coliform sites (6 to 30)	Daily
50,000 and greater	Half as many sites as samples. Example: A PWS collecting 60 samples must have 30 sites.	Daily

The number in the Table is only a minimum for coliform sites. Your mileage may vary. Every PWS is unique. If the number of sites is not adequate to represent the whole system, additional sites may be needed. If there are areas that you can demonstrate to be well-characterized by fewer sites, that may be acceptable to the TCEQ.

Locations of sites

Sites must be selected in a way that represents the whole distribution system—the 'service area' … wherever water is served.

Systems often use coliform sites for disinfection residual sites. This is acceptable, however, it is recommended that additional sites be identified, since disinfectant residual is a more useful process management tool than coliform compliance sampling.

Pressure planes

Enough sites must be selected to represent multiple pressure planes.

Water in pressure planes is hydraulically separate. Therefore, contamination in one pressure plane may be confined to that plane. If one of the pressure planes is not sampled—it could be contaminated without anyone knowing.

Critical control points

A critical control point is one that can be used effectively to respond to risk. For example, the entry point is a critical control point because samples taken there will immediately alert you to any chemical dosing problems.

It is recommended that critical control points be selected. In distribution, these may be at interconnections between major mains, storage facilities, pump stations, and interconnections with other PWSs.

Water age

Sites must represent the distribution system so they need to be located at places with average and high water-age.

Low water age

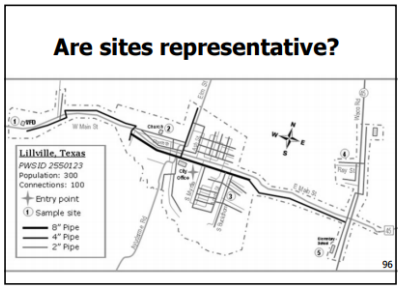
As long as we are sampling at entry points, low water age sites are the least important. Some sites can be at low water age, but not a preponderance. This is where the monochloramine is freshest, so the risk is lower. Higher risk sites are more useful.

Average water age

As a first estimate, average water-age can be estimated from historical data as locations with average total chlorine residual.

High water age

High water age sites are critical for disinfectant residual sampling. In that Appendix, it is recommended that all high water-age areas are fully represented in disinfectant residual sampling, and that combining it with flushing is a great way to save a trip.

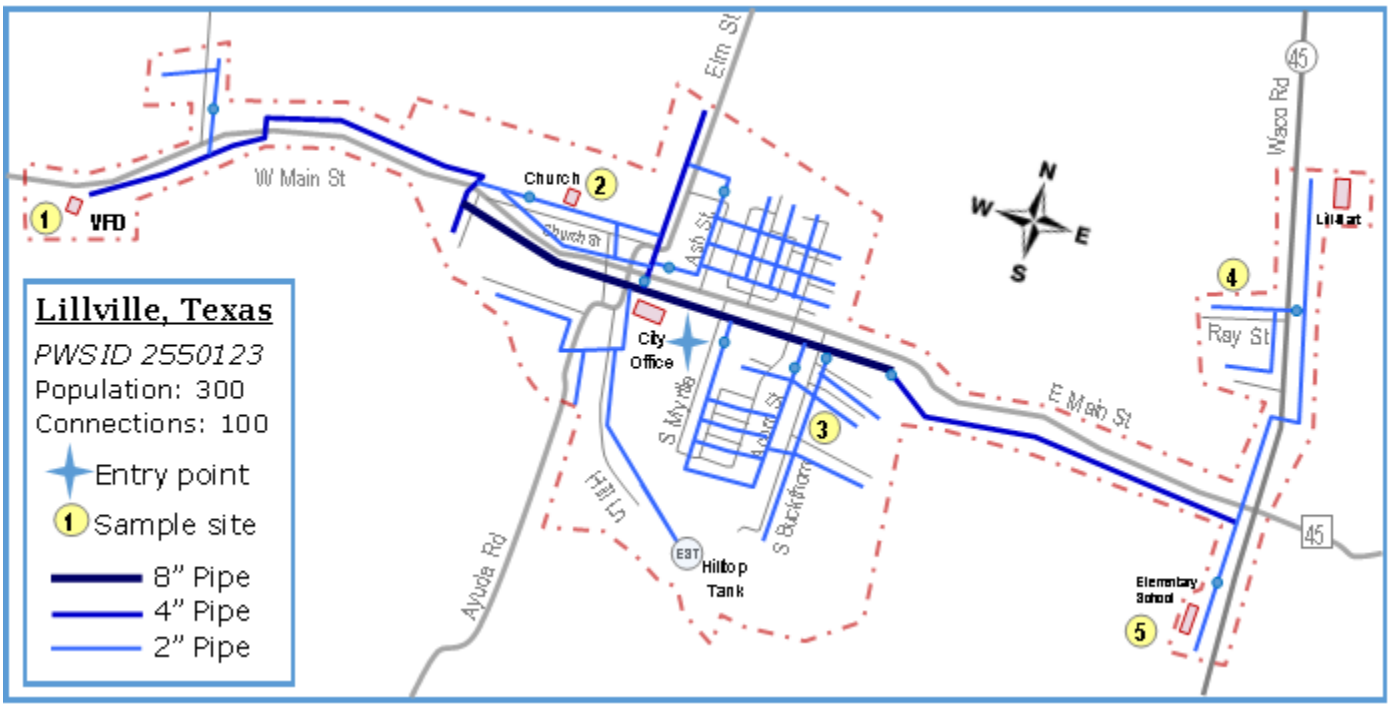


See Example, following:

Example: Setting sites for Lillville, Texas

A map of Lillville TX is shown below. Lillville's population is less than 750 people, and their number of connections is less than 250.

Therefore, they are required to have at least 5 total chlorine compliance sites that they rotate through for recording disinfectant residual for their DLQOR.



They want to use the same locations for both coliform and disinfectant residual because they plan to construct dedicated sampling stations in the future, when time permits.

Questions:

- Are all areas of the system represented with a sample site?
- Are critical control points represented?
- Do sites represent all high water-age areas?
- Are there areas that might have higher water-age because of hydraulic conditions, but are not dead ends?
- Is the map adequate?
  Can you figure out where everything is?
  Can you see improvements they could make to the locations?

Schedules

In this part of Chapter 3, we will talk about how frequently samples need to be collected.

Schedules

- Monochloramine and ammonia: Each weekly sampling event should represent the **entire** system.
  - A spread-out system will need more than one sample per week.
- Regulatory schedules are minimums.
  - Design schedules to fit your system.
    - Successful process management benefits the system.

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Just as we discussed in Part 1 of this chapter, we need to distinguish between sampling for compliance, versus sampling for process management.

The table that describes the MINIMUM required sampling is shown in Tables 11a and 11b. If your system is spread out, has multiple pressure planes, or has other complexity—you will need to take MORE than the minimum number of samples to be able to manage the system, and maintain stable chloramines.

The most common samples are total chlorine, monochloramine, and ammonia.

Minimum Sampling Requirements

Constituent	At the Treatment Plant	At the Entry Point	In the Distribution System
Total Chlorine	**Weekly** and prior to and after adjusting the chlorine or ammonia feed rate	**Weekly**	**Daily** or **Weekly** * Used to calculate compliance with min/max
Free Ammonia	**Weekly** and prior to and after adjusting the chlorine or ammonia feed rate	**Weekly**	**Weekly**
Mono-chloramine			

* Under 250 cnx/750 pop = Weekly, Over 250/750 = Daily

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Nitrate and nitrite routine sampling is less frequent.

Minimum Sampling Requirements

Chemical	At All Plants	At All Entry Points	In the Distribution System
Nitrite	Not required	Monthly for six months, *(to find NAP baselines)* then **Quarterly**	**Quarterly**, at representative sites, *(and also in response to NAP triggers)*
Nitrate			

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Compliance: Total chlorine compliance monitoring

The first kind of sampling we will talk about is:

- Total chlorine monitoring for compliance with maximum and minimum residual levels.

Note: Total chlorine compliance monitoring ONLY occurs in distribution—samples collected inside of a plant, are NOT compliance samples. Also, except under certain conditions (like surface water treatment plants) entry point samples are NOT considered for compliance (because entry points are not in distribution, they are before it).

The table below shows the table from the rules, with the non-compliance sampling highlighted in grey to emphasize that only the results from distribution system monitoring are used to determine compliance with total chlorine minimum and maximum levels [§290.110(c)(5)].

Table 11a. Total chlorine COMPLIANCE sample frequency and location

	At or after all Entry Point(s)	**In the distribution system —at representative sample sites**	**Before and after any chlorine or ammonia injection points, including booster plants**
Total Chlorine	At least weekly.	***Compliance monitoring:*** 1. Daily at large PWSs or Weekly at small PWSs. 2. Plus at the same time/place as coliform samples. [b]	At least weekly and before and after adjusting the chlorine or ammonia feed rate.

	At or after all Entry Point(s)	In the distribution system —at representative sample sites	Before and after any chlorine or ammonia injection points, including booster plants
Mono-chloramine	At least weekly.	At least weekly.[a]	
Free Ammonia	At least weekly.	At least weekly.	
Nitrite and Nitrate	AT LEAST monthly for the first six (6) months to set baselines, then at least quarterly.	In response to NAP action triggers to determine whether nitrification is happening; and at least quarterly	Routine sampling not required, but possibly needed as an action in response to NAP action triggers.

[a.] When collecting a routine sample such as a bacteriological or routine disinfectant residual sample.

[b.] Total chlorine must be collected weekly for systems serving fewer than 250 connections and fewer than 750 people, or weekly for systems serving at least 250 connections or at least 750 people, in accordance with §290.110.

Note: Additional sampling may be needed to follow up on results that are not as expected.

Sample sites and schedule for total chlorine compliance monitoring

The size cutoff for **weekly** versus **daily** total chlorine monitoring is 250 connections **or** 750 people. For example:

- A system with 249 connections and 751 people must monitor total chlorine **daily**.
- A system with 251 connections and 749 people must monitor total chlorine **daily**.
- A system with less than 250 connections **AND** less than 750 people can monitor total chlorine **weekly**.

Small *system (less than 250 connections* ***and*** *750 people)—****WEEKLY***

Total chlorine must be measured weekly at locations representing the entire system.

- Total chlorine result summary must be reported on the DLQOR or page 1 of the SWMOR (if the PWS has a SWTP).
- If 5% of total chlorine results are less than 0.5 mg/L, for two months in a row, that is a violation.
- If the monitoring is not done—that is a monitoring violation. If reporting is not done—that is a reporting violation.

Number of sites for WEEKLY compliance monitoring:

Each weekly sample event must represent the entire system. If there are two pressure planes, a weekly sample must be collected from each plane. If the system is very spread out, samples from areas that are far away from each other should be sampled each week.

In a larger system, rotating daily monitoring through the sites may provide enough data to manage the residual. In a smaller system, rotating through sites may not provide adequate data.

For example, if a PWS on weekly sampling has five (5) sites and rotates through them, it could be 5 weeks before an area is sampled. Five weeks is enough time for things to go very, very wrong.

Larger** system (more than 250 connections or 750 people)—**DAILY

Total chlorine must be measured daily at locations representing the entire system. Daily *includes* Saturday and Sunday.

- Total chlorine results must be reported on the DLQOR or page 1 of the SWMOR.
- If 5% of total chlorine results are less than 0.5 mg/L, for two months in a row, that is a violation.
- If the monitoring is not done—that is a monitoring violation; if reporting is not done, that is a violation.

Number of sites for DAILY compliance monitoring:

Each week samples must represent the entire system. If there are two pressure planes, samples must be collected from each plane at least once a week. If the system is very spread out, samples from areas that are far away from each other should be sampled at least once each week.

In a larger system, rotating through the sites may provide enough data to manage the residual.

Process management for chloramines: Monochloramine, ammonia, nitrite, and nitrate monitoring

To successfully manage chloramines, process management sampling is needed:

- **Monochloramine and free ammonia** monitoring are needed to determine the effectiveness of your chloramines, and
- **Nitrite and nitrate** monitoring are needed to identify the normal (baseline) conditions and then to provide clues to determine if nitrification is happening.
  (DAM 8 discusses how this information is part of the NAP.)

The results of this monitoring *don't* get sent to TCEQ monthly or quarterly. Instead, the results are reviewed by TCEQ investigators during periodic investigations.

Table 11b: Chloramine effectiveness process management sampling frequency and location

	At (or immediately after) all *Entry Point(s)*	**In the distribution system—*at representative sites***	**Before and after any chlorine or ammonia injection points, *including booster plants***
Total Chlorine	At least weekly.	***Compliance monitoring:*** *Daily at large PWSs* *Weekly at small PWSs.*[b]	At least weekly and before and after adjusting the chlorine or ammonia feed rate.
Mono-chloramine	At least weekly.	At least weekly. [a]	
Free Ammonia	At least weekly.	At least weekly.	
Nitrite and Nitrate	AT LEAST monthly for the first six (6) months to set baselines, then at least quarterly.	In response to NAP action triggers to determine whether nitrification is happening; and at least quarterly	Routine sampling not required, but possibly needed as an action in response to NAP action triggers.

[a.] When collecting a routine sample such as a bacteriological or routine disinfectant residual sample.

[b.] Total chlorine must be collected weekly for systems serving fewer than 250 connections and fewer than 750 people, or weekly for systems serving at least 250 connections or at least 750 people, in accordance with §290.110.

Note: Additional sampling may be needed to follow up on results that are not as expected.

Example schedule tables

In addition to the sites that we discussed in the previous section, we need to set schedules in the Monitoring Plan—specifically as part of the NAP (which is the section of your Monitoring Plan related to nitrification detection and control).

Therefore, the NAP will need both sites and schedules for samples. The following table applies for all distribution sampling.

Table 12. Requirements for (NAP) Sample Schedule Table

Site Code or Letter	Address of Routine Distribution Sample Site	Sample Schedule	Comments
Use a number or letter that corresponds to the dot showing the site on your Distribution System Map.	Provide a description of the site location. For example—a street address. For a sample station, flush valve, or other site, provide a dummy address or.	List the days or weeks that sampling should occur for each site or group of sites.	Make any notes relating to the sampling schedule or locations.

It is highly probable that you will want to combine your disinfectant residual and NAP sampling schedules. You may combine these with your coliform sampling schedule, if that works for you—usually this works for small systems.

You may have been told that you don't need to list any process management sampling in your Monitoring Plan. That is not true for the NAP part of the Monitoring Plan—you have to list the sites and schedules for chloramine-effectiveness and nitrification-detection process management sampling.

Exercises

- *Example for Daily Schedule, p _____*
- *Example for Weekly Schedule, p _____*

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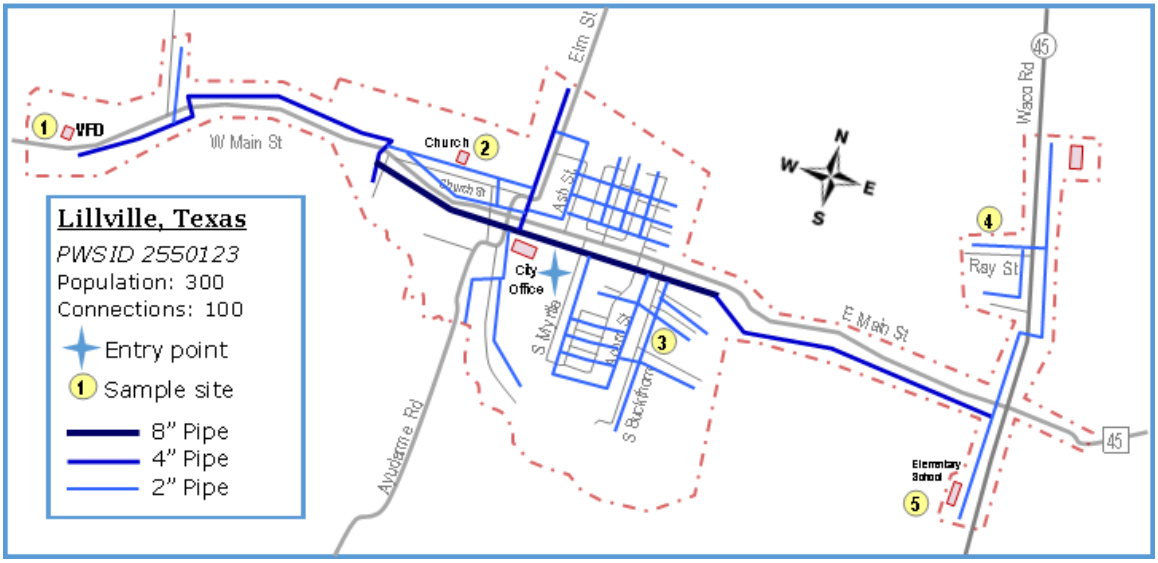
Example of schedule for small system: Lillville TX

For example, a map of Lillville TX is shown below (on the next page).

Lillville's population is 300 and number of connections is 100.

That is less than 750 people, *and* less than 250.

Therefore, they only are required to sample weekly (see tables above).



They are very proactive, so they would like to sample twice a week, but they have not been able to get another operator, so there just is not enough time.

Their schedule for Lillville's weekly sampling at their 5 distribution sites and their entry point is shown below:

Site #	**Address**	**Schedule**		
		Total chlorine	Monochloramine and Ammonia	Nitrite and nitrate
EP001	100 E Main St —City Hall	Daily	Every Monday, with the Total chlorine sample	Quarterly (check w TCEQ for timing)
SS 1	1202 W Main St —Volunteer Fire Dept	1st Monday of month	1st Monday of month	Quarterly (at the same time as EP sample)
SS 2	326 Church St —First Church	2nd Monday	2nd Monday	
SS 3	258 S Buckthorn St —Mayor's house	2nd Monday of month	2nd Monday of month	
SS 4	1626 Rey St —Operator's house	1st Monday of month	1st Monday of month	Quarterly (at the same time as EP sample)
SS 5	510 S Waco Rd —Elementary School	5th Monday (if one occurs)	5th Monday (if one occurs)	

This is a somewhat proactive sample schedule, because they take samples more than weekly.

However, there are still areas that may not be visited for long periods of time.

Can you identify any of those?

The same schedule information can be formatted differently.

	SS 1 VFD	SS 2 Church	SS 3 Mayor's	SS 4 Rey St	SS 5 School	EP001
Monday Week 1	**Total** Mono and ammonia					Take a Total residual daily* ALSO Take mono and ammonia every Monday*
Monday Week 2		**Total** Mono and ammonia*				
Monday Week 3			**Total** Mono and ammonia			
Monday Week 4				**Total** Mono and ammonia		
Monday Week 5 (if there is one)					**Total** Mono and ammonia	
Samples in **BOLD** are for compliance calculations						
*Process management sample—Total chlorine from the entry point is not used in compliance calculations for minimum or maximum distribution residuals						
Note: Nitrite and nitrate will be collected Quarterly by TCEQ's contractor. At that time, collect a nitrite/nitrate sample from SS2 and SS4 for analysis.						

Can you tell whether the two schedules are the same?

Which format would be better for your PWS?

Can you think of a format that works better for you?

Example: schedule for larger system sampling Daily

Here is an example of a NAP sample schedule for a PWS that serves more than 250 connections or more than 750 people.

In this example, the PWS takes two total chlorine samples for compliance every day, except on weekends. They do this because their system is spread out, and one sample would not represent the distribution system well enough.

Does their schedule meet the compliance requirements?

Example of Sample Schedule for a PWS Sampling Total Chlorine Daily

Site # on Map	Address	Type	Comment	Mon	Tues	Wed	Thurs	Fri	Sat	Sun
EP	281 Pump Station	HB	Source	T/M/A, *N/N*	T/M/A	T/M/A	T/M/A, *N/N*	T/M/A	T	T
1	55 E Railway St	HB	Average	T			T			
2	935 Pine St	HB	High	T			T			
3	200 W Lamar Blvd	HB	Low		T			T		
4	800 W Hwy 190	FV	Average		T			T		
5	700 Red River Rd	HB	High		T			T		
6	Hill Top Tank	HB	Storage	T/M/A, *N/N*	T	T	T/M/A, *N/N*	T		
7	10 W Main St	FH	High			T			T	
8	1164 E CR 400	HB	Average				T			T

T = Total chlorine from compliance sites must be reported on DLQOR or SWMOR.
Entry point samples are not included on the DLQOR or SWMOR.
Samples may be collected at other locations for process management.
Samples collected at locations OTHER than compliance sites do NOT need to be reported on the DLQOR or SWMOR

T/M/A = Total chlorine, monochloramine, and free available ammonia

N/N = Nitrite/nitrate

Is this schedule understandable?

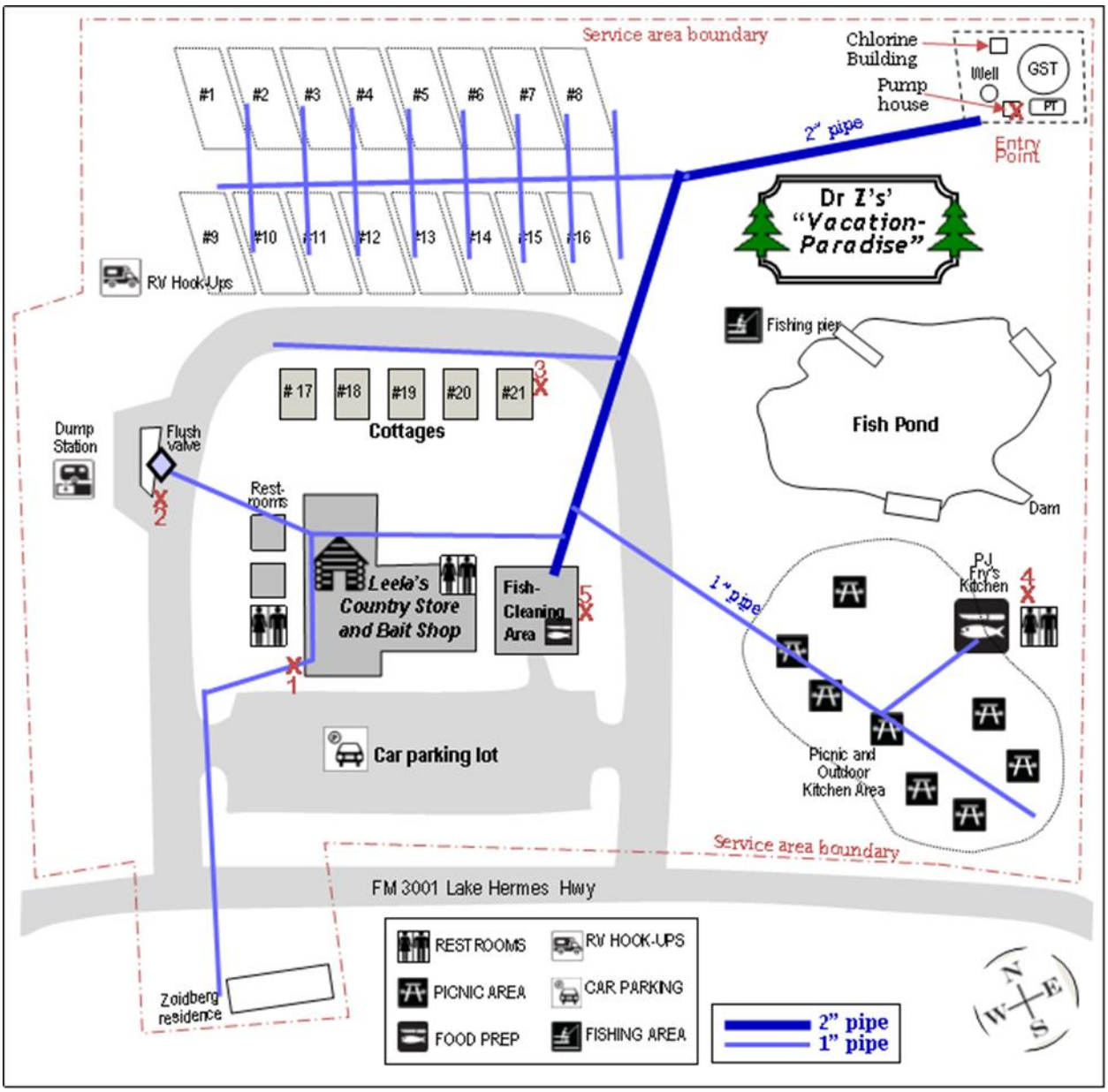
Does it matter what day the month starts on?

Would it be better to put the **Sites** across the top, and the **Day** down the side? What would that look like?

Example: Weekly Schedule for Dr Z's RV Park

Here is an example of a chloramine-effectiveness sample schedule for a small PWS.

Dr Z's RV Park has a restaurant, gift shop, convenience store, gas station, fish pond, five cottages, and 16 RV slots. Dr Z lives across the street. It has one-well and one-entry point. TCEQ's Drinking Water Watch web site lists their population as 25.



Dr Z's Vacation Paradise Map

On the map above, the five sample sites are marked with an X.

Can you find them?

Are the sites representative of the entire system?

If not, what sample sites could be changed to make them representative?

The sample schedule for this system is shown below.

Example: Dr. Z's Vacation Paradise Sample Schedule Table

Site Code	**Location** (coliform and total chlorine compliance sites)	**Type of sample site**	**Total, Monochloramine, and Ammonia**
EP001	Well after chlorine and ammonia injectors	Tap at plant	Every Friday
1	SW corner of stor	Hose bibb	First Friday in month
2	Dump station Flush	Hose for rinsing after dumping.	Second Friday in month
3	Cottage #2	Hose bibb	Third Friday in month
4	Restaurant	Ladies room sink	Fourth Friday in month
5	Fish-cleaning station	Sink tap	Fifth Friday in month

Does this schedule meet the rule requirements for frequency?

They are currently monitoring for total chlorine, monochloramine, and free ammonia every time they sample. Is this required?

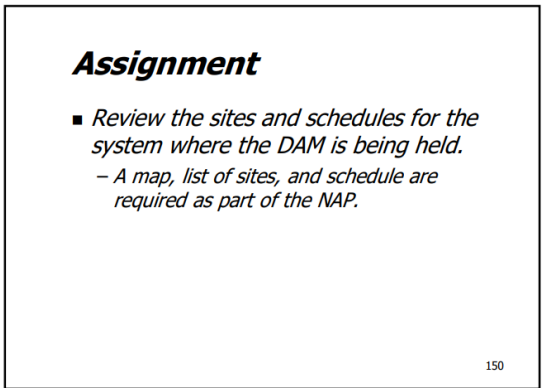
Are there any other issues with these sites?

Routes

Practically speaking, but outside the scope of this training, is the need to schedule sampling routes. There is a natural desire to group sites in one area together, but that does not meet the intent to know what is happening all over the system. Design routes as efficiently as possible, but also make sure that sampling represents the whole system.

Assignment: Review the systems sites and schedules

Every PWS that uses monochloramine for distribution system disinfection is required to have a map, a list of sample sites, and a schedule as part of their NAP.



If this DAM is being performed at a PWS, take out the system's NAP now.

Questions to consider in reviewing the system's NAP:

MAP:

Is the map easy to read?

- You should be able to show the map to a TCEQ investigator and have them understand it, even if they are unfamiliar with the system.

Does the map include the entire service area?

- Sometimes there are areas outside the city, district, or utility limits that get water service. These should be included.

Does the map

Are the sites shown clearly on the map?

Chapter 3 Review Questions

(Questions may have MULTIPLE correct answers.)

<u>The target for total chlorine should be:</u>

1. Equal to 0.5 mg/L at the entry point.
2. Whatever the wholesaler's source water has.
3. High enough to achieve exactly 0.5 mg/L at the far reaches of the system.
4. Have a safety factor so the residual is higher than 0.5 mg at the far reaches

<u>A purchased water system must perform chloramine-effectiveness sampling:</u>

1. At only one location in the distribution system
2. In the seller's source water
3. At the entry point to their distribution system
4. At critical control points
5. At locations representative of their distribution system

<u>Sample sites must be:</u>

1. Representative of bulk water from the main
2. At active service connections
3. At dedicated sample stations
4. Capable of producing a pencil-thin stream of water

<u>Which statements are true:</u>

1. Results of monitoring at process management sites must be reported to TCEQ.
2. Results of compliance monitoring must be reported to EPA
3. Compliance r esults must be documented on the DLQOR or SWMOR

<u>A system should schedule sampling:</u>

1. Taking into account the efficiency of travel routes
2. So that no potential trouble spots have too long a time between samples
3. At the locations that the TCEQ directs them to sample on the chloramine approval letter

Chapter 3 Checklist

Hopefully, after this chapter, you have a completed map and schedule that meets the sampling requirements.

Chapter 3

Part 1. Concept of compliance vs process management

- Do you understand the purpose of samples, based on how you document them?
- Do you understand that you can do additional samples to manage your system without reporting the levels, if the samples are not defined as compliance?

Part 2: Desired and required disinfectant residuals —including 'safety factors'

- Do you know required the minimum and maximum levels for total chlorine compliance?
- Do you know what your process management goals for monochloramine and free ammonia are?

Part 3. Sample sites and schedules

- Do your sites adequately represent the system? Are there any areas that are missing sites?
- Are all valves in the system set correctly? Do you know? Are closed valves in the system causing localized high water-age?
- Is your sample schedule table complete?
- Have you scheduled daily or weekly total chlorine compliance monitoring for reporting on the DLQOR or SWMOR?
- Have you scheduled at least weekly monochloramine and free available ammonia monitoring for process management?
- Does your process management schedule include sites representative of the distribution system—especially risky sites?

Follow up:

If you have a good map that regulators can understand, have schedules for compliance and process management, and know what levels you need to achieve, you are in very good shape to hold stable monochloramine residuals. If you DON'T blend in distribution, pat yourself on the back—that is a difficult situation.

Recommended actions?

If you are missing a map, sites, or schedules, make a plan for how you are going to address that and note it on your Plan of Action.

If you blend chlorinated and chloraminated water in distribution—make sure that you are doing it in a manner specifically approved in writing by TCEQ.

Chapter 4.
Dosing, mixing, and blending

In Chapter 1, we introduced the concept of the chlorine-to-nitrogen ratio. We calculated both the ideal chlorine-to-ammonia and ideal chlorine-to-nitrogen ratio. This section talks about how to control that ratio when dosing, and the related topics of mixing and blending.

Scope

This section builds on the previous chapters and presents ways to use molecular weights and conversion factors to be able to successfully dose chlorine and ammonia to form chloramines.

Part 1. Dosing calculations

We will look at examples using both the chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio, and also the chlorine-to-nitrogen (Cl_2:NH_3) ratio. This will help us be careful about which one we use for dosing calculations.

Part 2. Mixing

Also, this chapter discusses the importance of mixing when injecting chemicals. It On the one hand, good mixing can keep your chloramines stable; on the other hand, incomplete mixing can cause real problems from unknown, unseen ratios inside pipes or tanks.

Part 3. Blending

Finally, when water with chloramines and free chlorine is put in distribution it is called 'blending' and we will talk about the concerns related to blending in this Chapter.

Chapter 4 Scope

- **Part 1.** Practice the chemical feed math for chloramine dosing calculations;
- **Part 2.** Discuss how mixing impacts the stability of monochloramine.
- **Part 3.** Talk about blending chlorinated and chloraminated water in distribution, and the difficulties that can cause.

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Materials

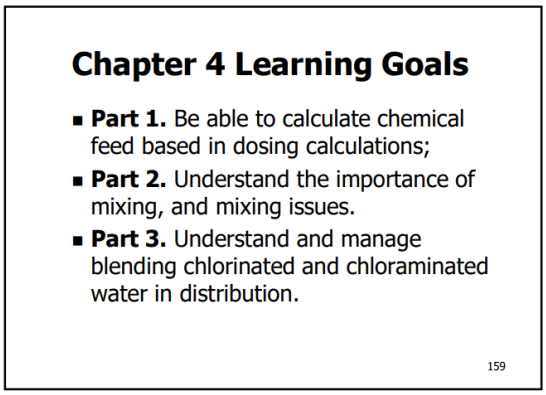
For this section, we will look at:

- The Student Guide,
- The system details—plant schematic, current feed rates, flow rates,
- Records of chemical types and concentration, feed rates, results.

Learning goals

The learning goals for this workshop are:

- **Part 1.** Be able to calculate how much chemical to feed based on the weight of chemical and water flow rate; and be able to use either the chlorine-to-ammonia-nitrogen (Cl2:NH3-N) ratio, and also the chlorine-to-nitrogen (Cl2:NH3) ratio in dosing calculations;
- **Part 2.** Understand the importance of mixing, and be able to troubleshoot existing mixing issues.
- **Part 3.** Be able to determine if your system blends chlorinated and chloraminated water in distribution and prepare to manage that concern.



Part 1: Feed-rate calculations using weight-based units

The molecular ratios of the different molecules or ions involved in the chloramination process are important, as shown in Chapter 1. However, we measure chemical feed rate mass—not molecules. For example, we use units of pounds per day (ppd) and chemical concentration in units of mg/L rather than in units of molecules/L (or more accurately moles/L).

Therefore, we have to convert molecules (moles) to a weight-based system of measurement in order to calculate dosage and feed rate. This conversion is accomplished using atomic and molecular weight.

For example, Table 13 shows the atomic or molecular weights of the chemicals that we are most concerned about during chloramination.

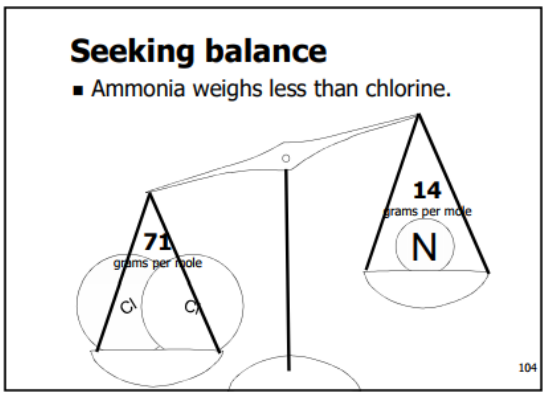
Table 13. Atomic and molecular weights of chloramination chemicals

Atom *	Atomic weight (grams per mole)	Molecule *	Molecular weight (grams per mole)
Chlorine (Cl)	35.45	Chlorine gas (Cl2)	71
Nitrogen (N)	14	Nitrogen gas (N2)	28
Hydrogen (H)	1	Ammonia (NH3)	17
Oxygen (O)	14	Ammonium (NH4)	18
Carbon (C)	12	Monochloramine (NH2Cl)	51
		Dichloramine (NHCl2)	85
		Trichloramine (NCl3)	119

* Molecules are groups of atoms, atoms are the smallest single particle of an elemental substance.

This table shows us that 71 lbs of chlorine gas (Cl2) contains the same number of molecules as 17 lbs of ammonia, 51 lbs of monochloramine, 12 lbs of carbon, etc.

As the equations in Figures 1 and 2 indicate, one molecule of chlorine will produce the one chlorine atom needed to react with one ammonia molecule to form one monochloramine molecule. The equations also show that each molecule of ammonia contains one nitrogen atom.



Therefore, when forming monochloramine, the ratio between the number of chlorine molecules and the number of ammonia molecules (1:1) is the same as it is for chlorine and nitrogen (also one chlorine molecule for every nitrogen atom).

However, ammonia has three hydrogen atoms attached to its nitrogen atom so it weighs more than nitrogen alone. Since the weight-based ratio depends on the weight of each molecule, the weight-based chlorine-to-ammonia (Cl_2:NH_3) ratio will be different than the weight-based chlorine-to-nitrogen (Cl_2:NH_3-N) ratio.

One way to visualize the mass ratio is as a see-saw, or teeter-totter. Only one person can be on each side—and if they are different weights, the see-saw will tilt toward the heavier person (Figures 19a and 19b).

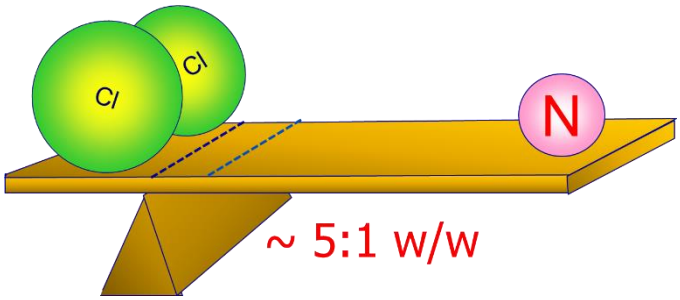


Figure 19a. Balance of optimum chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio.

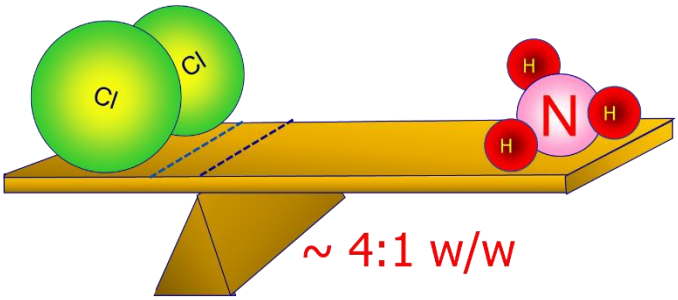


Figure 19b. Balance of optimum chlorine-to-ammonia (Cl_2:NH_3) ratio

In the case of the chlorine to nitrogen ratio (Cl_2:NH_3-N), a 1:1 molecular ratio results in a 5.06:1 weight-to-weight ratio between chlorine and ammonia-nitrogen as indicated in Equation 1.

Equation 1. Chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) weight ratio

slide

$$\frac{1\ \cancel{mol\ Cl_2}}{1\ \cancel{mol\ NH_3}} \cdot \frac{1\ \cancel{mol\ NH_3}}{1\ \cancel{mol\ N}} \cdot \frac{71\ lb\ Cl_2}{1\ \cancel{mol\ Cl_2}} \cdot \frac{1\ \cancel{mol\ N}}{14\ lb\ N} = \frac{71\ lb\ Cl_2}{14\ lb\ N} = \frac{5.06\ lb\ Cl_2}{1\ lb\ N}$$

In the case of the chlorine-to-ammonia ratio (Cl_2:NH_3), a one-to-one molecular ratio results in a 4.2:1 weight-to-weight ratio between chlorine and ammonia as indicated in Equation 2.

Equation 2. Chlorine-to-ammonia (Cl_2:NH_3) weight ratio

$$\frac{1\ \cancel{mol\ Cl_2}}{1\ \cancel{mol\ NH_3}} \cdot \frac{71\ lb\ Cl_2}{1\ \cancel{mol\ Cl_2}} \cdot \frac{1\ \cancel{mol\ NH_3}}{17\ lb\ NH_3} = \frac{71\ lb\ Cl_2}{17\ lb\ NH_3} = \frac{4.2\ lb\ Cl_2}{1\ lb\ NH_3}$$

(Note: in Equations 1 and 2, lb-moles instead of gr-moles are used. It does not matter as long as you are consistent and use the same units in the same equation.)

Watch the ratio!

Operating at the wrong ratio could result in unstable chloramines.

Be careful about whether you are calculating using the:

chlorine-to-ammonia-*nitrogen* (Cl_2:NH_3-*N*) or

chlorine-to-ammonia ratio (Cl_2:NH_3)!

For example, Table 8 shows how the numbers for the ratio are different if you use the ratio with *ammonia* (Cl2:NH3) versus the ratio with *nitrogen* (Cl2:NH3-N). The industry standard is to use the ratio with nitrogen.

Chlorine dose and feed rate examples

Chlorine is available in a variety of forms and concentrations.

For example, chlorine gas contains 100% available chlorine, calcium hypochlorite is a solid form that generally contains 60-75% available chlorine, and sodium hypochlorite (bleach) is a liquid that usually contains 5-12% available chlorine.

Consequently, the feed rate and dosage calculations must address both the weight of the material being applied and its concentration.

Examples of chlorine feed (Examples 4.1, 4.2, 4.3)

These following examples show that:

1) We need to base our chemical feed rate on the pounds of reactant that we want to add . . .
   even if we need to figure out how many gallons of solution we need to add.
2) To get the amount of reactant we want, we need different amounts of chemical
3) Our chemical feed rate depends on the concentration of the reactant in the chemical we're feeding and (in the case of liquid chemicals) the weight or specific gravity of the solution.

Example 4.1: Feeding 10 pounds per day of gas chlorine (Cl_2)

Let's compare the chemical feed rates for a plant that wants to feed chlorine at a rate of 10 lbs per day.

Gas Chlorine Data:

Gas chlorine contains 100% available chlorine

Calculation:

Rotameter setting = 10 ppd (pounds per day)

. . . that was easy.

The gas chlorine example is easy because you directly measure the pounds of chlorine used on a scale every day. Gas chlorine is ALL chlorine—but it gets a little more complicated when you feed a liquid solution, like shown in Examples 2 and 3.

Many PWSs feed liquid solutions like calcium hypochlorite or sodium hypochlorite in order to avoid the risks and reporting related to using gas chlorine.

Example 4.2:
Calcium Hypochlorite Dosage:

When dosing liquid calcium hypochlorite solution, it is more difficult because the solution is NOT 100% chlorine.

In this example, our calcium hypochlorite contains 65% available chlorine

We will create our feedstock by adding 10 lbs of calcium hypochlorite to 10 gallons of water.

Calculation:

1 lb $Ca(OCl)_2$ X 65% available chlorine = 0.65 lbs of chlorine per lb of Ca(OCl)2

$$\frac{10\ \cancel{\text{lb Cl}}}{\text{day}} \times \frac{\text{lb Ca(OCl)}_2}{0.65\ \cancel{\text{lb Cl}}} = 15.4 \text{ pounds of calcium hypochlorite per day}$$

$$\frac{15.4\ \cancel{\text{lb Ca(OCl)}_2}}{\text{day}} \times \frac{10 \text{ gal of solution}}{10\ \cancel{\text{lb Ca(OCl)}_2}} = 15.4 \text{ gallons of solution per day}$$

Instead of calcium hypochlorite, a system may wish to feed sodium hypochlorite. That is shown in Example 4.3.

Example 4.3:
Sodium Hypochlorite Dosage

When dosing liquid sodium hypochlorite solution, it is more difficult because the solution is NOT 100% chlorine.

Data:

Our sodium hypochlorite bleach contains 10% available chlorine

Our bleach has a specific gravity of 1.28

Each gallon of water weighs 8.34 lbs

Calculation:

1 lb bleach X 10% available chlorine = 0.10 lbs of chlorine per lb of bleach

$$\frac{10\ \cancel{\text{lb Cl}_2}}{\text{day}} \text{ X } \frac{\text{lb bleach}}{0.1\ \cancel{\text{lb Cl}_2}} = 100 \text{ pounds of bleach per day}$$

1 gallon bleach = 1.28 X 8.34 = 10.68 lbs of bleach per gallon of bleach

$$\frac{100\ \cancel{\text{lbs of bleach}}}{\text{day}} \text{ X } \frac{\text{gal of bleach}}{10.68\ \cancel{\text{lbs of bleach}}} = 9.4 \text{ gal of bleach per day}$$

In those examples we needed 10 ppd of chlorine gas, 15.4 ppd of calcium hypochlorite, or 100 ppd of sodium hypochlorite bleach to get 10 ppd of chlorine reactant depending on the type of chemical fed.

Example 2 showed how to calculate dosage for feeding calcium hypochlorite. Example 3 shows the same calculations, but for sodium hypochlorite. Since sodium is a different molecular weight, and since the solution may be a different strength, you can't use one set of equations for the other chemical.

Ammonia dose and feed rate

Ammonia, like chlorine, is available in many forms and concentrations. Consequently, the ammonia feed rate and dosage calculations must also address both the weight of the material being applied and its concentration.

However, dealing with ammonia calculations is even more complex than dealing with chlorine calculations. To understand why, we need to be aware of several issues.

Ammonia compound type

Different compounds contain different amounts of ammonia (and, therefore, different amounts of nitrogen). Consequently, the feed rate dosage calculations will differ depending on the type of chemical used and the number of ammonia (or nitrogen) atoms it contains.

Table 14. Percent available ammonia and nitrogen from common sources

Compound	Molecular Formula	Molecular Weight	% Available Ammonia as NH_3 (1)	% Available Ammonia as N (2)
Ammonia (gas)	NH_3	17	100 %	82.4 %
Ammonia hydroxide (dry)	NH_4OH	35	48.6 %	40.0 %
Ammonia sulfate (dry)	$(NH_4)_2SO_4$	132	25.8 %	21.2 %

(1) These values are obtained by dividing the weight of NH3 (which is 17) by the molecular weight of the compound we are feeding and then multiplying that result by the number of ammonia molecules the compound contains.

(2) These values are obtained by dividing the weight of N (which is 14) by the molecular weight of the compound we are feeding and then multiplying that result by the number of nitrogen atoms the compound contains.

Anhydrous ammonia (like anhydrous chlorine) is a pure liquid that is stored in a sealed cylinder and then vaporized and fed as a gas. Other liquid ammonia compounds are more like chlorine bleach; the calculations must address the density (weight) of the solution being applied, the concentration of the solution, and the ammonia content of the compound it contains.

However, liquid ammonium sulfate (LAS) and liquid ammonium hydroxide (LAH) differ from liquid bleach in one important respect. Bleach vendors almost always express their concentration in terms of "% available chlorine on a w/w (weight to weight) basis".

LAS and LAH vendors, on the other hand, often describe their products based on the amount of dry chemical present in the solution. While one pound of a 10% bleach almost always contains about 0.10 pounds of available chlorine, a pound of 25% LAS could contain 0.25 pounds of dry ammonium sulfate, 0.25 pounds of available ammonia, or 0.25 pounds of available nitrogen.

It is extremely important to know how our vendor specs their product!

An LAS solution that contains "25% ammonium sulfate on a w/w basis" only contains 6.45% available ammonia and 5.3% available nitrogen. (If the solution

contains 25% AS and AS is only 25.8% NH3, then the percent available ammonia (as NH3) is equal to 25.8% of 25%, or 6.45%).

Examples for ammonia feed

Let's compare the chemical feed rates for a plant that wants to feed ammonia (as NH3) at a rate of 2 lbs per day.

Example 4.4a
–Feeding anhydrous ammonia

A plant wants to feed ammonia (as NH_3) at a rate of 2 lbs per day.

Anhydrous Ammonia Data:

Anhydrous ammonia contains 100% available ammonia

Calculation:

Rotameter setting = 2 ppd NH_3 (as NH_3) . . . that was easy.

Example 4.4b
–Feeding anhydrous ammonia as Nitrogen

A plant wants to feed ammonia (**as N**) at a rate of 2 lbs per day.

Anhydrous Ammonia Data:

Anhydrous ammonia contains 100% available ammonia as NH_3

Amount of ammonia that is nitrogen:

Based on the molecular formula, there is one N atom in every NH_3.

The mass of N in NH_3 is the ratio of molecular weight.

N weighs 14 grams per mole.

NH_3 weighs 14 + 1+ 1+ 1 = 17

The fraction of nitrogen in ammonia = N/NH_3 = 14/17 = **0.82, or 82%**

Calculation:

We want to feed 2 lbs of N a day—not 2 lbs of NH_3…
but the rotameter reads in lbs NH_3/day!

We will need to INCREASE the rotameter setting
over 2 lbs/day ammonia to get 2 lbs /day of nitrogen!

$$\frac{2\ \cancel{\text{lbs N}}\ \text{(desired)}}{\text{day}} \times \frac{\text{lb NH}_3}{0.82\ \cancel{\text{lb N}}} = \frac{_\ _\ _\ \text{lb NH}_3}{\text{day}}$$

Just like with feeding chlorine, the calculations for feeding the pure chemical are the easiest. However, most people feed a liquid solution because of safety and other concerns.

Example 4.4c
. Liquid Ammonium Sulfate (LAS) as ammonia

Conditions:

Our LAS contains 38% ammonium sulfate on a weight/weight basis.

Based on the molecular formulas of the two compounds,
132 pounds of ammonium sulfate $(NH_4)_2SO_4$ contains
34 pounds of ammonia (as NH_3)

Our LAS has a specific gravity of 1.23.
Each gallon of water weighs 8.34 lbs.

Calculation:

$$\frac{2\ \cancel{\text{lb NH}_3}}{\text{day}} \times \frac{132\ \text{lb (NH}_4)_2\text{SO}_4}{34\ \cancel{\text{lb NH}_3}} = 7.76\ \text{lbs ammonium sulfate per day}$$

1 lb LAS X 38% ammonium sulfate = 0.38 lbs of pure AS per lb of LAS

$$\frac{7.76\ \cancel{\text{lb (NH}_4)\text{SO}_4}}{\text{day}} \times \frac{\text{lb LAS}}{0.38\ \cancel{\text{lb (NH}_4)\text{SO}_4}} = 20.4\ \text{lbs LAS per day}$$

1 gallon LAS = 1.23 X 8.34 = 10.26 lbs of LAS per gallon of LAS

$$\frac{20.4\ \cancel{\text{lbs of LAS}}}{\text{day}} \times \frac{\text{gal of LAS}}{10.26\ \cancel{\text{lbs of LAS}}} = 2.0\ \text{gal of LAS per day}$$

(Notice that "gpd of LAS" equals "ppd of ammonia (as NH3)" if you are feeding this chemical.)

Example 4.4d.
Feeding LAS as nitrogen

Conditions:

How would this calculation change if you needed to base the calculations on nitrogen dose—with the same LAS and desired dose?

You can use the same set of equations as above,
but use the weight of N, not NH_3, in the beginning:
132 pounds of ammonium sulfate $(NH_4)_2SO_4$,
contains 2 Ns at a weight of 14 each → 28 pounds of ammonia (as NH_3)

Calculation:

$$\frac{2\ \cancel{\text{lbs N}}\ \text{(desired)}}{\text{day}} \times \frac{132\ \text{lb}\ (NH_4)_2SO_4}{28\ \cancel{\text{lb N}}} = \frac{4.7\ \text{lb ammonium sulfate}}{\text{day}}$$

After that, you just follow the equations in example 4a.

1 lb LAS X 38% ammonium sulfate = 0.38 lbs ammonium sulfate per lb LAS

$$\frac{4.7\ \cancel{\text{lbs ammonium sulfate}}}{\text{day}} \times \frac{\text{lbs LAS}}{0.38\ \cancel{\text{lb ammonium sulfate}}} = \frac{12.4\ \text{lb LAS}}{\text{day}}$$

Our LAS specific gravity is 1.23 and a gallon of water weighs 8.34 lbs, so:

1 gallon LAS = 1.23 X 8.34 = 10.26 lbs of LAS per gallon LAS

$$\frac{12.4\ \cancel{\text{lbs LAS}}}{\text{day}} \times \frac{\text{gallons LAS}}{10.26\ \cancel{\text{lbs LAS}}} = \frac{1.2\ \text{gallons LAS}}{\text{day}}$$

The answer is 1.2 gallons per day of LAS.

Another way to feed ammonia is with a dry powder. No PWSs in Texas use that method, so we will skip it.

Always remember that when we are feeding liquid chemicals, our reactant dose depends on the concentration of the reactant in our liquid and the weight (or specific gravity) of the liquid. Since the specific gravity of liquid chemicals can vary slightly, we need to be able to measure the specific gravity of each batch of chemical when it is delivered. The hydrometer is a simple, inexpensive

instrument used to measure the specific gravity of a solution. Every plant that feeds liquid chemicals should have a hydrometer so the plant staff can measure the specific gravity

Dosing desk-top exercises

Three extra questions are provided on the following pages. You can work through these following the process above in order to strengthen your knowledge.

Exercise 4.5: Dosing—Bringing it all together

Let's use the information from the previous examples to demonstrate the difference between the applied chemical dose, the applied reactant dose, and the effective reactant dose.

Conditions:

Let's assume that our (water) flow rate is 166 gpm (which is about 240,000 gpd, or 2.00 million *pounds of water per day* (ppd)).

Calculation for ppd

Let's also assume that our raw water has a 2.0 mg/L chlorine demand which means that the chlorine residual that we measure at our ammonia application point is 2.0 mg/L less than the chlorine dose that we applied.

Exercise 4 Table: Data for three exercises

Data for exercise:	**Gas Cl_2**	**Calcium Hypochlorite**	**Sodium Hypochlorite Bleach**
Chemical Feed Rate (ppd) (from the example)	**10**	**15.4**	**100**
Water Flow Rate (Million ppd)	2.00	2.00	2.00
Applied Chemical Dose (ppm as Cl_2)	**5.0**	**7.7**	**50**
Reactant Feed Rate (ppd of Cl_2)	10	10	10
Applied Reactant Dose (ppm of Cl_2)	5.0	5.0	5.0
Chlorine Demand (mg/L of Cl_2)	2.0	2.0	2.0
Effective Reactant Dose (ppm of Cl_2)	3.0	3.0	3.0

Question

What doses should we apply?

Exercise 4.6

Conditions:

A system that normally uses chloramines is doing a free chlorine burn.
They have gas chlorine. The flow rate of the plant is 1 million gallons per day (MGD).
The residual they want to dose during the burn is 3 mg/L of free chlorine.
The raw water has a demand of 1 mg/L.

Question

How many pounds per day of chlorine will they need to feed?

Extra Dosing Exercise 4.7

Conditions:

A booster plant is located in distribution. It is able to feed

The water coming in has 0.5 mg/L total chlorine, 0.5 mg/L monochloramine, and 0.4 mg/L free ammonia.

The operator wants the total chlorine residual leaving the booster plant to be 2.0 mg/L.

How much chlorine and ammonia should be fed?

Question

Part 2. Mixing after dosing

The bulk calculations we did in Part 1 are important—but when we actually mix the chemicals into water, they may not react completely, which can cause issues.

Part 2.
Order of addition, mixing

- Order of addition:
  - At source:
    - Add chlorine first for dosing **raw water**
      - NOTE: SWTP can get exception to add ammonia first–with additional viral log inactivation.
    - Make sure that your source has no free ammonia.
  - Booster (in distribution):
    - Add **ammonia** first to water with **chloramines.**
    - Add **chlorine** first to water with **free chlorine.**

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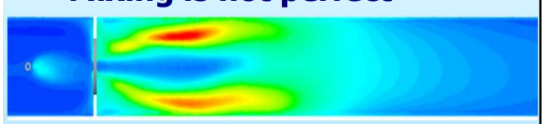
For example, higher dichloramine formation rates can occur if chlorine is applied just upstream of the ammonia. The chlorine solution that we inject into the water is often highly concentrated (4,000 mg/L or more). Unless we are using a buffered bleach, the chlorine solution usually has a very low pH because it contains a mixture of hydrochloric and hypochlorous acids, especially if we are using gas chlorine.

Mixing is not perfect



- Areas of different concentration can be present—resulting in unstable chloramine residuals

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At the application point, the chlorine solution can consume all of the alkalinity in the water and it may take a few seconds for the chlorine solution to disperse enough to allow the alkalinity in the rest of the water to react and restore a more neutral pH. This situation probably occurs in most natural waters, but especially in low alkalinity water.

These phenomena are why there are guidelines for mixing. In this part of this chapter, we will talk about:

- Mixing—how getting the chemicals mixed in well is accomplished to achieve stable monochloramine, and
- Reaction times, applied dose, and effective dose—why mixing is important.

Ideal mixing practice to achieve stability

The first consideration when injecting chemicals is which one goes in first.

Tips: When dosing to form monochloramine…

- The target CHLORINE feed should equal the desired MONOCHLORAMINE concentration.
  - Except for 'non-ammonia demand'
- If AMMONIA is present, you can add CHLORINE to 'tie it up' to get MONOCHLORAMINE.

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For source water, it is required that chlorine be added first. This is required in order to achieve some viral kill (inactivation) with free chlorine before the ammonia is added.

For boosting the monochloramine level is water that already has ammonia in it, you can add ammonia first. However, if you are transforming water with free chlorine into chloraminated water, you will want to add chlorine first (up to your desired total chlorine level) then add ammonia.

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Order of addition, mixing

- Order of addition:
  - At source:
    - Add chlorine first for dosing **raw water**
      - NOTE: SWTP can get exception to add ammonia first– with additional viral log inactivation.
    - Make sure that your source has no free ammonia.
  - Booster (in distribution):
    - Add **ammonia** first to water with **chloramines.**
    - Add **chlorine** first to water with **free chlorine.**

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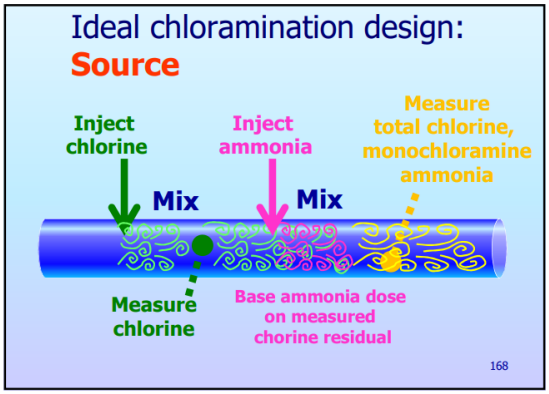
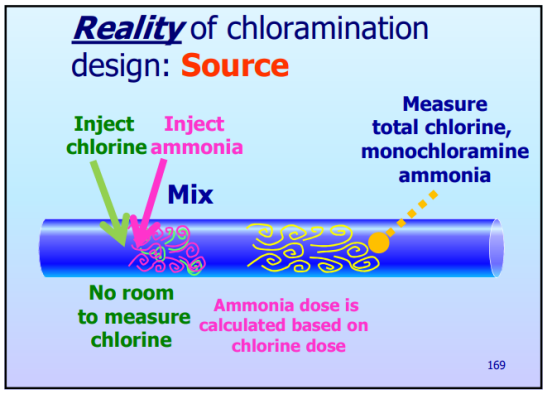
Some PWSs have received TCEQ approval (in writing) to add ammonia first because of their special needs—for example, if their source water has free ammonia in it already. If that is the case at your system, consult with TCEQ and/or request additional assistance.

Inside the pipe, you can't see what is going on. Mixing is never perfect—there are always some areas with stronger concentrations. If mixing is poor, the water may have unstable areas where dichloramine and trichloramine are formed. In that case, you will see a loss of total chlorine and monochloramine levels across the mixing zone.

In an ideal setting, you would always have a mixing zone and monitoring point after every point where chemical is injected.





Mixing when dosing source water

For example, in source water you would ideally add chlorine first—then measure it to see how much of the free chlorine has been lost to oxidation with iron, sulfur, etc. That way, you would know exactly how much ammonia to add to 'tie up' the chlorine.

Then, knowing the exact free chlorine residual, we would add ammonia. Then, after the ammonia had a chance to mix in, we would measure all of the process-management parameters (total chlorine, monochloramine, and ammonia).

In the real world, chlorine and ammonia are often injected closer together—with no room for a monitoring point in between. (For plants designed before 1/1/16, this is grandfathered in.)

This is not the best, because it is harder to figure out what might be causing instability. Without the ability to actually measure how much free chlorine is lost to permanent demand, we can't tell if low residuals after treatment are caused by permanent demand or by unstable areas of dichloramine and trichloramine in the contact zone between free chlorine and ammonia.

When ammonia and chlorine are added at close points, the amount are calculated theoretically (or guessed) and the way we determine whether they are okay is by the downstream monitoring for total chlorine, monochloramine, and free ammonia. The most common thing that happens in this situation is that the ammonia is too high.

When ammonia is high, it can cause nitrification—a problem covered by **"DAM 8: DEVELOPING A NITRIFICATION ACTION PLAN (NAP) FOR A PUBLIC WATER SYSTEM (PWS)".**

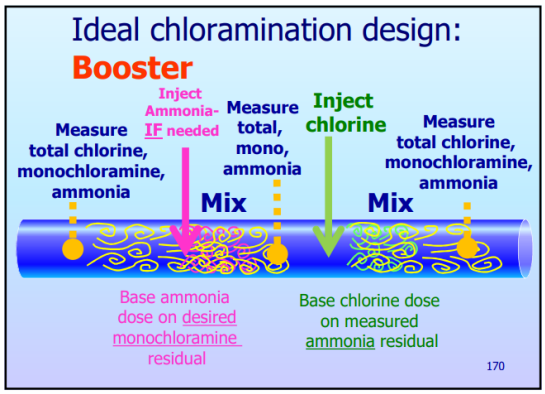
When dosing source water like this, the process management sampling downstream of the mixing point—for example, at the entry point—becomes extremely important. That is the only data that will tell you how to change doses to get stable monochloramine and an acceptable amount of free ammonia (0.05 to 0.1 mg/L).

'Boosting' chloraminated water

Things are different when you are treating treated water—boosting, as it is called.

When we are trying to increase monochloramine in distribution—or treating water purchased water from a wholesaler—there is already some free ammonia present. It would be silly (and cost more) to add too much additional ammonia.

In this case, it is really necessary to measure the ammonia that is already in the water to be boosted. Then, ammonia should be added to bring the level up to what you need to get the total chlorine level you want. Otherwise you are wasting money on ammonia and risking nitrification.



After adding the ammonia (IF needed) we will know exactly how much chlorine is needed. Then, downstream of the chemical injection points, monitoring the process management parameters (total chlorine, monochloramine, and free ammonia) will tell us whether we have been successful in creating stable monochloramine and not too much ammonia.

At least…

- Monitor before and after dosing
  - It's not just a good idea, it's the rule!

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Applied dose and effective dose

What you WANT is called the 'applied dose.' What you actually GET because of losses is called the 'effective dose.' That is discussed in the next part of this chapter.

Competing chemical reactions can consume some of the reactants that we apply. Therefore, we also need to understand the difference between the terms "applied dose" and "effective dose".

- The applied dose is equal to the amount of chemical we actually add to the unit of water
- The effective dose is the amount of reactant that remains (after competing reactions consume some of it) to form the products that we want to form.

Chemical dose and feed rate calculations must address the molecular formula and concentration of the chemical being applied. Many of the chemicals that we feed at the plant are molecular compounds that contain the materials other than the molecular group that we need to apply. This is particularly true when we are feeding liquid chemicals because these chemical solutions typically contain lots of water. As a result, there may be a difference between chemical dose and reactant dose.

If the chemical we are applying contains only the molecular group that participates in the reaction we want to achieve, the chemical dose and the reactant dose are equal. For example, chlorine gas and ammonia gas contain very little other material other than chlorine and ammonia, respectively. Consequently, the chemical and reactant doses are equal when we use these chemicals.

However, if the chemical that we apply is a chemical compound or solution, only part of what we add actually participates in our reaction. For example, liquid ammonium sulfate contains a sulfate group which does not participate in the chloramination process.

In addition, it is a solution and, therefore contains even less ammonia than pure ammonium sulfate. As a result, we have to apply more of the chemical than we would if it only contained the reactant that we need.

Sometimes, there is an important difference between the applied chemical dose and the effective reactant dose. For example, if we put 5 mg/L of pure chlorine into untreated water that has a 2 mg/L chlorine demand, we'll end up with water that contains 3 mg/L of free chlorine. In this case, our applied chlorine dose was 5 mg/L but our effective chlorine dose was only 3 mg/L.

Other times, there is an almost no difference between the applied reactant dose and the effective reactant dose. For example, water usually has a very low ammonia demand. Therefore, if we put 1 mg/L of pure ammonia (as NH3), we'll probably end up with close to a 1 mg/L effective free ammonia (as NH3) dose.

Similarly, our effective chlorine dose will be close to 1.0 mg/L if we put 1 mg/L of pure chlorine into water that has already been disinfected and has enough ammonia to react with the chlorine (since chlorine tends to combine with the ammonia before it reacts with other materials).

Why mixing is important: Speed of competing reactions

The reason mixing is important is…. Chemistry!

As noted previously, chemical reactions can occur simultaneously. However, some reactions will occur faster than others. A variety of factors (such as the pH and temperature of the solution and the relative concentration of the reactants and products) influence reaction rates.

For example, the breakpoint curve indicates that chlorine will react with strong reducing substances such ferrous iron and hydrogen sulfide much faster than it reacts with organic ammonia. Similarly, free chlorine will react with free ammonia before it will react with monochloramine.

However, if the free ammonia concentration is low and the monochloramine concentration is high, the reaction with monochloramine may dominate simply because there are many more monochloramine molecules present than there are free ammonia molecules. Although the chlorine would prefer to react with ammonia, it will react with whatever is present if it can't find an ammonia molecule.

It is sometimes difficult to precisely anticipate the impact of competing chemical reactions that can consume some of the chlorine before free chlorine begins to form or that can result in the decay of the monochloramine once it has formed.

Therefore, it's not enough to just know how much chemical we add. We also need to be able to measure how much of the chemical we add is present after the competing reactions have consumed some of it.

This is particularly important when we deal with free chlorine because there are a lot of competing reactions and a lot of these reactions can occur within 1–2 minutes (and many can occur within a few seconds). It's not so important when we deal with free ammonia because there are not many competing reactions that will consume our ammonia.

Reaction time

The available reaction time is also an important issue because it impacts how much free chlorine is available to react with our free ammonia. More reaction time means that each competing reaction moves further toward completion and also that more types of (slower) reactions can begin (and end) before adding ammonia (when chlorine is added first).

The water pH can have a big impact on formation of chemicals. Table 15 shows the reaction time as a function of pH.

Table 15. Time to 99% conversion of chlorine to monochloramine

pH	Time (seconds)
2	421
4	147
7	0.2
8.3	0.069
12	33.2

Figure 20 illustrates the impact that (competing reaction) reaction time has on the total and free chlorine residual.

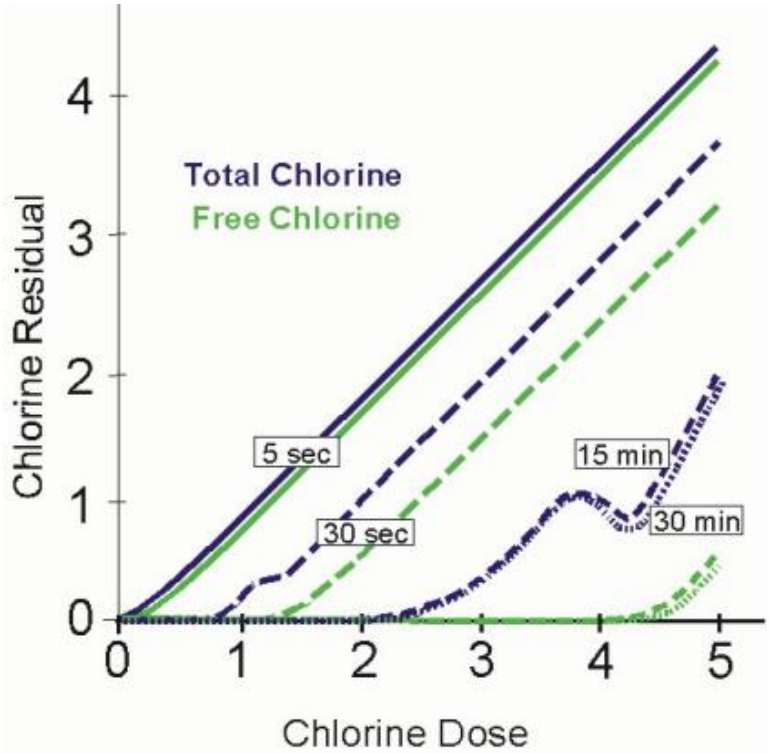


Figure 20. Impact of competing reaction time on total or free chlorine residual.

In Figure 20, we see that:

1) If we stop the reaction after just a few seconds,
    a) There has been very little chlorine demand because relatively few competing reactions have had time to progress very far, and
    b) The free and total chlorine levels will be pretty much the same;
2) If we allow the competing reactions to proceed for about 30 seconds,
    a) Reducing substances will have time to consume some of the chlorine and so we see the Stage 1 (using up free chlorine demand) response that we saw on the breakpoint curve (in Chapter 1)
    b) Chlorine has begun to react with organic and inorganic nitrogen and produced a small blip in the curve (that is similar to the Stage 2 (monochloramine formation) response shown on the breakpoint curve in Chapter 1 but there hasn't been enough time for the di and trichloramine formation reactions to proceed very far, and
    c) The total and free chlorine residuals will be lower than they would have been if we terminated the competing reactions after only a few seconds;
3) If we allow the competing reactions to occur for several minutes (usually 10 to 15 minutes or more),

a) The curve looks pretty much like the ideal breakpoint curve in Chapter 1 because all (or almost all) of the reducing substances and most of the initial reactions with organic and inorganic ammonia have reacted with chlorine,

b) Although some Stage 4 (di and trichloramine formations) reactions will continue if the reaction time is increased, the shape of the curve has become very stable (i.e., doesn't change much if the reaction time is further increased), and

c) The total and free chlorine residuals don't change much after 10 to 15 minutes unless we introduce a new source of demand.

As Figure 20 shows, competing reactions and available reaction time can also impact our ability to obtain and interpret test data. For example, if we are adding ammonia a couple of feet downstream of our chlorine, we do not have time to collect the sample and run the free chlorine test before the sampling and analytical time exceeds the time that the competing reactions can occur before the ammonia reacts with the chlorine.

Dosing and mixing bottom line

There are some key take away messages from this Chapter:

1) We always have to be aware of the potential impact of competing reactions and the time that is available for these competing reactions to occur.

2) We need to be aware of and understand how our instruments are reporting our results so that we can interpret our data. Instruments are almost always set to measure total chlorine and monochloramine 'as Cl_2' and measure ammonia, nitrate, and nitrite 'as N.'
Double check. Remember to convert to NH_3 for ammonia feed rates.

3) Chemical dose should be calculated on a weight-to-weight (w/w) basis. Remember 1 ppm (w/w) = 1 lb/106 lbs = 1 mg/L.

4) There is a difference between applied chemical dose, applied reactant dose, and effective reactant dose.

   a) **Applied Chemical Dose:** the amount of chemical we add divided by the amount of water we put it in

   b) **Applied Reactant Dose:** the amount of the reactant (contained in the chemical we add) divided by the amount of water we put it in

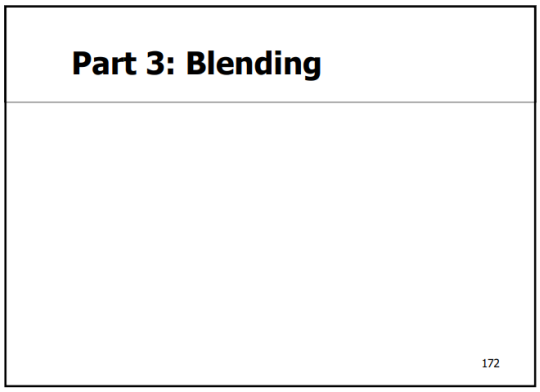
   c) **Effective Reactant Dose:** the amount of the reactant (contained in the chemical we add) that (after any competing reactions) is actually available to form product we want divided by the amount of water we put it in

5) Dose and feed rate calculations depend on the molecular formula and the concentration of the material we are adding.

6) It is okay—even best—to have a **little bit of free ammonia** (~0.05 to 0.1 mg/L) in the finished water. That way you know you are in the MONOCHLORAMINE zone (on the breakpoint curve).

Part 3. Blending chlorinated and chloraminated water

It is NOT recommended that systems blend chloraminated and chlorinated water streams in distribution.



If a system blends chlorinated and chloraminated water in distribution they should seek approval ***immediately*** by sending an exception request letter to the TCEQ, specifically:

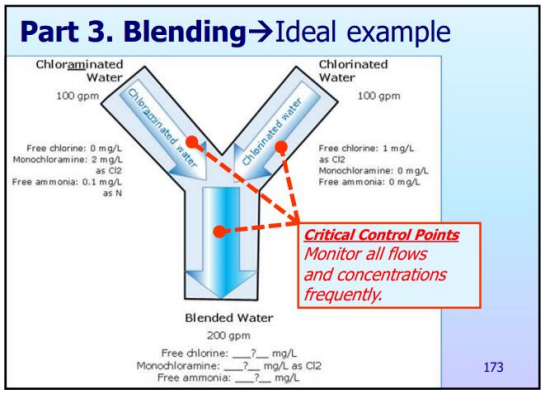
Attention: Technical Review and Oversight Team, MC 154

TCEQ, PO Box 13087

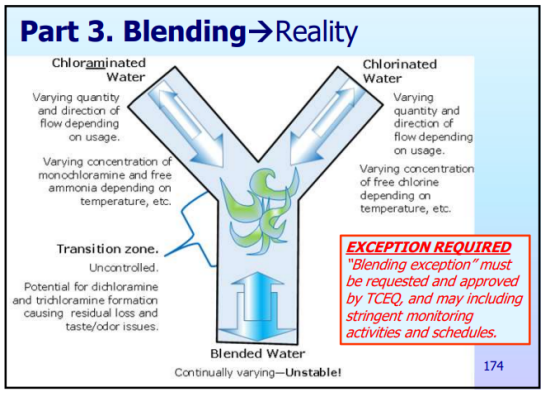
Austin TX 78711-3087

The reason for this is that problems are likely to happen when chlorinated water is mixed with chloraminated water without proper controls. The upstream levels of chemicals, and the flowrates, must be carefully controlled in order to produce a blended water of adequate quality.

Failure to blend correctly can result in loss of residual and/or taste and odor problems from di- and trichloramine.



In reality, blending is almost impossible to control, because of varying conditions.



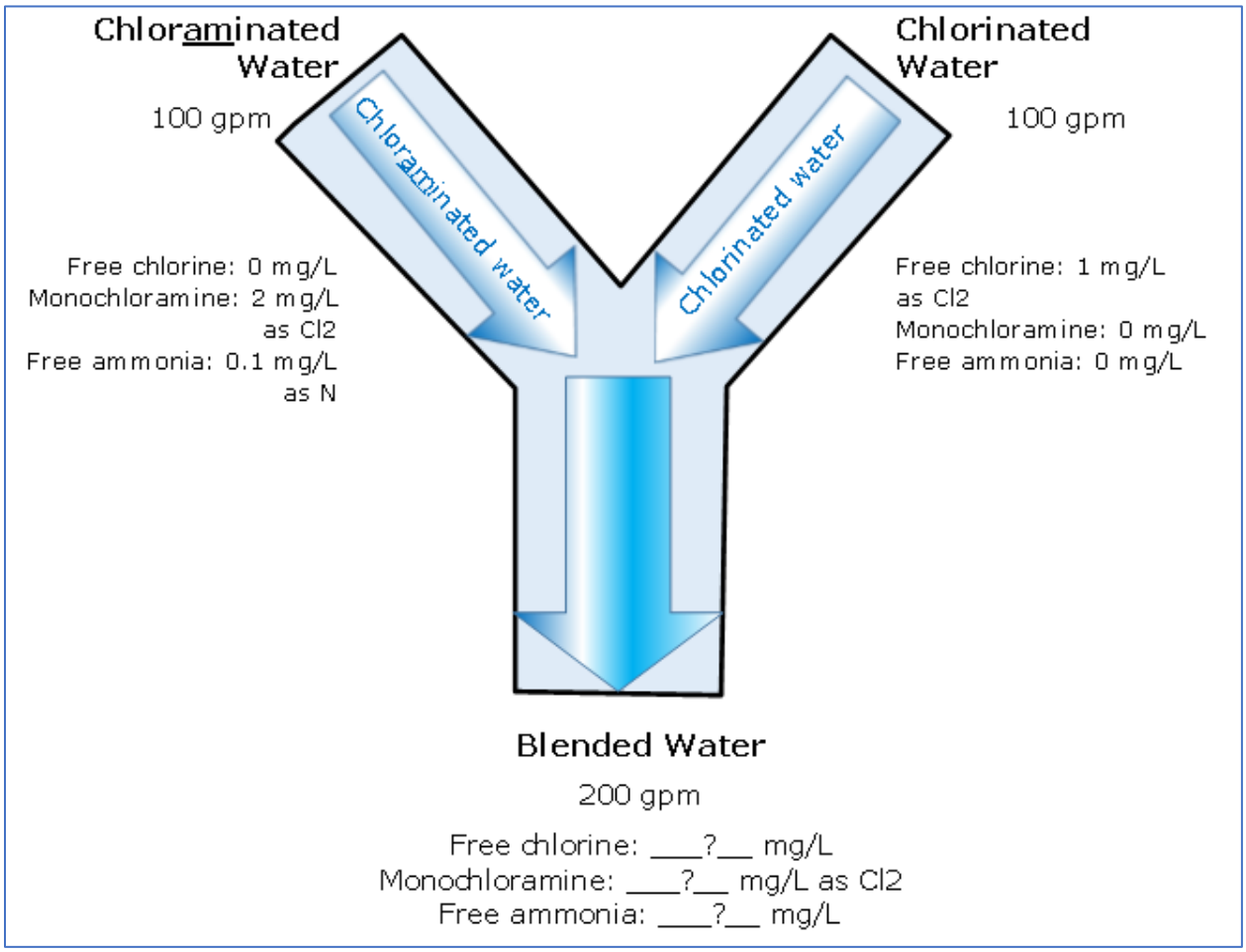


Figure 21. Ideal blending of chlorinated and chloraminated water in distribution.

Example: Ideal blending calculations

To illustrate the difficulty of maintaining a stable Cl_2:NH_3-N ratio, this example is provided. In this example, the incoming conditions for each water stream are shown below.

Free available ammonia in the chloraminated water:

0.1 mg/L as N,

can tie up (5 X 0.1) = 0.5 mg/L Cl2

But there is 1 mg/L of free ammonia more than that in the chloraminated water:

So: the 'leftover ratio' is 1 Cl_2: 0.1 N

Monochloramine at 2 mg/L includes

2 mg/L Cl_2, and

(1/5)X2 mg/L N = 0.4 mg/L N

The total available chlorine in the blended water can be expressed as:

2 (from mono) + 0.1 (from free) = 2.1 mg/L as Cl_2

and the free available ammonia–nitrogen can be expressed as:

0.4 (from mono) + 0 (from free) = 0.4 mg/L as N

So the Cl2:NH3-N ratio is

2.1:0.4 = 5.25,

starting to form dichloramine!

Monitoring needed to control blending

In order to control blending in distribution, the following monitoring is needed on a frequent enough basis to capture any significant changes.

Chemicals

Sample sites must be located to be able to measure chemicals at:

- Upstream in chlorinated stream,
- Upstream in chloraminated stream, and
- Downstream in blended stream.

The chemicals that MUST be measured are:

- Free chlorine upstream in chlorinated stream
- Monochloramine and free ammonia upstream in chloraminated stream, and

- Total chlorine, free chlorine, monochloramine, and ammonia downstream in blended water.

The upstream sample sites should be far enough from the blend-point so that backwash from turbulent mixing does not change results. However, they should be close enough to the blend-point that significant decay does not occur before the blend point.

The chemicals must be monitored frequently enough that any changes—either from dose changes, decay, or incipient nitrification—are not allowed to occur for a long time. For example, a daily frequency might be acceptable in a fairly stable system. Weekly sampling would probably be inadequate.

Flow rate

The Cl_2:NH_3-N ratio will be significantly impacted by changes in flow rate in either or both upstream flows.

Going back to the example, you can see that this was a very simple example because both the water streams were flowing at exactly 100 gpm. That situation is unlikely to occur in a real-life situation.

At a minimum, a system that is blending must monitor flow rate:

- Upstream in chlorinated stream,
- Upstream in chloraminated stream, and
- Downstream in blended stream for verification.

Modeling

It may be possible to produce computational fluid dynamic results to support flow rate monitoring and predict a range of acceptable operating parameters. When seeking an exception using modeling or computational fluid dynamics, it is recommended that a PWS set up a face-to-face meeting with the TCEQ engineers who will be reviewing the blending exception request.

Chapter 4 Review Questions

(There are multiple answers to some questions, select all)

<u>When boosting chloramines in water that is already chloraminated:</u>

1) Add chlorine before ammonia
2) Add ammonia before chlorine
3) Measure the monochloramine and ammonia in the influent water before setting the dose.

<u>When chloraminating raw water:</u>

1) Add chlorine before ammonia
2) Add ammonia before chlorine
3) Measure the monochloramine and ammonia in the influent water before setting the dose.

<u>The best of the mixing sequences below for dosing raw water is:</u>

1) Add chlorine first, add ammonia second, then measure total chlorine

2) Measure ammonia, add chlorine, then add ammonia, then measure monochloramine

3) Measure ammonia, add ammonia, then measure ammonia again, then add chlorine

<u>Inadequate mixing can cause:</u>

1) Higher total chlorine residuals
2) Formation of di-and tri-chloramine
3) Lower total chlorine residuals
4) Waste of money

Chapter 4 Checklist

Hopefully, after this chapter, you have a completed map and schedule that meets the sampling requirements.

Chapter 4 checklist

Part 1. Calculating feed rates

- Do you understand how the weight and number of chemicals are related?
- Do you know how to calculate the amount of chemical you are dosing?
- Can you do the calculations to switch between chlorine-to-ammonia (Cl_2:NH_3) or chlorine-to-ammonia-nitrogen (Cl_2:NH_3-N) ratio as needed?

Part 2. Mixing and dosing

- Do you know how your chemicals are mixed?

If so, do you know how well they are mixing?

- Do you know how much time each chemical is mixed for?

If not, are you able to calculate that?

- Are you monitoring well enough to know your applied dose?

Effective dose?

Follow up:

If you are doing dosing calculations correctly, using the correct ratio for your situation, and mixing in a manner that achieves a stable monochloramine residual—congratulations, you are making your own life easier.

Recommended actions?

If you have unanswered questions about mixing and dosing, make a plan for how you are going to address that and note it on your Plan of Action.

Chapter 5. Treatment plants: Applying the dosing concepts

In a booster or groundwater treatment plant, there are concerns like pH and source water quality (especially free ammonia).

There are more concerns in a surface water treatment plant, for example, it is better to try to avoid trying to form monochloramine in parts of the plant (like the rapid mix) where we are trying to suppress the pH in order to improve particle and TOC removal.

If we are going to use monochloramine as a pre-disinfectant, we need to add the chlorine and ammonia either before or after the alum injection point in a surface water treatment plant.

We have just reviewed many of the important issues related to chloramination chemistry, analytical methods, and chemical dose and feed rate calculations. Now it's time to use the concepts to help us evaluate and control the chloramination process at our plant.

This section is most important for surface water treatment plants (SWTPs). It can also be helpful for systems re-chloraminating purchased water, chloraminating groundwater, or boosting the monochloramine residual in distribution.

Operators who want to increase skills to include treatment concepts are encouraged to work through this section, even if it does not apply to your current job. Knowledge can open doors. A self-directed activity is provided at the end of the Chapter for this purpose.

Scope

During this section we will:

- Review the process control loop and discuss how the approach can be applied to effectively control the chloramination process.
- Discuss the different types of data that the operator will need to obtain.
- Address the relationships between sampling sites, laboratory testing, and goal setting to help the participants identify appropriate sampling sites and laboratory tests for each chlorine and ammonia application point at the plant.
- Explain how operators can use the collected data to evaluate the status of the chloramination process and develop a response to unacceptable operating conditions.
- Ensure that the plant staff understands how the data is used make appropriate feed rate adjustments and to verify the impact of each adjustment after it is made.

- Review the 11 Steps in the manual step-by-step approach for evaluating and adjusting the chloramination process. The participants will: work with the instructor to identify suitable chlorine and ammonia feed points and appropriate sampling sites within the plant.

Materials

For this section, the student should look at the materials provided for the course, particularly:

- The Student Guide,
- Plant description and plant tour notes.

Chapter 5. Scope

- Part 1: A process management loop is how many technical decisions are made. We will talk about how this technique is used for dosing.
- Part 2. For a SWTP, we can use the changing breakpoint curve to visualize the way that the process management loop works.

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Learning goals

The learning goals for this workshop are:

- Be able to describe a process control or process management loop (they are synonymous);
- Identify desired process management process for making changes to chemical dosing in the treatment plant—either the 11-step method, or the Chloramine Spreadsheet;
- If a feed rate change is needed, ensure that the change is made properly.
- Be able to choose the right type of adjustments to feed rates based on results.

Chapter 5 Learning Goals

- Be able to describe a process management loop.
- Be able to calculate chemical dosing changes using:
  - 11-step method, or the
  - Chloramine Spreadsheet.
- Be able to troubleshoot residual issues at a SWTP and choose the right feed rate adjustments.

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Part 1. The Process Control (or "Process Management") Loop

Several years ago, one of the TCEQ staff members (a very wise fellow named Chuck Schwarz) gave a presentation in which he discussed a simple process control loop. This process control loop can be applied to the chloramination process in the manner shown in Figure 18.

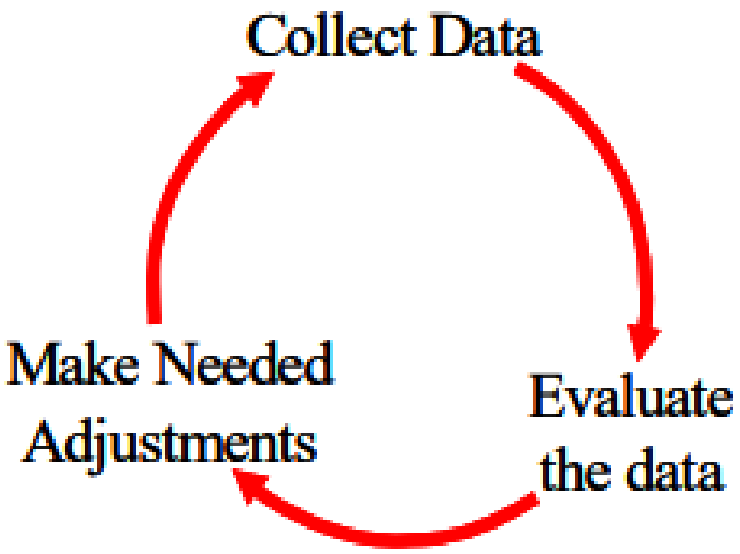


Figure 22. Process control loop (AKA process management loop).

This process control loop can be applied to the chloramination process in the following manner:

1. Collect Data

Collect Data means that, at each chemical application point, we need to gather the applicable information about:

1) our initial target free chlorine, total chlorine, and monochloramine residuals and our desired free ammonia level,
2) our current free chlorine, TAC, monochloramine, and FAA levels,
3) our current chemical feed rates and water flow rates,
4) the molecular weight and formula of the chemicals we use to form monochloramine, and
5) the concentration (on a w/w basis) and specific gravity of any liquid chemical we are using.

Evaluate Data

Evaluate the Data means:

6) asking ourselves if we got the results we wanted to get and, if not,
7) determining what changes we need to make to reach our target initial free chlorine, monochloramine, or FAA level.

Make Adjustments

Make Needed Adjustments is pretty self explanatory, but it's important to realize that the loop does not end with the adjustment. We must collect more data to verify that:

8) We actually made the precise adjustment that we intended to make and
9) The adjustment produced the outcome we wanted to produce.

As we can see, the basic questions we need to ask ourselves are:

- What do we need to measure to control the chloramination process?
- Where is the best spot to test for it?
- What results are we looking for?
- What do we do when we don't get it?

We have two feed-rate adjustment process management methods to talk about:

- The 11-step method, and
- Spreadsheet method, using the DAM 8 Excel file.

Any method that achieves the result of stable, long-lasting monochloramine is a good method.

Many operators use a step-by-step method to calculate their target chlorine and ammonia feed rates rather than using a computer and spreadsheet. The step-by-step calculation uses the same conversion factors as the "mash it all together in a single step" approach used by the spreadsheets. Consequently, both approaches will give the same results.

11 step process-management loop for adjusting feed rate

When using the step-by-step approach, we can use the following 11 steps:

Step 1—Set Targets:
Decide what monochloramine residual and free ammonia level we want to have in the water after we add the chlorine and ammonia.

Step 2—Run Tests:
Measure total chlorine, monochloramine, and free available ammonia (and free chlorine, if desired) and determine if we need to make any adjustments.

A) If we are at our targets, repeat step 2 periodically.

B) If adjustments are needed, proceed to step 3.

Step 3—Calculate Flow Rate:
Figure out how many million pounds of water we would produce during 24 hours if we ran continuously at the current flow rate.

Step 4—Measure Feed Rates and Calculate Doses and Ratio:
If we are currently feeding chlorine and ammonia at this application point—measure our current feed rates, calculate the current chlorine and ammonia doses, and determine our current Cl_2:NH_3-N ratio.

Step 5—Calculate Desired Monochloramine Dose:
Figure out how much we need to raise the monochloramine residual (in mg/L) to reach our target so that we know what our effective chlorine dose needs to be.

Step 6—Determine Chlorine Demand:
Figure out how much chlorine demand we have in the water so that we can determine what our actual chlorine dose needs to be.

Step 7—Determine Desired Chlorine Feed Rate:
Figure out what our chlorine feed rate should be based on the type of chemical we are using and its concentration (and if we're feeding bleach, its specific gravity).

Step 8—Set Target Ratio:
Decide what our target Cl_2:NH_3-N ratio should be.

Step 9—Determine Ammonia Dose:
Figure out what our ammonia dose (as mg/L of NH_3-N) needs to be to achieve our target ratio or our desired free ammonia concentration.

Step 10—Calculate Desired Ammonia Feed Rate:
Figure out what our ammonia feed rate should be based on the type of chemical we are using and its concentration (and if we're feeding a liquid, its specific gravity).

Step 11—Go back to Step 1, repeat as needed.

Example 5.1: Detailed example of using the 11-step method

Step 1: Set Targets

The first step of setting targets will be different for different systems. In general, we want to set plant levels high enough to not have problems in distribution—it is unusual to see targets much less than 2 mg/L.

Example conditions: Let's say that we want to have a monochloramine residual of 2.2 mg/L but are willing to accept a reading of 2.0 – 2.5 mg/L (as Cl_2). We also want to maintain a free ammonia level of 0.05 – 0.07 mg/L as NH_3 to minimize dichloramine and trichloramine formation.

Step 2: Run Tests

Example conditions:

We collect a sample at the tap upstream of our chlorine and ammonia injection point and find:

Total chlorine	= 1.9 mg/L
Free chlorine	= 0.1 mg/L
Monochloramine	= 1.0 mg/L
Free ammonia	= 0.05 mg/L as NH_3

We also collect a sample at the tap downstream of our chlorine and ammonia injection point and find:

Total chlorine	= 3.0 mg/L
Free chlorine	= 0.1 mg/L
Monochloramine	= 1.6 mg/L
Free ammonia	= 0.0 mg/L as NH_3

Interpreting results: Based on our results, we should not assume that we really have free chlorine in either sample because the monochloramine levels are high enough to interfere with the free chlorine test and because monochloramine and free ammonia cannot coexist with free chlorine for very long.

However, we also cannot assume that the free chlorine residual in the downstream sample is really 0.0 mg/L because we have no free ammonia present. If FAA is really 0.0 mg/L, then we may have run out of ammonia before all of the chlorine reacted.

Furthermore, the difference between the total chlorine and monochloramine levels increased after we added our chlorine and ammonia. As a result, we should be worried that we may be adding too much chlorine (or not enough ammonia) and forming a little dichloramine. We should also assume that we

probably have not formed any trichloramine because our monochloramine level is still pretty high.

Based on these test results, we realize that we need to adjust either (or maybe even both) our chlorine and ammonia feed rates so that we can achieve our target monochloramine residual and free ammonia level.

Step 3: Calculate Flow Rate

Example conditions: Our current flow rate at this injection point is 830 gpm. This flow rate is equivalent to 1.195 MGD, or about 10 million pounds per day.

$$\frac{830 \text{ x } 1440}{1{,}000{,}000} = 1.195 \text{ MGD x } 8.34 = \frac{9.967 \text{ million pounds } H_2 0}{\text{day}}$$

Step 4: Measure Feed Rates and Calculate Doses and Ratio

(Note: This scenario uses the Cl2:NH3 ratio, not the Cl2:NH3-N ratio)

Example conditions: At this application point, we are currently feeding 6.0 ml/min of LAS followed by 15 ppd of gas chlorine at few feet downstream. The specification sheet on our LAS says that the product contains 38% ammonium sulfate (w/w) and a specific gravity of 1.23.
Therefore, we are applying 2.3 ppd of ammonia and 15 ppd of chlorine.

$$1.23 \text{ X } 8.34 \text{ lb}/\text{gal} = \frac{10.26 \text{ lb LAS}}{\text{gal LAS}}$$

$$\frac{10.26 \text{ lb LAS}}{\text{gal LAS}} \text{ X } \frac{0.38 \text{ lb } (NH_4)SO_4}{\text{lb LAS}} \text{ X } \frac{0.258 \text{ lb } NH_3}{\text{lb } (NH_4)SO_4} = \frac{1.005 \text{ lb } NH_3}{\text{gal LAS}}$$

$$\frac{6.0 \text{ ml LAS}}{\text{min}} \text{ X } \frac{1{,}440 \text{ min}}{\text{day}} \text{ X } \frac{\text{gal LAS}}{3{,}785 \text{ mL LAS}} \text{ X } \frac{1.005 \text{ lb } NH_3}{\text{gal LAS}} = \frac{2.3 \text{ lb } NH_3}{\text{day}}$$

Using our feed rate and flow rate information, we can determine that our current chlorine and ammonia dosages are about 1.5 ppm and 0.23 ppm, respectively.

$$\frac{15 \text{ lb } Cl_2}{10 \text{ M lb } H_2 0} = 1.5 \text{ ppm } Cl_2 \qquad \frac{2.3 \text{ lb } NH_3}{10 \text{ M lb } H_2 0} = 0.23 \text{ ppm } NH_3$$

Interpreting results: Because we are applying ammonia upstream of chlorine at this application point, we should probably base our Cl_2:NH_3 ratio on our chlorine and ammonia feed rates (since we should assume that most of the chlorine demand results from the ammonia we have put in the water).
Based on this assumption, our (applied) Cl_2:NH_3 ratio is 6.5:1.

$$\frac{15 \text{ ppm } Cl_2}{2.3 \text{ ppm } NH_3} = 6.52$$

x

Remember (from Step 2) we were worried that we might be adding too much chlorine or not enough ammonia because the difference between the total chlorine and monochloramine levels increased after we added our chemicals. Since higher ratios (more chlorine and less ammonia) favors the formation of dichloramine, we should not be too surprised to find that we are operating at a ratio that is higher than the theoretical ratio of 4.2:1.

Step 5: Calculate Desired Monochloramine Dose

To reach our monochloramine target of 2.2 mg/L, we'll need to increase the monochloramine residual by 1.2 mg/L at this application point.

This means that we need to apply an effective chlorine dose of 1.2 mg/L (since 1 mg/L of chlorine will produce 1 mg/L of monochloramine if there are no competing reactions).

However, since we are willing to accept any monochloramine residual that falls between 2.0 and 2.5 mg/L, our effective chlorine dose can be as low as 1.0 or as high 1.5 mg/L.

Step 6: Determine Chlorine Demand

Example conditions: Because we are applying ammonia upstream of chlorine at this application point, we should assume that most of the chlorine demand results from the ammonia we have put in the water. Still, there might be a little naturally-occurring chlorine demand left after our earlier processes. In addition, we have a relatively high monochloramine target and a relatively low free ammonia target. As a result, we are probably not going to be able to completely eliminate the formation of dichloramine and, therefore, we have a little chlorine demand.

Let's assume that we're going to lose about 0.1 mg/L of the chlorine we add to a competing reaction. If the demand is much higher than we estimated, we'll get more free ammonia than we expect after we make our change. If the demand is far lower than we expected, we'll continue to see elevated combined chlorine levels and no free ammonia.

Interpreting results: In Step 4, we determined that we were adding 1.5 ppm (mg/L) of chlorine. Therefore, based on estimated chlorine demand, our effective chlorine dose will be about 1.4 mg/L. Although this effective dose is within the acceptable range we identified in Step 5, let's assume that we decide to lower it to 1.2 ppm so that we can reach our chloramine target of 2.2 mg/L exactly. Based on our estimated chlorine demand, an effective dose of 1.2 mg/L is equivalent to an applied dose of 1.3 mg/L.

Step 7: Determine Desired Chlorine Feed Rate

Calculation: Based on our flow rate and our 1.3 ppm (applied) dose, we calculate that our gas chlorine feed rate needs to be about 13 ppd instead of 15 ppm.

$$\frac{10\ \text{M lb}\ H_2O}{\text{day}} \times \frac{1.3\ \text{lb}\ Cl_2}{1\ \text{M lb}\ H_2O} = \frac{13\ \text{lb}\ Cl_2}{\text{day}} = 13\ \text{ppd}\ Cl_2$$

Step 8: Set our target Cl_2:NH_3

(Note: This scenario uses the Cl_2:NH_3 ratio, not the Cl_2:NH_3-N ratio)

Example conditions: For this scenario, because our results were so far from our targets, we should probably select a Cl_2:NH_3 ratio that is pretty close to the theoretical value of 4.2:1.

If we had been more on target, we might have selected a ratio that is closer to where we were currently operating (i.e., 6.5:1) than to theoretical.

If we want to make sure that we minimize dichloramine formation, we may even decide to try a ratio that is closer to 4:1 or even 3.5:1.

Step 9: Determine our Ammonia Dose (as mg/L of NH_3)

Since we are applying ammonia upstream of chlorine at this injection point, we'll need to base our target Cl_2:NH_3 ratio of 4.2:1 on the chlorine and ammonia dosages that we are applying rather than the measured residuals. We would also need to do this if we were injecting chlorine only a few feet upstream of the ammonia. However, if we had several minutes of free chlorine contact time upstream of our injection point, we would want to base our ammonia dose on the chlorine residual at the ammonia injection point so that we could account for the actual chlorine demand of the water. Since our free ammonia level upstream of this application point is right where we want it to be, we will need to add enough ammonia to maintain this level after the chlorine has been added. Therefore, based on our target ratio, our ammonia feed rate needs to be 3.1 pounds per day.

$$\frac{13\ \text{lb}\ Cl_2}{\text{day}} \times \frac{1\ \text{lb}\ NH_3}{4.2\ \text{lb}\ Cl_2} = \frac{3.1\ \text{lb}\ NH_3}{\text{day}} = 3.1\ \text{ppd}\ NH_3$$

If our free ammonia level at the upstream tap was higher than our target, we would want to lower our ammonia feed rate enough to allow the chlorine to consume some of the extra ammonia that is already present at our ammonia application point. Similarly, if the ammonia level at the upstream tap was below our target range, we would have to increase the ammonia dose slightly so that we could reach our target after applying the chlorine.

Step 10: Calculate Desired Ammonia Feed Rate

In step 4, we calculated that 1 gallon of our LAS solution contains 1.0 lbs of ammonia (as NH_3). Since we need to add 3.1 ppd of NH_3, we need to set our feed pump so that it feeds 3.1 gpd of LAS, or 8.1 mL/min.

$$\frac{3.1 \text{ lb } NH_3}{\text{day}} \times \frac{1.0 \text{ lb } NH_3}{\text{gal LAS}} \times \frac{3{,}785 \text{ mL LAS}}{\text{gal LAS}} \times \frac{\text{day}}{1{,}440 \text{ min}} = \frac{8.1 \text{ mL LAS}}{\text{min}}$$

Step 11: Go back to Step 1 and Begin Again

This time through we get the following:

Step 1: No change in our goals

Step 2: This time we find the following in the sample we collect from the upstream tap:

Total chlorine	= 1.9 mg/L
Free chlorine	= 0.1 mg/L
Monochloramine	= 1.0 mg/L
Free ammonia	= 0.05 mg/L as NH_3

The sample we collect at the tap downstream of our chlorine and ammonia injection point shows:

Total chlorine	= 2.9 mg/L
Free chlorine	= 0.1 mg/L
Monochloramine	= 2.1 mg/L
Free ammonia	= 0.06 mg/L as NH_3

Based on the sample results, we should realize that we got pretty close to optimizing the feed rates and Cl_2:NH_3 ratio at this application point. The combined chlorine residual remained fairly constant at about 0.8 – 0.9 mg/L. The monochloramine level is now within our target zone and we were able to maintain a FAA residual after adding chlorine.

If we decide to make additional changes, we would need to increase the dose of both chlorine and ammonia feed so that we would maintain our 4.2:1 ratio.

Now we just keep repeating step 2.

Chloramination Spreadsheets for feed rate adjustment

TCEQ has created a pair of Chloramination Spreadsheets to help us set our chemical feed rates. One spreadsheet was designed for plants that feed liquid ammonium sulfate and the other one was designed for plants that feed anhydrous ammonia.

Each of the spreadsheets contain three pairs of worksheets; one pair for plants that feed gas chlorine (one for gas chlorine first and one for gas chlorine second), one pair for plants that feed bleach (bleach first, bleach second), and one pair for plants that feed calcium hypochlorite (hypochlorite first, hypochlorite second).

After we enter data about our current operating conditions for each injection point into the proper worksheet, the spreadsheet will tell us what adjustments we will probably need to make to our chemical feed rates at each injection point.

Working with the Chloramination Spreadsheet may take up to an hour to get the plant started using it.

The process includes:

1) Install the Chloramination Spreadsheet on one of the plant's computers. If possible, the spreadsheet will be installed on the "Desktop" of the computer nearest the laboratory or the control room.
2) Move the appropriate worksheets to the front of the spreadsheet.
3) The instructor will demonstrate how the spreadsheet can be used as a tool to help the plant staff make appropriate changes to the various chemical feed rates.
4) Operators should enter data for the application point where data was collected onto one of the worksheets. In future, they can use the spreadsheet to evaluate the impact of possible changes to the chlorine and ammonia feed rates.

Part 2. Visualization using the breakpoint curve and process control loop

1) The breakpoint chlorination curve helps us visualize what will happen during the various stages of the chloramination process.
2) We need to be able to measure free available chlorine, total available chlorine, monochloramine, and free available ammonia.
3) We can use our free chlorine, TAC, monochloramine, and FAA data to figure out where we are on the curve and what general adjustments we need to make to get where we want to be.
4) The TAC residual should not change simply because we add ammonia . . . if we add enough ammonia to combine with all of our FAC.
5) However, if we have too much free chlorine present after we add our ammonia,
    a) Our monochloramine will be lower than we expected,
    b) Our TAC residual will drop, and
    c) Our combined chlorine level will increase (the difference between monochloramine and TAC will be greater than the difference between FAC and TAC).
6) Chlorine, chlorine dioxide, or ozone needs to be added to undisinfected water before we add our ammonia.
7) Ammonia should be added before chlorine if we are boosting the chloramine residual in water that has already been disinfected with free chlorine, chlorine dioxide, or ozone.
8) Competing reactions (such as dichloramine formation) can affect the shape of our breakpoint curve. In addition, these competing reactions may mean that we have to add slightly more than 1.0 mg/L of chlorine to get 1.0 mg/L of monochloramine when we are booster chlorinating water that contains a free ammonia residual.

Collect the data

In order assure that we collect the data we need (and to avoid collecting unnecessary data), we need to identify our important monitoring sites, the type of data we need to collect at each site, and our target results. (Yeah, this does sound an awful lot like data we need to include in our Monitoring Plan.)

Some of the data we need (like the molecular weight, formula, concentration, and specific gravity of the chemicals we are using) must be obtained from our chemical supplier and other sources. However, most of the data (like target and current residual levels, current feed and flow rates, etc) we have to determine ourselves. For example, we may need to set our target residual at one of our

injection points based on the disinfectant residual we need maintain at the end of that disinfection zone but set the target residual at another point based on the residual we want leaving the plant (which, in turn, might be based on the residual we want to maintain in the distribution system).

What do we need to measure in a treatment plant?

By now, we should realize that we need to be able to test for at least four different things:

1. Free chlorine . . . to find out:
    a. if we added the right amount of chlorine to get the monochloramine residual we want and
    b. exactly how much ammonia we need to apply.
2. Free ammonia . . . to find out:
    a. if we applied too much ammonia or
    b. exactly how much chlorine we should apply to reduce the ammonia level
3. Monochloramine . . . our target disinfectant, to find out:
    a. if we added the right amount of chlorine and ammonia.
4. Total chlorine . . . to find out:
    a. if we made any di- or trichloramine and
    b. how much difference we should expect between our monochloramine and total chlorine results.

However, it is also pretty helpful if we can also be able to determine our chemical/reactant feed rate and water flow rate at each of our injection points

Where should we test for it (in the treatment plant)?

Obviously, we have to monitor at each sampling point that is required by regulations. For example, we have to monitor at the end of each disinfection zone, at the entry point to the distribution system, and at designated sites in the distribution system. However, we also need to collect process control samples in addition to the regulatory samples. Process control samples are particularly important because they can detect problems before they reach the regulatory sampling point. In general, process control sampling points will depend on where we are adding each chemical but it is always helpful if we have:

1) an upstream tap so that we can determine much chemical we need to add before we add it, and
2) a downstream tap so that we can determine if we added the right amount of chemical after we added it.

Figure 23 shows an example of the ideal way to see how well the chlorine and ammonia are mixing to form chloramines.

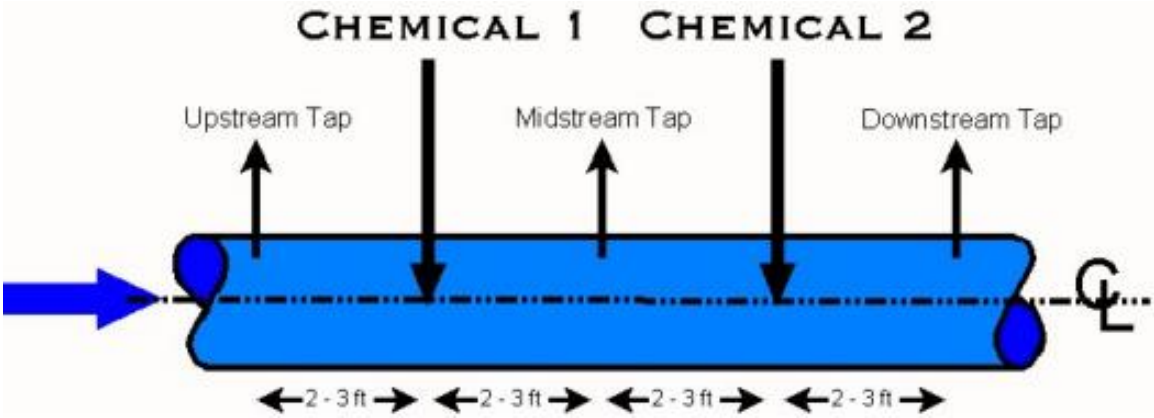


Figure 23. Ideal way to see how well the chlorine and ammonia are mixing to form chloramines.

Regardless of which chemical (chlorine or ammonia) we inject first, we should try to separate the injection points by several feet or at least ensure that the injection stingers are placed at about the same depth in the pipe. This arrangement helps us get as much chemical dispersion and mixing as we can when adding each chemical. As the figure indicates, it is usually helpful to have a sample tap upstream of each pair of (chlorine and LAS) injection points, one between the two points, and one after the two points. If we don't have enough room to put the midstream tap, we may be able to run the "midstream tests" by temporarily turning off Chemical 2 and making our measurement at the downstream tap.

We need to remember that competing chlorine reactions can occur very quickly. Consequently, it may not be possible to get an accurate free chlorine reading if chlorine is being applied first and ammonia is being injected only a few feet later. This is because the amount of time it takes to collect and analyze the sample will be much longer than the 10 – 15 seconds it takes for the chlorinated water to reach the ammonia injection point. Since the competing reactions continue to occur during collection and analysis, the free chlorine residual detected in the sample could be much lower than the residual that actually exists at the time that the ammonia is injected.

On the other hand, if it takes 4 or 5 minutes for the chlorinated water to reach the ammonia injection point, we may be able to get a reasonably accurate reading if we collect the sample quickly and run the test at the sampling site. This is because the very rapid reactions occur within the first couple of minutes of chlorine exposure; after a few minutes of chlorine exposure, the minute or so that it takes to collect and test the sample has less of an impact on the results. If there is 10 – 15 minutes of free chlorine contact time between the chlorine

and ammonia injection points, the free chlorine residual in the water will have stabilized enough for sampling and analysis time to have a minimal impact.

What are our targets (at the plant)?

As we just noted, our performance targets for the monitoring sites at each application point are usually based on a performance goal somewhere else in the plant or in the distribution system. These goals tend to vary on a system-by-system basis and even on a seasonal basis within a single system. However, there are some rules of thumb that we can use.

1) We need to set performance targets for free chlorine, total chlorine, and monochloramine residuals at each application point.
    a) The targets within the plant should usually be based on our CT requirements. Therefore, we need to develop a correlation between the disinfectant residuals at the end of each zone and the levels we need to achieve at the application point.
    b) The targets at the high-service pump station should usually be based on the disinfectant levels that we want to maintain in the far reaches of the distribution system or at our next re-chlorination point. Again, we need to understand the relationships that exist between the sample sites. However, we also need to realize that it is going to much more difficult to use the results at a distant point to control the process because the distribution residuals are influence by a lot more than just the residual leaving the plant.
2) Although we may also need to set a free ammonia target for each application point, the one we set at the entry point to the distribution system is the most important. Free ammonia is a food for nitrifying bacteria. In addition, free ammonia levels in distribution tend to be significantly higher than those at the plant because monochloramine decays in the distribution system and this decay can release ammonia back into the water. Consequently, we need to keep the ammonia level as low as possible in the water leaving the plant. The target free ammonia level at the high-service pump station should be no greater than 0.05 – 0.10 mg/L.
3) Our performance targets need to include:
    a) an acceptable range . . . what results will we allow before we are willing to make a change in the treatment process
    b) critical levels . . . what reading(s) would prompt us to make a change and what adjustments would we make if we reached that unacceptable level of performance.

Evaluate the data—troubleshooting

This step in the process control loop is where we compare our test results to our performance targets, determine if we are over-feeding or under-feeding one or more reactants, and then decide what adjustments (if any) we need to make.

Figure 24 describes how to troubleshoot by evaluating the data

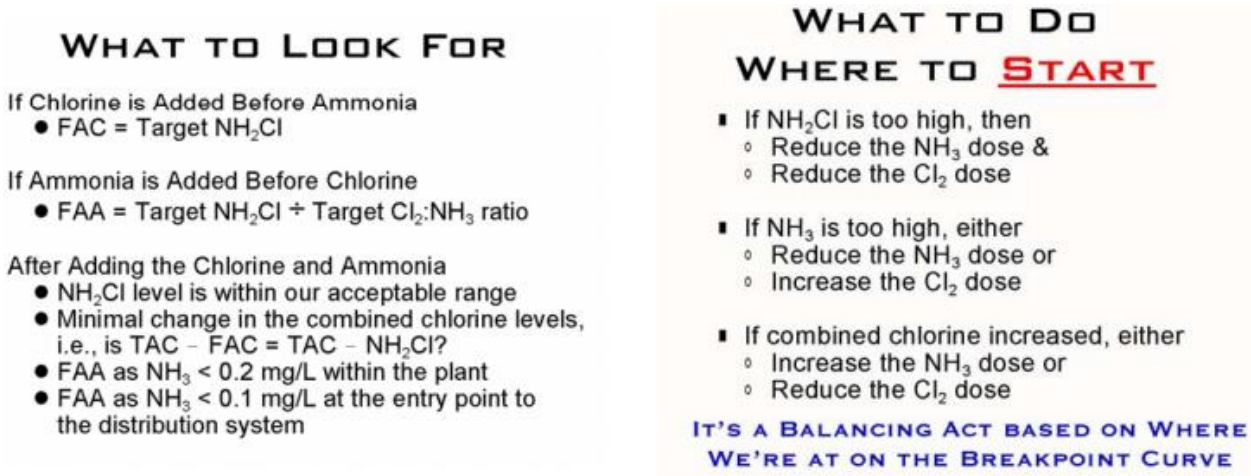


Figure 24: Troubleshooting

Breakpoint curve scenarios

One of the benefits of the breakpoint curve is that we can use it to help us understand the chloramination process and interpret the results of our laboratory tests. The breakpoint curve allows us to visualize where we are in the process and what adjustments we need to make to optimize our disinfection process.

Let's consider the two disinfection scenarios that operators are likely to use on a routine basis.

- Scenario 1 describes adding chlorine before ammonia, and
- Scenario 2 describes adding ammonia before chlorine.

Scenario 1: Chlorine is added before ammonia

For any operator that uses chloramines, it is important to understand how the treatment plant is making decisions about what chemicals to add. Even if you are purchasing and redistributing chloraminated water, you will be able to manage your system better if you understand what is happening upstream. Also, it will help you ask questions of the treatment plant operators—and understand their answers.

NOTE: This is the sequence that chlorine and ammonia must be applied if you are disinfecting untreated water with chloramines. In this scenario, there is no (or very little) ammonia in the raw water that we are treating.

We want to add enough chlorine to go past the breakpoint and move far enough up the free chlorine curve so that, when we add the ammonia, we get the monochloramine residual we want. This way we can oxidize iron, manganese, sulfide and some of the organic nitrogen—basically get past any little bit of 'demand' that is in the raw water.

As the Schulze breakpoint curve in Figure 4 indicates, the process will also allow us to determine about how much difference there will probably be between our monochloramine and total chlorine residuals.

Figure 25 shows the condition that the water is in when free chlorine is added to water that does not have (much) ammonia in it using the breakpoint curve.

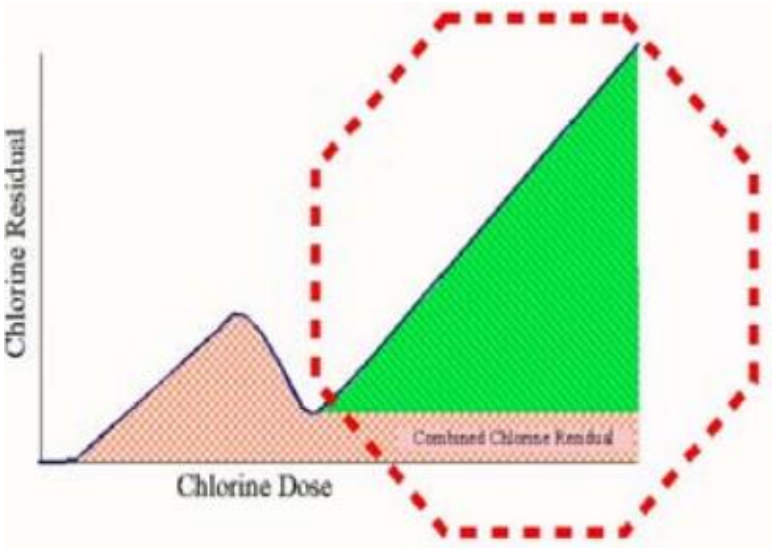


Figure 25. When you add free chlorine to water with very little ammonia, you are in Stage 6 of the Schulze breakpoint curve (Figure 4).

Scenario 1 Conditions

Let's assume that we want to achieve a monochloramine residual of about 2.3 mg/L (or so).

Let's also assume that our current operating conditions produce the following results:

- Total Chlorine = 4.6 mg/L
- Free Chlorine = 4.0 mg/L
- Monochloramine = trace mg/L
- Free Ammonia = 0 mg/L as NH3

Figure 26 shows the conditions for Scenario 1 at the beginning of the process. Since we said we wanted just 2.3 mg/L of total/mono… you can see that we have more free chlorine than we need.

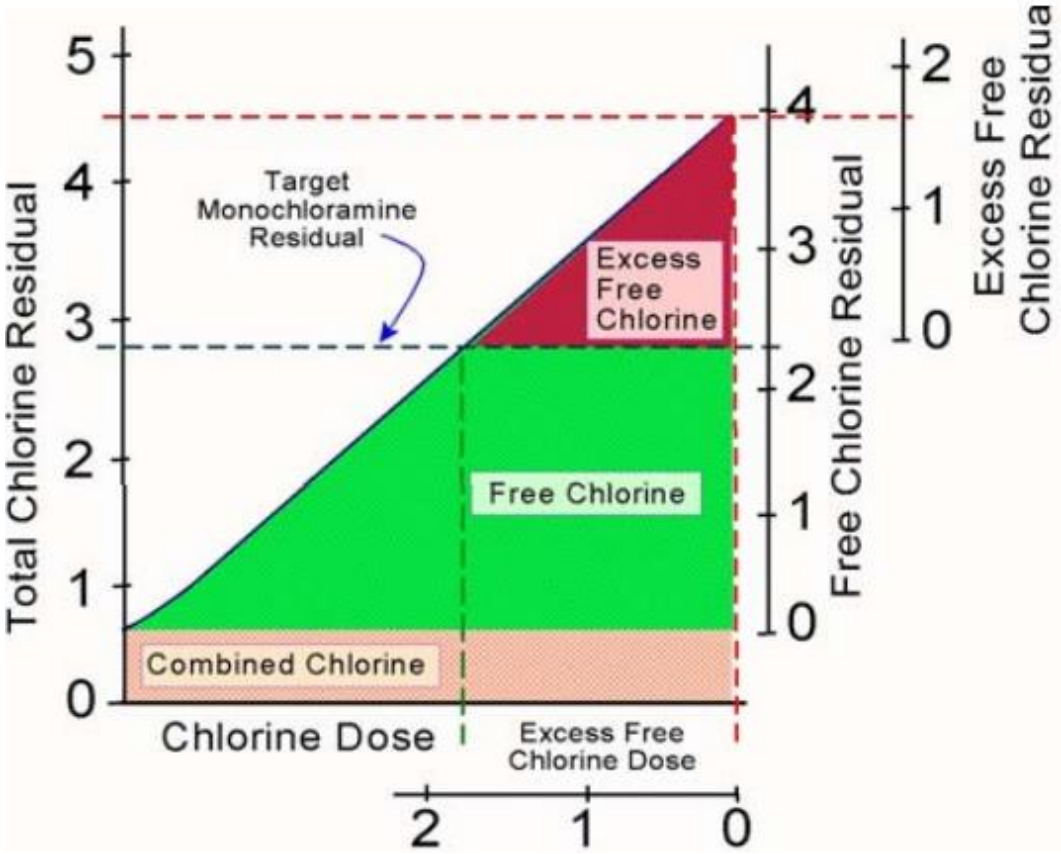


Figure 26. Conditions for Scenario 1 at the beginning of the process.

<u>Question 1: What does the data tell us about our conditions?</u>

The data indicates that:

1. Our current chlorine dose produces a free chlorine residual that is 1.7 mg/L higher than our target monochloramine level.
2. We will need to lower the chlorine feed rate enough to drop the free chlorine residual to our 2.3 mg/L monochloramine target.
   As the curve indicates, there is a 1:1 relationship between chlorine dose and residual once we have reached breakpoint.
   Therefore, a 1.0 mg/L change in chlorine dose results in a 1.0 mg/L change in the free chlorine residual.
3. Our total chlorine residual is 0.6 mg/L higher than our free chlorine residual.
4. If we make the right adjustments, the total chlorine residual will probably remain about 0.6 mg/L higher than our monochloramine residual because:

a. Although the total chlorine test kit measures all forms of chloramines (including some organic chloramines), the monochloramine test kit only measures monochloramine;

b. The combined chlorine will contain very little mono chloramine since the monochloramine and free chlorine cannot coexist; and

c. Adding ammonia does not affect the combined chlorine that formed during the breakpoint chlorination process.

<u>Question 2: What will happen if we reduce our chlorine dose by 1.7 mg/L?</u>

When we reduce the chlorine dose:

1. Our free chlorine residual will drop from 4.0 mg/L to 2.3 mg/L (our target monochloramine residual).
2. Our total chlorine residual will drop from 4.6 mg/L to 2.9 mg/L (because the combined chlorine that was formed during breakpoint chlorination will still be there).
   In essence, we want to slide back down the free chlorine part of the breakpoint curve until we reach our 2.3 mg/L free chlorine target.

In essence, we want to slide back down the free chlorine part of the breakpoint curve until we reach our 2.3 mg/L free chlorine target.

Figure 27 shows the graphic view of what this would look like on the breakpoint curve. (Note that the left vertical axis is total chlorine, and the right vertical axis is free chlorine.)

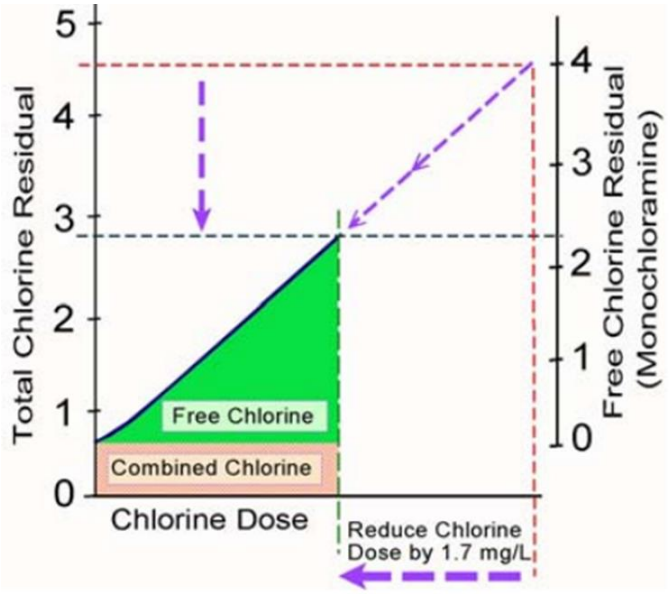


Figure 27. Scenario 1—reducing the free chlorine dose, how that changes the breakpoint curve.

Question 3: What will happen if add the right amount of ammonia after reducing our chlorine dose by 1.7 mg/L?

Once we add the right amount of ammonia:

1. Our 2.3 mg/L of free chlorine will combine with the ammonia to form 2.3 mg/L of monochloramine;
2. Our total chlorine residual will remain at about 2.9 mg/L because all we did was convert the free chlorine to monochloramine and the total chlorine tests measures both kinds of molecules; and
3. In theory, our free chlorine residual will drop to 0.0 mg/L or so because it will be reacting with the ammonia to form monochloramine.
   (In the real world, we often get a positive free chlorine test because monochloramine will interfere with the DPD method and give a false positive reading. Measuring free chlorine is NOT essential for managing chloramines IF you maintain a stable monochloramine residual.)

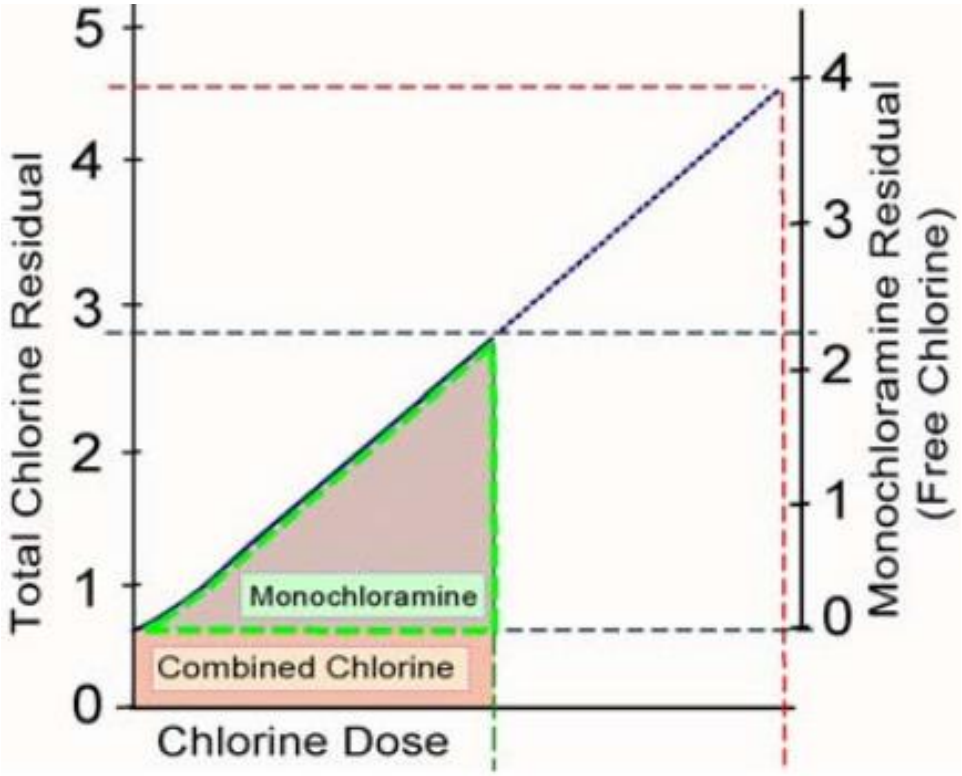


Figure 28. Scenario 1—Adding the right amount of ammonia to tie up 2.3 mg/L of chlorine, how that changes the breakpoint curve.

Question 4: What will happen if add the too much ammonia after cutting our chlorine dose by 1.7 mg/L?

In this case, chlorine is the "limiting reactant" because we will run out of free chlorine before all the ammonia has reacted. Therefore:

1. We will get the same total chlorine and monochloramine residuals we would get if we hadn't fed too much ammonia;
2. We will have unreacted ammonia which means that:
    a. We could end up having a problem with biofilm in the distribution system because some bacteria use free ammonia as a food source,
    b. If a biofilm bacteria get established, we could have trouble maintaining a chloramine residual in distribution because the bacteria exert a chlorine demand and can be difficult to completely eliminate; and
3. We extend the breakpoint curve (or more accurately, extend a new breakpoint curve) so that both the total chlorine and monochloramine residuals would go up if we add more chlorine. How far up the curve we could go depends on how much excess ammonia we put in and then how much additional chlorine we apply to form additional chloramine.

Figure 29 shows what this would look like on the breakpoint curve.

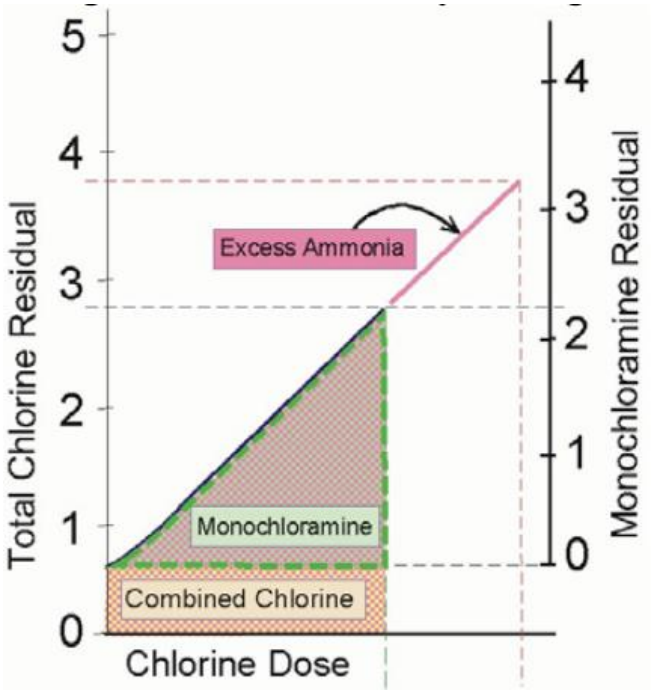


Figure 29. Scenario 1—Adding more ammonia than needed, how that changes the breakpoint curve.

Question 4b: Why does adding ammonia effectively begin a new breakpoint curve?

As soon as we consume all of the available free chlorine, we have basically created a new Section 2 of the breakpoint curve (on page 7) because we have created an additional chlorine demand. However, in this case:

1. There should be no chlorine demand due to readily-oxidizable compounds because they will have been completely oxidized when first added chlorine; and
2. There should be very little demand from organic ammonia since it was satisfied when we went through breakpoint the first time; and
3. Therefore, a 1.0 mg/L increase in the chlorine dose should produce about a 1.0 mg/L increase in the total chlorine and monochloramine … at least until we run out of either chlorine or ammonia. In the real world, we may find that we have to add slightly more than 1.0 mg/L of chlorine to produce 1.0 mg/L of monochloramine because competing reactions (such as dichloramine formation) will consume some of our chlorine.

Figure 30 shows what this would look like on the breakpoint curve.

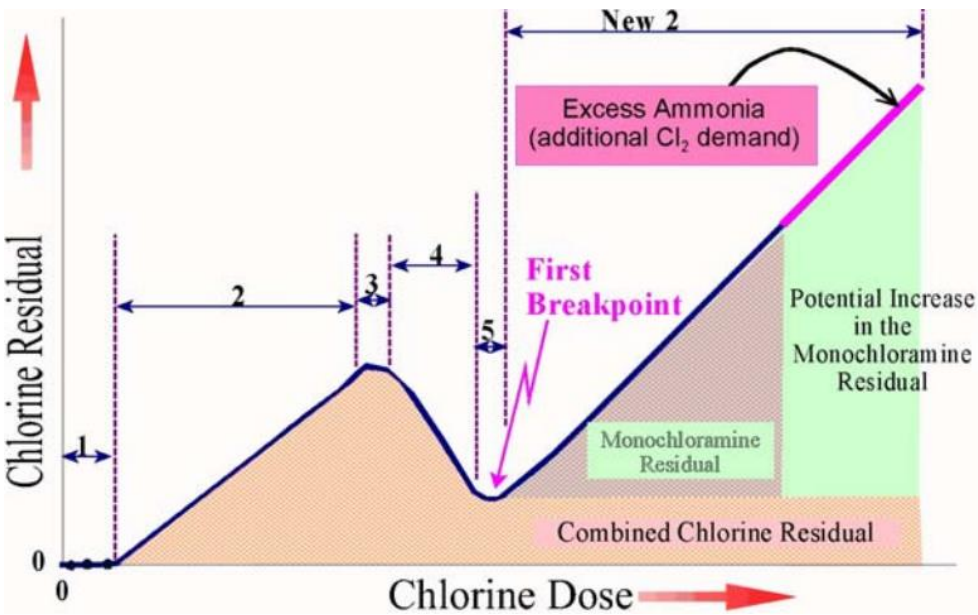


Figure 30. Scenario 1—Adding more ammonia than needed creates a new breakpoint curve.

Question 5: What will happen if we do not lower the chlorine feed rate but add enough ammonia to tie up all the free chlorine?

Three things will happen if we add enough additional ammonia to tie up all the free chlorine,

1) The monochloramine residual will rise to about 4.0 mg/L as the free chlorine reacts with the ammonia;
2) The free chlorine residual will drop to almost 0.0 mg/L at the same rate that the monochloramine residual increases (because 1.0 mg/L of free chlorine turns into 1.0 mg/L of monochloramine); and
3) The total chlorine residual will remain at about 4.6 mg/L since total chlorine test measures both combined chlorine and monochloramine.

If we added even more ammonia, we'd end up with the potential for extending the breakpoint curve just as we did in Question 3. However, this extension would begin at the 4.0 mg/L monochloramine point because that's where we ran out of chlorine.

Figure 31 shows the graphic view of what this would look like on the breakpoint curve. (Note that the left vertical axis is total chlorine, and the right vertical axis is monochloramine.)

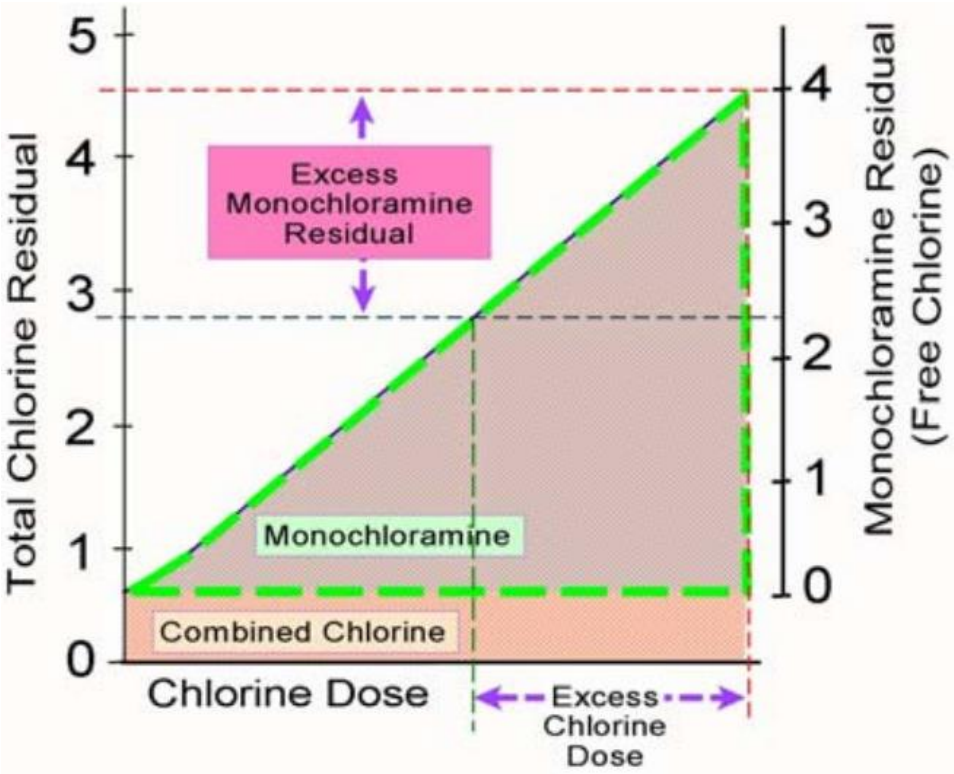


Figure 31. Scenario 1—Leaving the chlorine addition at 4.6 mg/L and adding enough ammonia to form monochloramine from all that chlorine —how that appears on the breakpoint curve.

Question 6: What will happen if we don't reduce the chlorine feed rate before we add the right amount of ammonia?

In this case, ammonia becomes the "limiting reactant" because we will run out of ammonia before all of the chlorine has reacted. However, as we discussed previously, monochloramine and free chlorine cannot coexist at any significant concentration for a significant period of time because the excess chlorine will react with monochloramine to form di- and trichloramine. Therefore, if the we add the proper amount of ammonia without reducing the chlorine dose, we will probably see several things happen. Initially, we will find that:

1. The free chlorine level will rapidly drop from 4.0 mg/L to 1.7 mg/L as it reacts quickly with the free ammonia; and
2. The monochloramine level will simultaneously rapidly rise to our target level (of 2.3 mg/L) as the ammonia and chlorine react.

Figure 32 shows how this results in an excess of free chlorine available for further reaction to monochloramine.

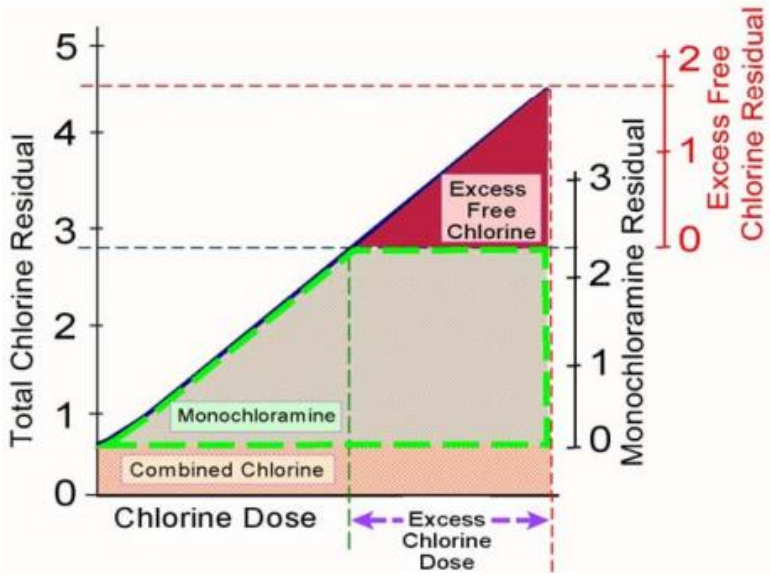


Figure 32. Scenario 1—Excess free chlorine.

Since monochloramine and free chlorine cannot coexist to any significant degree, chemical reactions will continue until all (or almost all) of the free chlorine is consumed. Consequently, as the reaction continues we will see that:

3. The free chlorine level will continue to drop from 1.7 mg/L to 0.0 mg/L as it reacts with the monochloramine to form dichloramine and with the dichloramine to form trichloramine;
4. The monochloramine residual will start to fall as the excess chlorine converts it to di- and trichloramine;

5. The monochloramine residual will probably not drop to zero since we will run out of excess chorine before the mono is converted entirely to di- and trichloramine;

Using the breakpoint curve, we can see that what has happened is that we have basically flipped the “Excess Free Chlorine” part of the graph over and covered part of the “Monochloramine” section of the graph. This tells us that the free chlorine is reacting with monochloramine. (However, Figure 32 does not show the whole picture because it does not show what happens to the monochloramine once it is converted to dichloramine or trichloramine.)

Figure 33 shows getting rid of the excess chlorine.

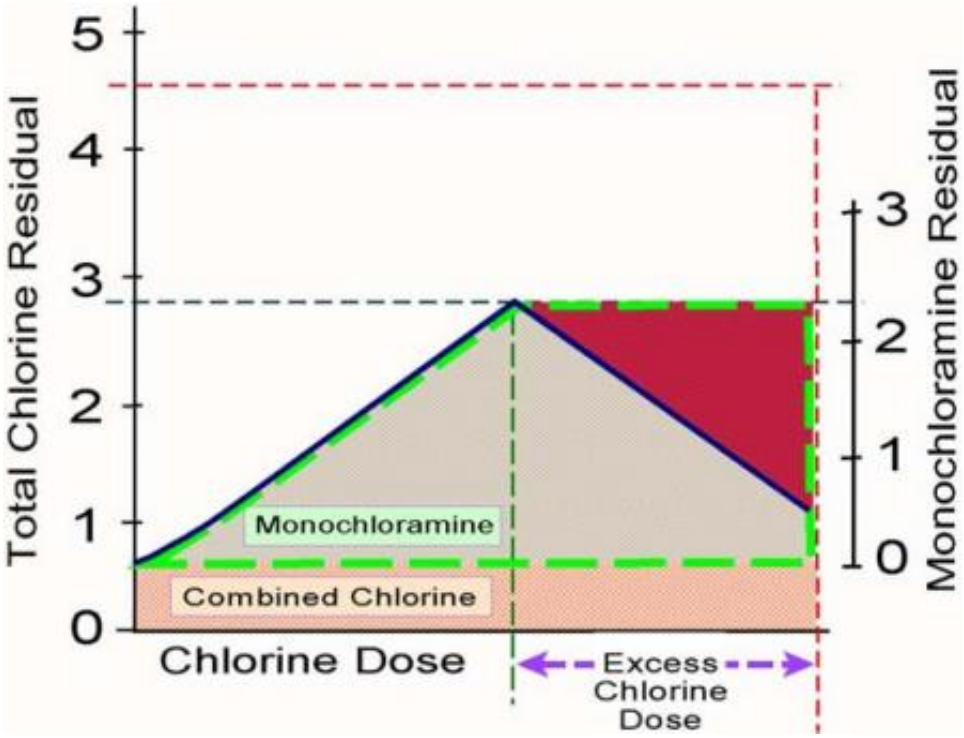


Figure 33. Scenario 1—getting rid of the excess chlorine.

In reality, we will probably see a few more things happen:

6. The point on the breakpoint curve is more rounded than pointed because the destruction of monochloramine actually begins before all the ammonia is consumed;
7. The monochloramine residual may not actually reach our target of 2.3 mg/L because of this destruction;
8. The combined chlorine level will begin to increase when the destruction of mono begins;

9. The monochloramine residual will probably fall faster than the total residual because the monochloramine test does not detect di- and trichloramine while the total test kit does; and
10. The difference between the monochloramine and total chlorine residuals will gradually increase to greater than 0.6 mg/L.

Figure 34 is shown below.

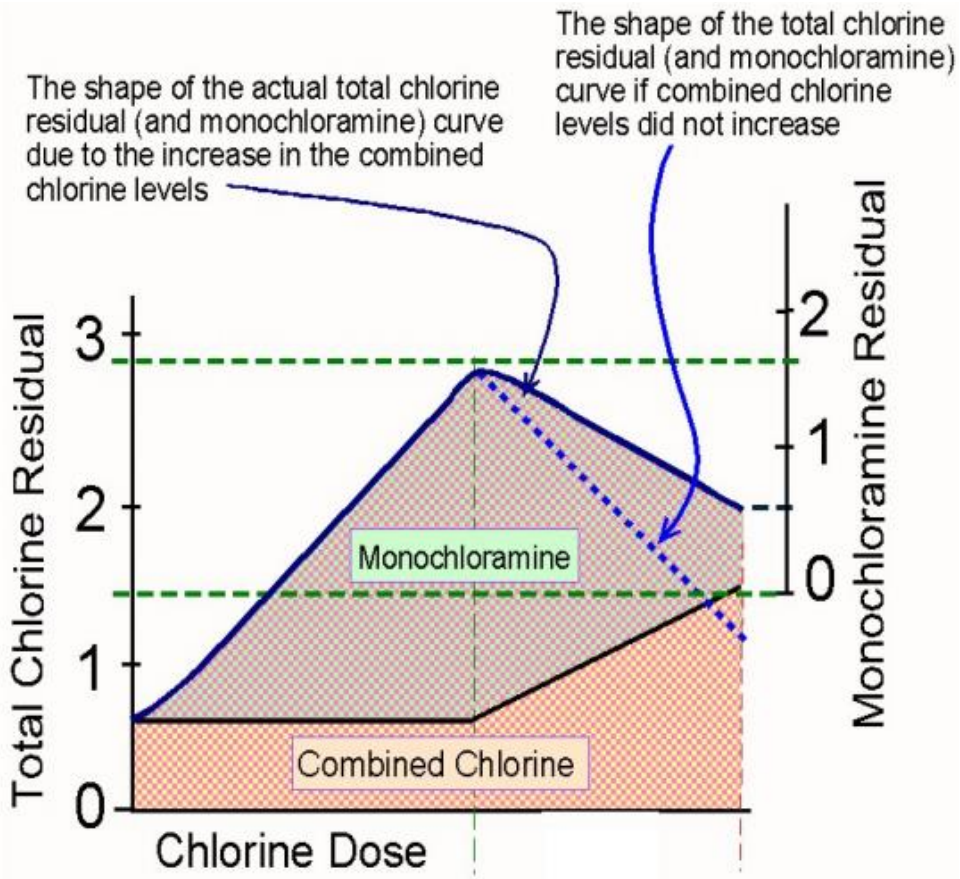


Figure 34. Scenario 1—continued.

The actual data (and therefore the shape of the curve) we get will vary based on a lot of factors that we will discuss later.

In this illustration, monochloramine destruction began long before we reached 2.3 mg/L. By the time the reaction was complete, the monochloramine residual was only 0.5 mg/L (or -1.8 mg/L) but only dropped the total chlorine to 1.5 mg/L (or -1.4 mg/L). As a result, the difference between monochloramine and total chlorine rose to 1.0 mg/L.

Scenario 2: Ammonia is added before chlorine

Ammonia may be added before chlorine for booster plants.

Also, some raw water has a significant amount of naturally-occurring free ammonia—this scenario applies to that situation, too.

NOTE: This is the sequence that chlorine and ammonia should be applied if you are boosting the disinfectant residual in water that has already been treated with free chlorine, chlorine dioxide, or ozone. It should not be used to disinfect untreated water.

In the second scenario, we—or our treated water wholesaler—used pre-chlorine, pre-chlorine dioxide, or pre-ozone in their plant to meet the oxidant demand and establish a measurable free or total chlorine residual in the water before distribution.

Now, we just want add enough chlorine and ammonia to complete the disinfection process or to raise the chloramine level. In this case, we want to add ammonia before we add chlorine. By adding ammonia first, we minimize the chance the chlorine we are adding will react with (destroy) the monochloramine that we are forming or that is already in the water.

Figures 35a and 35b show the difference between adding chlorine (to raw water with insignificant free ammonia) first versus boosting with ammonia first.

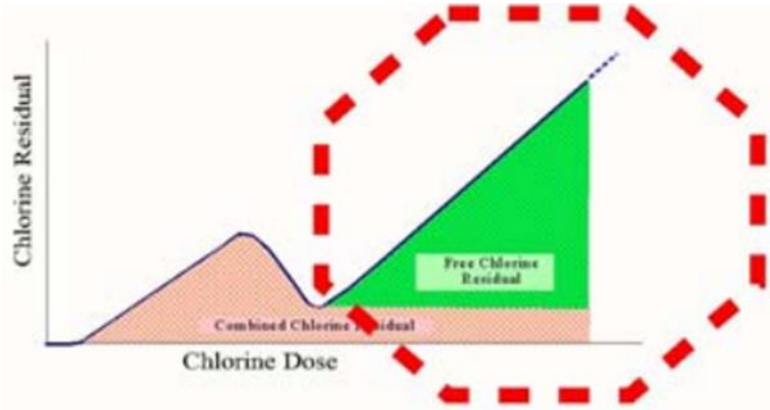


Figure 35a. Free chlorine added to water with no significant free ammonia.

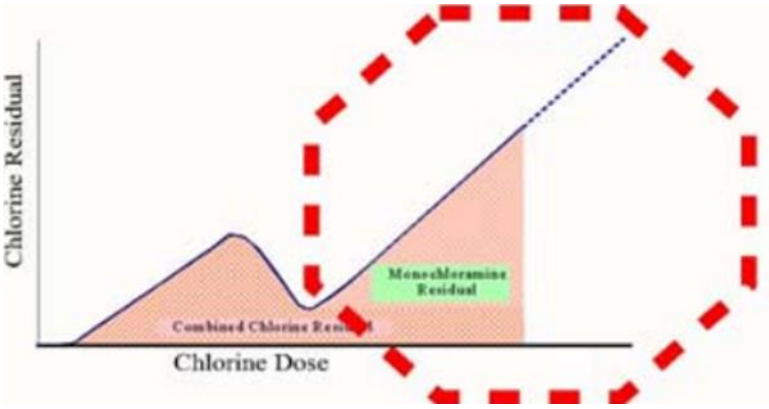


Figure 35b. Ammonia added to water that contains an existing monochloramine residual (plus possibly free ammonia).

Scenario 2 conditions

In this scenario, let's assume that we want to achieve a monochloramine residual of about 2.3 mg/L. (Note—this scenario uses a Cl2:NH3 ratio, NOT a Cl2:NH3-N ratio)

Current operations produce the following data:

- Total chlorine = 2.3 mg/L
- Free chlorine = 0 mg/L
- Monochloramine = 1.6 mg/L
- Free ammonia = 0.2 mg/L as NH_3

The first question we need to ask ourselves is: Do we need to add more ammonia or is there already enough present to get us to our target monochloramine residual of 2.3 mg/L if we just add chlorine.

This is a question is similar to the one that we should have asked ourselves in Scenario 1. What is "the right amount of ammonia for a 2.3 mg/L free chlorine residual"?

The second question we need to ask ourselves is: Once we have the right amount of ammonia, how much chlorine do we need to add to reach our target monochloramine residual?

To answer these question in practical terms, we need to understand the difference between molecular-based measurements (such as the chemical equations shown on in Chapter 1, and weight-based units that we use at the plant on a daily basis.

Our assumptions are:

1. We are adding ammonia before chlorine because the water has already gone through breakpoint chlorination;

2. We want to achieve a monochloramine residual of about 2.3 mg/L or so; and
3. Current operations produced the following data:

Total chlorine	= 2.3 mg/L
Free chlorine	= 0 mg/L
Monochloramine	= 1.6 mg/L
Free ammonia	= 0.2 mg/L as NH_3 (Note: this example uses the Cl_2:NH_3 ratio).

We need to answer these two questions:

1. Is there already enough ammonia present to get us to our target monochloramine residual of 2.3 mg/L if we just add chlorine or do we need to add more ammonia?
2. Once we have the right amount of ammonia, how much chlorine do we need to add to reach our target monochloramine residual?

To answer these questions, we need to remember that 1.0 mg/L of chlorine (as Cl2) will produce 1.0 mg/L of monochloramine (as Cl2) if we have enough ammonia present. Therefore, we will need to add about 0.7 mg/L of chlorine raise our monochloramine level from 1.6 mg/L to 2.3 mg/L.

We also need to remember that the chemical monochloramine reaction involves one chlorine molecule and one ammonia molecule. Since chlorine (measured as Cl2) molecules have a molecular weight of 71 and ammonia (NH3) molecules have a molecular weight of 17, the chlorine:ammonia ratio (Cl2:NH3) is 71:17, or 4.2:1.

To find out if we have enough ammonia present, we divide the amount of chlorine we need to add by our chlorine:ammonia (Cl2:NH3) ratio. As the equation below indicates, we'll need about 0.17 mg/L of free ammonia (as NH3) to react with the chlorine we add if there are no competing reactions.

Therefore, if there are no competing reactions, we will need to add 0.7 mg/L of chlorine and no ammonia to reach our 2.3 mg/L monochloramine target.

After we add the chlorine, we expect to get the following results:

- Total chlorine = 3.0 mg/L
- Free chlorine = 0.0 mg/L
- Monochloramine = 2.3 mg/L
- Free ammonia = 0.03 mg/L as NH_3

Because:

1. Adding the chlorine should also raise our total chlorine residual by 0.7 mg/L (since the total chlorine test kit will detect monochloramine),

2. The combined chlorine level will remain 0.7 mg/L (since we didn't form any dichloramine or trichloramine), and
3. Consuming 0.17 mg/L of our free ammonia should leave us with an ammonia level of about 0.03 mg/L (which we may not be able to see since it is near the lower detection limit of our test kit)

All of these parameters (monochloramine residual, change in total chlorine, and free ammonia level) fall within our desired parameters. Now we have our starting point for making feed rate adjustments.

Activity:
Surface water treatment plant dosing evaluation (optional)

To identify whether your dosing is working as you want it to, you can evaluate it using this dosing activity. However, this is probably too time-consuming to do while you are working through this DAM for the first time.

In this activity, you will evaluate the actual conditions at the plant. ***Depending on how big the plant is, this may take several hours to a day or more.***

Procedure:

1. Select an application point where there are currently upstream and downstream sample taps/sites. (Note: If possible, utilize an application point where it will be possible to evaluate a change in operating conditions. An optimum application point would allow detection of a change in the downstream tap within about 15 minutes of a feed-rate adjustment.)
2. Identify appropriate performance targets for total chlorine, monochloramine, and free ammonia that are applicable to the selected application point.
3. Evaluate the results and determine what adjustments should be made to the chlorine and ammonia feed rates.
4. Make any necessary adjustments to the chlorine and ammonia feed rates.
5. Collect a sample from two application point sample taps and the sample tap at the point of entry to the distribution system.
6. Run the laboratory analysis for free chlorine, total chlorine, monochloramine, and free available ammonia.
7. Identify and correct any sampling or analytical errors observed.
8. Verify the accuracy of the calculations.
9. If a feed rate change is needed, ensure that the change is made properly.
10. Identify appropriate performance targets (total chlorine, free chlorine, monochloramine, and free ammonia) that are applicable to the remainder of the current application and monitoring points.
11. Verify the impact on the treatment process by running another set of samples from the upstream and downstream sample taps.
12. Interpret the second set of data and assess the impact adjustments were made to the chlorine and ammonia feed rates.

Optimization

For a plant with challenges, or operators who want to optimize treatment, future work is recommended. This can be accomplished as a self-directed activity, or by requesting additional assistance from the TCEQ's FMT assistance program at 512-239-4691.

Chapter 5 Review Questions

There are no Chapter 5 review questions.

Chapter 5 checklist

Part 1. Process Management Loop

- Do you understand the Process Management Loop?
- Have you used the 11-step process or Chloramine Spreadsheet to help figure out the right dosing strategy?
- Can you troubleshoot any dosing issues you are having?

Part 2. Breakpoint visualizations

- Can you use your understanding of the breakpoint curve to evaluate whether your chemical dosing strategy is optimized?
- Can you apply the Process Management concepts to your breakpoint curve visualizations?

Follow up:

If you are successfully applying the concepts to your dosing strategy—good for you.

Recommended actions?

If you need to do further study to successfully dose chloramines, make a plan for how you are going to do that and note it on your Plan of Action.

Wrapping it up:

Final thoughts

We have gone through a lot of material today, and hopefully it will help you be successful at achieving stable, adequate chloramine levels.

To finish up the day, we will:

- Do the Post-Test,
- Review the answers,
- Complete an evaluation of the training, and
- Double check our Plan of Action to address any future needs.

Next step: NAP

The work we did today included the first steps in creating the system's required NAP. There is a second DAM for finishing the NAP: **"DAM 8: CREATING A NITRIFICATION ACTION PLAN (NAP) FOR A PUBLIC WATER SYSTEM (PWS)."** You can ask your instructor about scheduling that DAM, or contact the TCEQ Water Supply Division at 512-239-4691 to schedule it.

Post-test

When you do the Post-test, notice the answers that come to you more easily than they did in the morning on the Pre-test. If there are still unclear concepts, plan on how you will get more information.

Training evaluation

Please fill out the training evaluation form with recommendations to TCEQ on how we can keep making this DAM better for you. TCEQ staffers really do read your comments and try to incorporate your ideas in future versions.

Plan of Action

At the end of the day, everyone just wants to go home—but take a minute or two to list actions you will take to:

- Achieve more stable chloramines,
- Learn more, and
- Help others to learn more.

Thanks!

And good luck in your future endeavors.

Notes

Attachment 1: Chemicals of interest

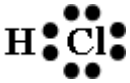
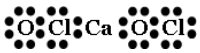
This is not an exhaustive list of chemicals, but includes some that are used in the context of chloramination.

Note regarding Lewis structure:

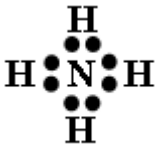
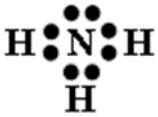
The Lewis structure is a way of drawing chemicals with dots for electrons. A modified form is used in the table below, with dots for electrons, dots with a **"+"** sign indicating holes where an electron is needed to balance the charge, and dots with a **"-"** sign indicating extra electrons that cause a charge on the molecule or atom

Chemical Name	**Chemical Formula**	**Description**
Water species		
Water	H_2O	Water (H_2O) is necessary for life as we know it—humans must consume water to remain alive. Water is mostly H_2O, but small amounts of other chemicals are almost always present in it—and that can make things complicated. It is called the universal solvent—though it does not dissolve everything.
Hydrogen ion	H^+	The hydrogen ion (H+) is the smallest chemical—just one lonely proton, no neutron, no electron. It is positively charged (missing its only electron). The concentration of hydrogen ions defines pH: If there are lots of H+, a water solution is called acidic, and the pH is low. If there are very few H+, the water is basic (alkaline), and the pH is high. In the picture, the dot with the "+" sign on it is basically saying—"I lost my electron, now my one proton's positive charge is what you see".

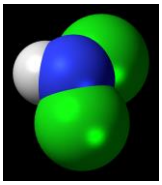
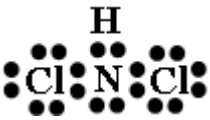
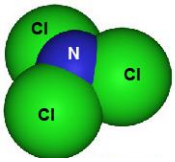
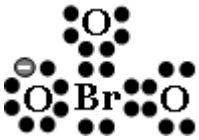
Chemical Name	Chemical Formula	Description
Hydroxide ion	OH-	The hydroxide ion (OH-) is what's left when you take a proton off of water. It is negatively charged (has an extra electron it stole from hydrogen) The concentration of hydroxide ion is the inverse of the concentration of hydrogen ion (protons). If there are lots of OH- in water, the solution is basic, and the pH is high. If there are very few OH- in water, it is acidic, and the pH is low. In the picture, the dot with the "-" is saying "I have an extra electron, so I am negative."
Chlorine species		
Chlorine (elemental)	Cl	You don't find a single (uncharged) chlorine atom running around loose. Chlorine (Cl) is the most electronegative element, so it is extremely reactive—when you find it in the environment, it will have reacted with something and **not** be present as just Cl. It really wants one more electron to fill its outer ring (valence) up to eight electrons.
Chlorine (gas)	Cl_2	Chlorine gas exists as Cl_2. It is very common for PWSs to use chlorine gas to form chloramines. Chlorine gas has 100% available chlorine, which makes the dosing math easy.
Chloride (ion)	Cl^-	If you run into a single chlorine atom in water, it won't be alone—it will have picked up an electron from somewhere and be floating around in its ionic form: chloride (Cl-). The minus charge is what tells you it has an extra electron to make it stable. High chloride (>300 mg/L) can make water taste salty.

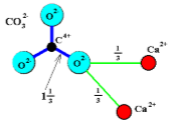
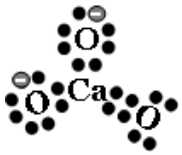
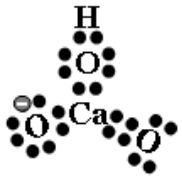
Chemical Name	Chemical Formula	Description
'Free chlorine'	Not a specific chemical	The "free chlorine" is a measure of the amount of chlorine gas (Cl_2) that would yield the same oxidizing power as the HOCl/ClO^- in solution. It is not a specific chemical—it is the sum of HOCl and ClO- (and dissolved Cl_2, if the pH is less than 4).
Hypochlorous acid	HOCl 	When chlorine is in water, it is in two forms: hypochlorous acid (H OCl) and hypochlorite ion (OCl-). Hypochlorous acid dominates below pH 7.5 and is the desired form for disinfection strength.
Hypochlorite ion	OCl^- 	When chlorine is in water, it is in two different forms: hypochlorous acid (H OCl) and hypochlorite ion (OCl-). Hypochlorite ion is the weaker disinfection and dominates above pH 7.5.
Hydrochloric acid	HCl 	Hydrochloric acid (HCl) is a strong acid made of the H+ and Cl-. It exists in solution with water, not as a solid. In water, it is dissociated into hydrogen ion (H+) and chloride (Cl-).
Sodium hypochlorite	NaOCl 	Sodium hypochlorite solution ($NaOCl_{aqueous}$) is bleach. When used for disinfection at PWS's it is often called 'hypo.' It is sold as a 5% to 12.5% solution in water—but it degrades, so it may not be as strong as it says on the label. It is a strong base, so it can increase pH in some waters. In water, it disassociates rapidly into sodium ion (Na+) and hypochlorite ion (HOCl-).
Calcium hypochlorite	$Ca(OCl)_2$ 	Calcium hypochlorite ($Ca(OCl)_2$) is usually sold as powder or pellet. It is basically also bleach. It is more stable and has more available chlorine than sodium hypochlorite. In water, it disassociates rapidly into calcium (Ca+) and two hypochlorite ions (2 HOCl-).

Ammonia species

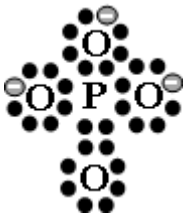
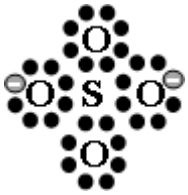
Chemical Name	Chemical Formula	Description
Ammonia	NH_3+	In water, ammonia and ammonium are in equilibrium. In water at pH less than 9.26 Ammonium (NH4) dominates; at pH greater than 9.26, ammonia (NH3+) dominates. Ammonia
Ammonium	NH_4 	In water, ammonia and ammonium are in equilibrium. In water at pH less than 9.26 Ammonium (NH4) dominates; at pH greater than 9.26, ammonia (NH3+) dominates. Ammonia
Anhydrous ammonia	NH_3 (gas) 	Anhydrous ammonia is the gas form of ammonia (NH3), sold as a pressurized liquid, with 100% available ammonia. It is a colorless, odorless, extremely reactive and dangerous gas. The term 'anhydrous' stresses the point that no water is present.
Liquid ammonium sulfate (LAS)	$(NH_4)_2SO_4$	LAS is a liquid and is the most common chemical that PWSs use to make chloramines. It has 30 to 40% available ammonium. It is a stable, moderately hazardous, water-based liquid. In water, LAS dissociates immediately into two ammonium ions (NH_4^-) and one sulfate ion (SO_4^{2-}).
'Free ammonia'	Not a specific chemical	'Free ammonia' is a measurement of sum of ammonia (NH_3) and ammonium ion (NH_4^+) in water, measured as mg/L nitrogen (N_2). It does not include any ammonia/ammonium that is part of organic molecules—like proteins in bacteria. That 'organic ammonia' can't participate in the chloramine reactions. Only 'free ammonia' can.

Chloramine species

Chemical Name	Chemical Formula	Description
Monochloramine	NH_2Cl	Monochloramine (NH_2Cl) is the desired chemical when using chloramines for disinfection. It is a long-lasting disinfectant often used in drinking water distribution systems.
Dichloramine 	$NHCl_2$ 	Dichloramine ($NHCl_2$) is an undesirable member of the chloramine family that forms when the chlorine-to-ammonia-nitrogen (Cl2:NH3-N) ratio is wrong.
Trichloramine 	$NHCl_3$	Triichloramine ($NHCl_3$) is a very undesirable member of the chloramine family that forms, then decays rapidly, when the chlorine-to-ammonia-nitrogen (Cl2:NH3-N) ratio is very wrong.
Other disinfectants		
Chlorine dioxide	ClO_2	Chlorine dioxide (ClO_2) is a useful disinfectant because it does not form regulated trihalomethanes and haloacetic acids. It does not have a stable residual so it is not used in distribution systems.
Chlorite (ion)	ClO_2^-	Chlorite (ClO_2^-) is an undesirable side effect of using chlorine dioxide for disinfection. it is a regulated disinfection byproduct that can cause acute respiratory effects.
Ozone	O_3	Ozone (O_3) is a highly reactive disinfectant sometimes used in surface water treatment plants. It does not have a stable residual so it is not used in distribution systems.
Bromate (ion)	BrO_3^- 	Bromate (BrO_3^-) is an undesirable side effect of using ozone for disinfection if there is bromide in the source water. It is a regulated disinfection byproduct and known carcinogen.
Ultraviolet (UV) light	UV light is photons, not chemicals	Ultraviolet (UV) light can be used to disinfect clear water.

Chemical Name	Chemical Formula	Description
		It does not have a residual, so it can't be used for distribution system disinfection.
Other chemicals		
Calcium, Divalent calcium (ion)	Ca Ca^{2+} 	In water, calcium is usually present as a 'divalent cation' meaning it has lost its two outer electrons and has 2 positive charges. (Lots of metals or minerals do this). Calcium can react with other stuff in water—particularly things with a negative charges. (The "+" signs on the ion show where an electron would go, but it is not there to balance the charge of the protons in the nucleus.)
Calcium carbonate	Ca_2CO_3 	Calcium carbonate is one of the main chemicals in pipe scale. It tends to be a whitish, chalky, hard solid—darker when mixed up with a lot of rust, mud, manganese, etc.
Carbonate (ion)/ Bicarbonate (ion)	CO_3^{2-}  HCO_3^- 	Carbonate ion is in equilibrium with bicarbonate (which we are supposed to call hydrogen carbonate) in water. They are dissolved—but if the concentration gets too high, and the pressure is lowered—you get bubbles of carbon dioxide.

Chemical Name	Chemical Formula	Description
Carbon	C	Carbon is a fundamental building block of organic things—like people. Organic carbon comes in so many forms it is difficult to describe or list what it might look (or smell) like. Inorganic carbon is easier to describe. For example, granular activated carbon (and powdered activated carbon) are brittle, black solids with the molecular form C_4. In air, carbon monoxide (CO) and carbon dioxide (CO_2) are inorganic forms of carbon. In water, inorganic carbon is present as carbonate (CO_3^{2-}) and all the various ions formed with carbonate, such as calcium carbonate—see 'pipe scale'.
Hydrogen	H	Hydrogen (H) is the most abundant element in the universe. It is found in the sun and most of the stars. It is the most common element in the universe by number but not by mass, because it is the lightest element. On Earth, hydrogen is found in its greatest quantities in the form of water. Hydrogen is the first chemical on the periodic table, with an atomic weight of 1. Hydrogen exists as hydrogen gas (H_2 in air, for example) or as positively charged ions (H+) in water.
Hydrogen (gas)	H_2	Hydrogen gas (H_2) is a colorless, odorless, flammable gas. It blows up pretty easy, so it is not used much in the drinking water industry. Maybe someday our flying cars will run on hydrogen gas.
Hydrogen sulfide (gas)	H_2S	Hydrogen sulfide (H_2S) is a gas that can be present underground—thus in well water. It is mainly of interest in drinking water treatment because it smells like 'rotten eggs' and people complain about it.

Chemical Name	Chemical Formula	Description
Oxygen	O	Oxygen (O) does not hang around loose in the environment we work in… it is unstable and wants to react add 2 electrons to fill its outer ring (valence) with 8 electrons.
Oxygen gas	O_2	Oxygen gas (O2) makes up 21% of the air we breathe. It dissolves in water, where aquatic animals can also 'breathe' it through their gills. It is a colorless, odorless gas. Surface water treatment plants that use ozone sometimes have tanks of condensed oxygen gas to make ozone out of.
Phosphate (ion)	PO_4^{3-} 	Phosphate ion (PO_4^{3-}) is a trace element for plant and animal growth. PWSs may feed some form of phosphate for corrosion control or to sequester iron/manganese.
Sodium, Sodium ion	Na, Na+	When sodium (Na) is present in water it is generally always in the form of sodium ion (Na^+).
Sulfate (ion)	SO_4^{2-} 	Many sulfate (SO_4^{2-}) salts are highly soluble in water. They combine with positive ions (cations) to form salts. Excessive sulfate in water can cause 'travelers disease'—temporary diarrhea.

Chemical Name	Chemical Formula	Description
Other parameters		
Alkalinity	Not a specific chemical	Alkalinity is not just one chemical. Alkalinity refers to the capability of water to neutralize acid. This is really an expression of buffering capacity. A buffer is a solution to which an acid can be added without changing the concentration of available H+ ions (without changing the pH) appreciably. These include hydroxides, carbonates and bicarbonates. Alkalinity is measured "as mg/L $CaCO_3$" just like hardness even though it is totally different than hardness. Think of alkalinity as the CO_3^{2-} part of the $CaCO_3$.
Hardness	Not a specific chemical	Hardness is not just one chemical. The simple definition of water hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, both calcium and magnesium. The reason it is called 'hard' is because it is hard to get soap to foam in hard water. Hardness is measured as "mg/L of $CaCO_3$" just like alkalinity—even though it is totally different from alkalinity. You can think of hardness as the Ca^{2+} part of the $CaCO_3$.
pH	pH units, (related to H+ concentration)	pH is defined as the negative log concentration of hydrogen ions (protons) in water. It does not have a definition in any other context—for example, you can't say "My couch is pH 7."
Total dissolved solids	Not a specific chemical	Total dissolved solids (TDS) is not just one chemical. "Dissolved solids" refer to any minerals, salts, metals, cations, and anions dissolved in water. TDS measures all of the inorganic salts: mainly calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates; and some small amounts of organic matter that are dissolved in water.

Chemical Name	Chemical Formula	Description
Conductivity	Not a specific chemical	Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water. Conductive ions come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds. Therefore—conductivity is directly related to total dissolved solids (TDS): Conductivity = 2 x TDS
Temperature	Not a specific chemical	Temperature is important—clearly ice is very different than boiling water. More importantly for drinking water distribution is that reactions happen faster in warm water. For example, in warm water: • chlorine decays faster, • bacteria grows faster, and • corrosion is more rapid.

Chemical equilibria

Several chemical processes discussed in this DAM are 'equilibrium' reactions.

Generally, for equilibrium, the ratio of the molar concentrations of products to reactants is a constant (ignoring possible constants that the concentrations may be raised to in higher order reactions):

K = [Products] / [Reactants]

In order for this ratio to stay constant, if the concentrations of [Reactants] goes down, then the concentrations of [Products] will go down. That just makes sense, if there is less reactant available, then it is logical that we won't form as much product.

For monochloramine:

$K = [NH_2Cl] / [HOCl] * [NH_3]$

Attachment 2: Parts per million

Except for a few cases (usually involving proprietary liquid coagulants), we should always describe our chemical dose on a weight-to-weight (w/w) basis. Since we are dealing with relatively low chemical levels, we usually describe our chemical dose in terms of parts of chemical per million parts of water (ppm). For example, we often describe the dose in terms of pounds of chemical per million pounds of water or milligrams of chemical per million milligrams of water (which is the same as mg/L since one liter of water weighs a million milligrams).

Proof that 1 mg/L = 1 ppm (in water)

It is important to understand that, on a weight-basis,

1 ppm = 1 lb per 10^6 lbs = 1 mg/L as shown below:

By definition, 1 ppm (w/w) = 1 pound of chemical per million (10^6) pounds of water.

Where 1.0 lb = 454 g

Therefore,

1 ppm = 454 g per 10^6 lbs of water.

Where 1.0 g = 1,000 mg

Therefore,

454 g per 10^6 lbs of water = 454,000 mg per 10^6 lbs of water

1.0 gallon of water weighs 8.34 lbs

Therefore,

10^6 lbs of water = 1,000,000/8.34, or 119,900 gallons of water

And therefore,

454,000 mg per 10^6 lbs of water

= 454,000 mg per 119,900 gallons of water

1.0 gallon = 3.785 L

Therefore,

454,000 mg per 119,900 gallons of water

= 454,000 mg per 454,000 L of water,

or 1.0 mg/L

and we just proved that **1.0 ppm = 1 lb/106 lbs = 1 mg/L**

Although we can also use the term “ppm” to describe a volumetric dose (such as gallons of liquid chemical per million gallons of water), we should probably avoid that approach since liquid chemicals are usually dilute solutions of a pure chemical and we need to know what our actual chemical dosage is rather than the solution dosage we are applying.

Attachment 3: Applicable Rule Language

***Disclaimer**: This Appendix copies the regulatory requirements of Title 30, Texas Administrative Code (30 TAC) Chapter 290, relating to chloramines. Should there be any inadvertent discrepancy between this Appendix and the rules of 30 TAC Chapter 290, the rules shall apply.*

The following rule language is provided to support TCEQ's Directed Assistance Module 5: Process Management for PWSs using Chloramines. The rules include:

- Laboratory requirements, including calibration/verification and method accuracy;
- Dosing requirements, including order of addition and recommended mixing;
- Record-keeping requirements;
- Monitoring requirements; and
- Minimum and maximum residuals.

Subchapter D: Rules and Regulations for Public Water Systems

§290.38. Definitions

§290.38(6) Approved laboratory--A laboratory approved by the executive director to analyze water samples to determine their compliance with certain maximum or minimum allowable constituent levels.

§290.38(12) Certified laboratory--A laboratory certified by the commission to analyze water samples to determine their compliance with maximum allowable constituent levels. After June 30, 2008, laboratories must be accredited, not certified, in order to perform sample analyses previously performed by certified laboratories. **(NOTE: This constitutes the regulatory definition of the term "Accredited laboratory".)**

§290.38(14) Chemical disinfectant--Any oxidant, including but not limited to chlorine, chlorine dioxide, chloramines, and ozone added to the water in any part of the treatment or distribution process, that is intended to kill or inactivate pathogenic microorganisms.

…

§290.42. Water Treatment.

…

§290.42(b) Groundwater.

…

§290.42(b)(4) Appropriate laboratory facilities shall be provided for controls as well as to check the effectiveness of disinfection or any other treatment processes employed.

…

§290.42(c) Groundwater under the direct influence of surface water, springs, and other water sources.

…

§290.42(c)(3) Appropriate laboratory facilities shall be provided for controls as well as for checking the effectiveness of disinfection or any other treatment processes employed.

…

§290.42(d) Surface water.

…

§290.42(d)(15) An adequately equipped laboratory shall be available locally so that daily microbiological and chemical tests can be conducted.

§290.42(d)(15)(A) For plants serving 25,000 persons or more, the local laboratory used to conduct the required daily microbiological analyses must be accredited by the executive director to conduct coliform analyses.

§290.42(d)(15)(B) For plants serving populations of less than 25,000, the facilities for making microbiological tests may be omitted if the required microbiological samples can be submitted to a laboratory accredited by the executive director on a timely basis.

§290.42(d)(15)(C) All surface water treatment plants shall be provided with equipment for making at least the following determinations:

§290.42(d)(15)(C)(i) pH;

§290.42(d)(15)(C)(ii) temperature;

§290.42(d)(15)(C)(iii) disinfectant residual;

§290.42(d)(15)(C)(iv) alkalinity;

§290.42(d)(15)(C)(v) turbidity;

§290.42(d)(15)(C)(vi) jar tests for determining the optimum coagulant dose; and

§290.42(d)(15)(C)(vii) other tests deemed necessary to monitor specific water quality problems or to evaluate specific water treatment processes.

…

§290.42(e) Disinfection.

…

§290.42(e)(7) Chloramine disinfection shall be performed in a manner which assures that the proper chlorine to ammonia (as nitrogen) ratio is achieved in order to maintain a monochloramine residual and limit nitrification.

…

§290.42(e)(7)(E) When using chloramines, the public water systems shall provide equipment for making at least the following determinations for purposes of complying with the requirements in §290.110 of this title:

§290.42(e)(7)(E)(i) free ammonia (as nitrogen);

§290.42(e)(7)(E)(ii) monochloramine;

§290.42(e)(7)(E)(iii) total chlorine;

§290.42(e)(7)(E)(iv) free chlorine; and

§290.42(e)(7)(E)(v) nitrite and nitrate (both as nitrogen). The public water systems must either obtain equipment for measuring nitrite and nitrate or identify an accredited laboratory that can perform nitrite and nitrate analysis and can provide results to the public water systems within 48 hours of sample delivery.

…

§290.46. Minimum Acceptable Operating Practices for Public Drinking Water Systems

§290.46(f) Operating records and reports.

§290.46(f)(1) The public water system's operating records must be organized, and copies must be kept on file or stored electronically.

§290.46(f)(2) The public water system's operating records must be accessible for review during inspections and be available to the executive director upon request.

§290.46(f)(3) All public water systems shall maintain a record of operations.

…

§290.46(f)(3)(B) The following records shall be retained for at least three years:

…

§290.46(f)(3)(B)(iii) the disinfectant residual monitoring results from the distribution system;

§290.46(f)(3)(B)(iv) the calibration records for laboratory equipment, flow meters, rate-of-flow controllers, on-line turbidimeters, and on-line disinfectant residual analyzers;

…

§290.46(f)(3)(E) The following records shall be retained for at least ten years:

…

§290.46(f)(3)(E)(ii) the results of chemical analyses; *(Note: This is not generally taken to mean disinfectant chemical analyses, but instead is taken to mean the regulated suite of inorganic chemicals (IOCs) in 290.10x)*

…

§290.46(f)(3)(E)(ix) any Sample Siting Plans required by §290.109(d)(6) of this title and monitoring plans required by §290.121(b) of this title (relating to Monitoring Plans); and (Note: This

…

§290.46(s) Testing equipment.
Accurate testing equipment or some other means of monitoring the effectiveness of any chemical treatment or pathogen inactivation or removal processes must be used by the system.

…

§290.46(s)(2) Laboratory equipment used for compliance testing shall be properly calibrated.

§290.46(s)(2)(A) pH meters shall be properly calibrated.

§290.46(s)(2)(A)(i) Benchtop pH meters shall be calibrated according to manufacturer specifications at least once each day.

§290.46(s)(2)(A)(ii) The calibration of benchtop pH meters shall be checked with at least one buffer each time a series of samples is run, and if necessary, recalibrated according to manufacturer specifications.

§290.46(s)(2)(A)(iii) On-line pH meters shall be calibrated according to manufacturer specifications at least once every 30 days.

§290.46(s)(2)(A)(iv) The calibration of on-line pH meters shall be checked at least once each week with a primary standard or by comparing the results from the on-line unit with the results from a properly calibrated benchtop unit. If necessary, the on-line unit shall be recalibrated with primary standards.

…

§290.46(s)(2)(C) Chemical disinfectant residual analyzers shall be properly calibrated.

§290.46(s)(2)(C)(i) The accuracy of manual disinfectant residual analyzers shall be verified at least once every 90 days using chlorine solutions of known concentrations.

§290.46(s)(2)(C)(ii) The accuracy of continuous disinfectant residual analyzers shall be checked at least once every seven days with a chlorine solution of known concentration or by comparing the results from the on-line analyzer with the result of approved benchtop method in accordance with §290.119 of this title.

§290.46(s)(2)(C)(iii) If a disinfectant residual analyzer produces a result which is not within 15% of the expected value, the cause of the discrepancy must be determined and corrected and, if necessary, the instrument must be recalibrated.

§290.46(s)(2)(D) Analyzers used to determine the effectiveness of chloramination in §290.110(c)(5) of this title shall be properly verified in accordance with the manufacturer's recommendations every 90 days. These analyzers include

monochloramine, ammonia, nitrite, and nitrate equipment used by the public water system.

…

§290.46(z) Nitrification Action Plan (NAP).
Any water system distributing chloraminated water must create a NAP. The system must create a written NAP that:

§290.46(z)(1) contains the system-specific plan for monitoring free ammonia, monochloramine, total chlorine, nitrite, and nitrate levels;

§290.46(z)(2) contains system-specific action levels of the above monitored chemicals where action must be taken;

§290.46(z)(3) contains specific corrective actions to be taken if the action levels are exceeded; and

§290.46(z)(4) is maintained as part of the system's monitoring plan in §290.121 of this title.

Source Note: The provisions of this §290.46 adopted to be effective September 13, 2000, 25 TexReg 8880; amended to be effective May 16, 2002, 27 TexReg 4127; amended to be effective February 19, 2004, 29 TexReg 1373; amended to be effective January 9, 2008, 33 TexReg 198; amended to be effective October 16, 2008, 33 TexReg 8533; amended to be effective December 10, 2009, 34 TexReg 8744; amended to be effective June 10, 2010, 35 TexReg 4726; amended to be effective May 15, 2011, 36 TexReg 2860; amended to be effective November 8, 2012, 37 TexReg 8849; amended tobeeffectiveSeptember 11, 2014, 39 TexReg 7145; amended to be effective July 30, 2015, 40 TexReg 4769; amended to be effective December 10, 2015, 40 TexReg 8793; amended to be effective March 30, 2017, 42 TexReg 1466

§290.47(h) Appendix H.

§290.47(h) Appendix H. Sample Language for Notification Upon Changing from Free Chlorine to Chloramines.

A public water system (PWS) must notify its customers, in writing, at least 14 days before starting to use chloramines. This notification must contain the Sample Language for Notification Upon Changing from Free Chlorine to Chloramines included below. The notification should be provided to the news media, renal disease facilities, dialysis clinics, hospitals, physicians, local health departments, pet stores, zoos, and any other facilities that may be impacted by the change.

Sample Language for Notification Upon Changing from Free Chlorine to Chloramines

"On <Date>, the <Water System Name> will be changing the disinfectant that we use from chlorine to chloramines. This change is intended to benefit our customers by reducing the levels of disinfection byproducts in the system, while still providing protection from waterborne disease.

However, the change to chloramines can cause problems to persons dependent on dialysis machines. A condition known as hemolytic anemia can occur if the disinfectant is not completely removed from the water that is used for the dialysate. Consequently, the pretreatment scheme used for the dialysis units must include some means, such as a

charcoal filter, for removing the chloramine prior to this date. Medical facilities should also determine if additional precautions are required for other medical equipment. In addition, chloraminated water may be toxic to fish. If you have a fish tank, please make sure that the chemicals or filters that you are using are designed for use in water that has been treated with chloramines. You may also need to change the type of filter that you use for fish tanks."

Optional: "When the chloraminated water first flushes out the chlorinated water there may be a slight taste and odor, and possibly discoloration for a short period of time. This will not compromise the safety of the water."

Important notes:

1. The PWS may not begin using chloramines prior to the date shown in the notice.

2. The Texas Commission on Environmental Quality does not require the PWS to include the name or contact telephone number of a PWS employee that the customers can contact if they have questions; however, several PWSs have included this information as a courtesy to its customers.

Source Note: The provisions of this §290.47 adopted to be effective November 3, 1995, 20 TexReg 8620; amended to be effective March 3, 1997, 22 TexReg 1809; amended to be effective February 4, 1999, 24 TexReg 731; amended to be effective September 13, 2000, 25 TexReg 8880; amended to be effective May 16, 2002, 27 TexReg 4127; amended to be effective February 19, 2004, 29 TexReg 1373; amended to be effective January 9, 2008, 33 TexReg 198; amended to be effective October 16, 2008, 33 TexReg 8533; amended to be effective December 10, 2009, 34 TexReg 8744; amended to be effective May 15, 2011, 36 TexReg 2860; amended to be effective July 30,2015, 40 TexReg 4769; amended to be effective December 10, 2015, 40 TexReg 8793; amended to be effective March 30, 2017, 42 TexReg 1466

Subchapter F: Drinking Water Standards Governing Drinking Water Quality and Reporting Requirements for Public Water Systems.

§290.101. Purpose

The purpose of these standards is to assure the safety of public water supplies with respect to microbiological, chemical and radiological quality and to further efficient processing through control tests, laboratory checks, operating records and reports of public water supply systems. These standards are written to comply with the requirements of the Federal "Safe Drinking Water Act," 42 USC §300f et seq., and the "Primary Drinking Water Regulations" which have been promulgated by the United States Environmental Protection Agency.

Source Note: The provisions of this §290.101 adopted to be effective September 13, 2000, 25 TexReg 8880; amended to be effective January 9, 2008, 33 TexReg 198

§290.103. Definitions

…

§290.103(10) DPD--Abbreviation for N,N-diethyl-p-phenylenediamine, a reagent used in the determination of several residuals. DPD methods are available for both volumetric (titration) and colorimetric determinations, and are commonly used in the field as part of a colorimetric test kit.

…

§290.103(14) Entry point--Any point where a source of treated water first enters the distribution system. Entry points to the distribution system may include points where chlorinated well water, treated surface water, rechlorinated water from storage, or water purchased from another supplier enters the distribution system.

§290.103(15) Entry point sampling site--A sampling site representing the quality of the water entering the distribution system at each designated entry point.

…

§290.103(19) Finished water--Water that is introduced into the distribution system of a public water system and intended for distribution and consumption without further treatment, except as necessary to maintain water quality within the distribution system (e.g., booster disinfection, addition of corrosion control chemicals).

…

§290.103(29) Maximum contaminant level (MCL)--The maximum concentration of a regulated contaminant that is allowed in drinking water before the public water system is cited for a violation. MCLs for regulated contaminants are defined in the applicable sections of this subchapter.

§290.103(30) Maximum residual disinfectant level (MRDL)--The disinfectant concentration that may not be exceeded in the distribution system. There is convincing evidence that addition of a disinfectant is necessary for control of waterborne microbial contaminants.

§290.103(31) Minimum acceptable disinfectant residual--The lowest disinfectant concentration allowed in the distribution system for microbial control.

…

§290.103(33) Raw water--Water prior to any treatment including disinfection that is intended to be used, after treatment, as drinking water.

§290.103(33)(A) Raw groundwater is water from a groundwater source.

§290.103(33)(B) Raw surface water is any water from a surface water source or from a groundwater under the direct influence of surface water source.

…

§290.110. Disinfectant Residuals

§290.110(a) Applicability. All public water systems shall properly disinfect water before it is distributed to any customer and shall maintain acceptable disinfectant residuals within the distribution system.

§290.110(b) Minimum and maximum acceptable disinfectant concentrations. All public water systems shall provide the minimum levels of disinfectants in accordance with the provisions of this section. Public water systems shall not exceed the maximum residual disinfectant levels (MRDLs) provided in this section.

§290.110(b)(1) The disinfection process used by public water systems must ensure that water has been adequately disinfected before it enters the distribution system.

§290.110(b)(1)(A) The disinfection process used by public water systems treating surface water sources or groundwater sources that are under the direct influence of surface water must meet the requirements of §290.111(d) of this title (relating to Surface Water Treatment).

§290.110(b)(1)(B) The executive director may require the disinfection process used by public water systems treating groundwater sources that are not under the direct influence of surface water to meet the requirements of §290.116 of this title (relating to Groundwater Corrective Actions and Treatment Techniques).

§290.110(b)(1)(C) The disinfection process at other types of treatment plants shall provide the level of disinfection required by the executive director.

§290.110(b)(2) The residual disinfectant concentration in the water entering the distribution system shall be at least 0.2 milligram per liter (mg/L) free chlorine or 0.5 mg/L chloramine (measured as total chlorine).

§290.110(b)(3) The chlorine dioxide residual of the water entering the distribution system shall not exceed an MRDL of 0.8 mg/L.

§290.110(b)(4) The residual disinfectant concentration in the water within the distribution system shall be at least 0.2 mg/L free chlorine or 0.5 mg/L chloramine (measured as total chlorine).

§290.110(b)(5) The running annual average of the free chlorine or chloramine residual (measured as total chlorine) of the water within the distribution system shall not exceed an MRDL of 4.0 mg/L.

§290.110(c) Monitoring requirements. All public water systems shall monitor the performance of the disinfection facilities to ensure that appropriate disinfectant levels are maintained. All monitoring conducted pursuant to the requirements of this section must be conducted at sites designated in the public water system's monitoring plan.

§290.110(c)(1) Entry point compliance monitoring for surface water and groundwater under the direct influence of surface water. Public water systems that treat surface water or groundwater under the direct influence of surfacewater must verify that they meet the disinfection requirements of subsection (b)(2) of this section.

§290.110(c)(1)(A) Public water systems that treat surface water or groundwater under the direct influence of surface water and sell treated water on a wholesale basis or serve more than 3,300 people must continuously monitor and record the

disinfectant residual of the water at each entry point. If there is a failure in the continuous monitoring equipment, grab sampling every four hours may be conducted in lieu of continuous monitoring, but for no more than five working days following the failure of the equipment.

§290.110(c)(1)(B) Public water systems that treat surface water or groundwater under the direct influence of surface water, serve 3,300 or fewer people and do not sell treated water on a wholesale basis must monitor and record the disinfectant residual of the water at each entry point with either continuous monitors or grab samples.

§290.110(c)(1)(B)(i) If a system uses grab samples, the samples must be collected on an ongoing basis at the frequency prescribed in the following table.

Entry Point Disinfectant Residual Monitoring Frequency for Grab Samples

System Size by Population	Samples/day
500	1
501 to 1,000	2
1,001 to 2,500	3
2,501 to 3,300	4

§290.110(c)(1)(B)(ii) The grab samples cannot be taken at the same time and the sampling interval is subject to the executive director's review and approval.

§290.110(c)(1)(B)(iii) Treatment plants that use grab samples and fail to detect an appropriate disinfectant residual must repeat the test at four-hour or shorter intervals until compliance has been reestablished.

§290.110(c)(1)(C) Continuous monitors must record the disinfectant residual of the water every 30 minutes.

§290.110(c)(2) Entry point compliance monitoring for groundwater and purchased water. Public water systems that treat groundwater or that purchase and resell treated water must, upon the request of the executive director, verify that they meet the disinfection requirements of subsection (b)(2) of this section.

§290.110(c)(2)(A) A public water system that uses free chlorine must measure free chlorine.

§290.110(c)(2)(B) A public water system that has a chloramine residual must measure total chlorine.

...

§290.110(c)(4) Distribution system compliance monitoring. All public water systems shall monitor the disinfectant residual at various locations throughout the distribution system.

§290.110(c)(4)(A) Public water systems that use groundwater or purchased water sources only and serve fewer than 250 connections and fewer than 750 people daily,

must monitor the disinfectant residual at representative locations in the distribution system at least once every seven days.

§290.110(c)(4)(B) Public water systems that serve at least 250 connections or at least 750 people daily, and use only groundwater or purchased water sources must monitor the disinfectant residual at representative locations in the distribution system at least once per day.

§290.110(c)(4)(C) Public water systems using surface water sources or groundwater under the direct influence of surface water must monitor the disinfectant residual tests at least once per day at representative locations in the distribution system.

§290.110(c)(4)(D) All public water systems must monitor the residual disinfectant concentration at the same time and at the same sampling site a bacteriological sample is collected, as specified in §290.109 of this title (relating to Microbial Contaminants) in addition to the residual disinfectant concentration monitoring requirements as described in this subsection and chapter.

§290.110(c)(4)(E) All public water systems with a chloramine residual must monitor the total chlorine residual downstream of any chlorine and ammonia injection points, in conjunction with the chloramine effectiveness sampling in paragraph (5)(C) of this subsection, in the distribution system weekly and whenever the chemical dose is changed.

§290.110(c)(5) Chloramine effectiveness sampling. Public water systems with a chloramine residual shall monitor to ensure that monochloramine is the prevailing chloramine species and that nitrification is controlled. Sample sites and procedures used for chloramine effectiveness sampling must be documented in the system's nitrification action plan (NAP) required by §290.46(z) of this title (relating to Minimum Acceptable Operating Practices for Public Drinking Water Systems). Sample results determined by monitoring required under this paragraph will not be used to determine compliance with the maximum contaminant levels, MRDLs, action levels, or treatment techniques of this subchapter.

§290.110(c)(5)(A) Source water. Public water systems must monitor source water (including raw and treated purchased water) to establish baseline ammonia, nitrite, and nitrate levels (all as nitrogen) at least once to determine the availability of ammonia for chloramine formation and to provide a reference for downstream nitrite and nitrate levels that may indicate nitrification. If any source has more than 0.5 mg/L free ammonia (as nitrogen) in the initial sample, then raw water ammonia (as nitrogen) shall be monitored monthly for six months to determine the baseline free ammonia level.

§290.110(c)(5)(B) Water entering distribution system. All public water systems that have chloramines present shall perform sampling to represent the water entering the distribution system.

§290.110(c)(5)(B)(i) Total chlorine, free ammonia (as nitrogen) and monochloramine shall be monitored weekly at all entry points to the distribution system or at a location before the first customer.

§290.110(c)(5)(B)(ii) Nitrite and nitrate (as nitrogen) levels at the first customer shall be monitored monthly for at least six months to determine baseline nitrite and nitrate levels in the water prior to consumption. Nitrite and nitrate samples collected at the first customer will not be used for compliance with §290.106 of this title (relating to Inorganic Contaminants).

§290.110(c)(5)(B)(iii) Nitrite and nitrate (as nitrogen) shall be monitored quarterly at the first customer after establishing the baseline. Nitrite and nitrate samples collected at entry points for compliance with §290.106 of this title may be used for these quarterly samples.

§290.110(c)(5)(C) Treatment sampling. Public water systems that inject chlorine at any location to form chloramines or to convert from chloramines to free chlorine must monitor to ensure that chemical addition is effective and the proper chlorine to ammonia (as nitrogen) ratio is achieved. Samples must be collected and analyzed weekly and whenever the chemical dosage is changed.

§290.110(c)(5)(C)(i) Sampling must be performed upstream of the chlorine or ammonia chemical injection point, whichever is furthest upstream.

§290.110(c)(5)(C)(ii) Sampling must be performed downstream of all the chlorine and ammonia chemical injection points.

§290.110(c)(5)(C)(iii) The residual of the chemical injected upstream must be determined to properly dose the downstream chemical where sample taps are present or required under §290.42(e)(7)(C)(ii) of this title (relating to Water Treatment).

§290.110(c)(5)(C)(iv) The total chlorine, ammonia (as nitrogen), and monochloramine residuals must all be monitored if the treatment occurs before the entry point.

§290.110(c)(5)(C)(v) The ammonia (as nitrogen) and monochloramine residuals must all be monitored if the treatment occurs in the distribution system. The monitoring must occur at the same time as a compliance sampling required under paragraph (4)(E) of this subsection.

§290.110(c)(5)(D) Distribution system. Public water systems that distribute water and have a chloramine residual must ensure the efficacy of disinfection within the distribution system.

§290.110(c)(5)(D)(i) Monochloramine and free ammonia (as nitrogen) must be monitored weekly at the same time as a compliance sample required under paragraph (4) of this subsection.

§290.110(c)(5)(D)(ii) Nitrite and nitrate (as nitrogen) must be monitored quarterly.

***Disclaimer**: The following table shows the requirements of 290.110(c)(5) in tabular form. The table is intended to reproduce the regulatory requirements of Title 30, Texas Administrative Code (30 TAC) Chapter 290, 290.110(c)(5). Should there be any inadvertent discrepancy between this Appendix and the rules, the rules shall apply.*

Required Sample Frequency of 290.110(c)(5)

	At or after all Entry Point(s)	In the distribution system	Before and after any chlorine or ammonia injection points
Total Chlorine	At least weekly.	Daily at large PWSs Weekly at small PWSs. [b]	At least weekly and before and after adjusting the chlorine or ammonia feed rate.
Mono-chloramine	At least weekly.	At least weekly. [a]	
Free Ammonia	At least weekly.	At least weekly.	
Nitrite and Nitrate	Monthly for the first six (6) months to set baselines, then quarterly.	In response to action triggers; and at least quarterly	Routine sampling not required.

[a.] When collecting a routine sample such as a bacteriological or routine disinfectant residual sample.

[b.] Total chlorine must be collected weekly for systems serving fewer than 250 connections and fewer than 750 people, or weekly for systems serving at least 250 connections or at least 750 people, in accordance with §290.110.

Note: Additional sampling may be needed to follow up on results that are not as expected.

§290.110(d) Analytical requirements.
All monitoring required by paragraphs (1) and (2) of this subsection must be conducted at a facility approved by the executive director and using methods that conform to the requirements of §290.119 of this title (relating to Analytical Procedures). All monitoring for chloramine effectiveness required by paragraphs (3) - (6) of this subsection must be analyzed to the accuracy provided therein.

§290.110(d)(1) The free chlorine or chloramine residual (measured as total chlorine) must be measured to a minimum accuracy of plus or minus 0.1 mg/L. Color comparators may be used for distribution system samples only. When used, a color comparator must have current reagents, an unfaded and clear color comparator, a sample cell that is not discolored or stained, and must be properly stored in a cool, dark location where it is not subjected to conditions that would result in staining. The color comparator must be used in the correct range. If a sample reads at the top of the range, the sample must be diluted with chlorine-free water, then a reading taken and the resulting residual calculated.

…

§290.110(d)(3) The free ammonia level must be measured to a minimum accuracy of plus or minus 0.1 mg/L.

§290.110(d)(4) The monochloramine level must be measured to a minimum accuracy of plus or minus 0.15 mg/L using a procedure that has the ability to distinguish between monochloramine and other forms of chloramine.

§290.110(d)(5) The nitrate (as nitrogen) level must be measured to a minimum accuracy of plus or minus 0.1 mg/L.

§290.110(d)(6) The nitrite (as nitrogen) level must be measured to a minimum accuracy of plus or minus 0.01 mg/L.

§290.110(e) Reporting requirements.
Any owner or operator of a public water system subject to the provisions of this section is required to report to the executive director the results of any test, measurement, or analysis required by this section.

...

§290.110(e)(2) Public water systems that use surface water sources or groundwater sources under the direct influence of surface water must submit a Surface Water Monthly Operating Report (commission Form 0102C), a Surface Water Monthly Operating Report (commission Form 0102D) for alternative technologies, or a Surface Water Monthly Operational Report for Plants That Do Not Have a Turbidimeter on Each Filter (commission Form 0103) each month.

...

§290.110(e)(4) Public water systems that use purchased water or groundwater sources only must complete a Disinfection Level Quarterly Operating Report (commission Form 20067) each quarter.

§290.110(e)(4)(A) Community and nontransient, noncommunity public water systems must submit the Disinfection Level Quarterly Operating Report each quarter, by the tenth day of the month following the end of the quarter.

§290.110(e)(4)(B) Transient, noncommunity public water systems must retain the Disinfection Level Quarterly Operating Reports and must provide a copy if requested by the executive director.

§290.110(e)(5) Systems that use chloramines must retain their NAP required under §290.46(z) of this title and must provide a copy upon request by the executive director.

§290.110(e)(6) Monthly and quarterly reports required by this section must be submitted to the Water Supply Division, MC 155, Texas Commission on Environmental Quality, P.O. Box 13087, Austin, Texas 78711-3087 by the tenth day of the month following the end of the reporting period.

§290.110(f) Compliance determinations.
Compliance with the requirements of this section shall be determined using the following criteria.

§290.110(f)(1) All samples used for compliance must be obtained at sampling sites designated in the monitoring plan.

§290.110(f)(1)(A) All samples collected at sites designated in the monitoring plan as microbiological and disinfectant residual monitoring sites shall be included in the compliance determination calculations.

§290.110(f)(1)(B) Samples collected at sites in the distribution system not designated in the monitoring plan shall not be included in the compliance determination calculations.

§290.110(f)(2) A public water system that fails to conduct the monitoring tests required by this section commits a monitoring violation.

§290.110(f)(3) A public water system that fails to report the results of the monitoring tests required by this section commits a reporting violation.

§290.110(f)(4) A public water system that uses surface water sources or groundwater sources under the direct influence of surface water and fails to meet the requirements of subsection (b)(2) of this section for a period longer than four consecutive hours commits a nonacute treatment technique violation. A public water system that fails to conduct the additional testing required by subsection (c)(1)(B)(iii) of this section also commits a nonacute treatment technique violation.

...

§290.110(f)(6) A public water system that fails to meet the requirements of subsection (b)(4) of this section, in more than 5.0% of the samples collected each month, for any two consecutive months, commits a nonacute treatment technique violation. Specifically, the system commits a nonacute violation if the value "V" in the following formula exceeds 5.0% per month for any two consecutive months:

$$V = b \times 100\ a$$

Where:

a = number of instances where the residual disinfectant concentration is measured during the month; and

b = number of instances during the month where the residual disinfectant concentration is measured but is detected at less than 0.2 milligrams per liter (mg/L) free chlorine or less than 0.5 mg/L chloramine (measured as total chlorine).

§290.110(f)(7) A public water system violates the MRDL for chlorine or chloramine (measured as total chlorine) if, at the end of any quarter, the running annual average of monthly averages exceeds the level specified in subsection (b)(5) of this section.

§290.110(f)(8) Public water systems shall increase residual disinfectant levels of free chlorine, or chloramines measured as total chlorine, (but not chlorine dioxide) in the distribution system to a level and for a time necessary to protect public health to address specific microbiological contamination problems caused by circumstances such as distribution line breaks, storm runoff events, source water contamination, or cross-connections. Public water systems shall consult with the executive director upon increasing residual disinfectant levels in the distribution system in order to maintain compliance with the MRDLs listed in subsection (b) of this section.

§290.110(f)(9) If a public water system's failure to monitor makes it impossible to determine compliance with the MRDL for chlorine or chloramines (measured as total chlorine), the system commits an MRDL violation for the entire period covered by the annual average.

§290.110(f)(10) A public water system that fails to issue a required public notice or certify that it has issued that notice commits a violation.

§290.110(g) Public notification requirements. The owner or operator of a public water system that violates the requirements of this section must notify the executive director and the people served by the system.

...

§290.110(g)(2) A public water system that uses surface water sources or groundwater sources under the direct influence of surface water and fails to meet the minimum disinfection requirements of subsection (b)(2) of this section shall notify the executive director by the end of the next business day and the customers in accordance with the requirements of §290.122(b) of this title.

§290.110(g)(3) A public water system that fails to meet the requirements of subsection (b)(4) of this section in more than 5.0% of the samples collected each month for two consecutive months must notify its customers in accordance with the requirements of §290.122(b) of this title.

§290.110(g)(4) A public water system that fails to meet the requirements of subsection (b)(5) of this section shall notify the executive director by the end of the next business day and the customers in accordance with the requirements of §290.122(b) of this title.

§290.110(g)(5) A public water system which fails to conduct the monitoring required by subsection (c)(1) - (4) of this section must notify its customers of the violation in accordance with the requirements of §290.122(c) of this title.

§290.110(g)(6) A public water system that uses chloramines shall notify their retail and wholesale customers of the use of chloramines.

§290.110(g)(6)(A) This notification must contain the exact wording included in Appendix H of §290.47 of this title (relating to Appendices).

§290.110(g)(6)(B) Prior to initially providing the chloraminated water to its existing customers, the water system must provide notification by mail or direct delivery at least 14 days before the change.

§290.110(g)(6)(C) Additionally, the notification must be provided to the news media, hospitals, renal disease facilities, dialysis clinics, physicians, local health departments, and entities which maintain live fish directly by letter, e-mail, or hand delivery.

§290.110(g)(6)(D) New customers must also be notified before they begin receiving water from the water system.

§290.110(g)(6)(E) Where appropriate, the notice must be multilingual.

Source Note: The provisions of this §290.110 adopted to be effective September 13, 2000, 25 TexReg 8880; amended to be effective May 16, 2002, 27 TexReg 4127; amended to be effective January 9, 2008, 33 TexReg 198; amended to be effective November 8, 2012, 37 TexReg 8849; amended to be effective July 30, 2015, 40 TexReg 4769; amended to be effective March 30, 2017, 42 TexReg 1466

§290.119 Analytical Procedures

§290.119(a) Acceptable laboratories.
Samples collected to determine compliance with the requirements of this chapter shall be analyzed at accredited or approved laboratories.

§290.119(a)(1) Samples used to determine compliance with the maximum contaminant levels, samples used to determine compliance with action level, and raw groundwater source monitoring requirements of this subchapter, and samples for microbial contaminants must be analyzed by a **laboratory accredited by the executive director** in accordance with Chapter 25, Subchapter A and B of this title (relating to General Provisions; and Environmental Testing Laboratory Accreditation) using acceptable analytical methods as specified in subsection (b) of this section. These samples include:

§290.119(a)(1)(A) compliance samples for synthetic organic chemicals;

§290.119(a)(1)(B) compliance samples for volatile organic chemicals;

§290.119(a)(1)(C) compliance samples for inorganic contaminants;

§290.119(a)(1)(D) compliance samples for radiological contaminants;

§290.119(a)(1)(E) compliance samples for microbial contaminants;

§290.119(a)(1)(F) compliance samples for total trihalomethanes (TTHM);

§290.119(a)(1)(G) compliance samples for haloacetic acid-group of five (HAA5);

§290.119(a)(1)(H) compliance samples for chlorite;

§290.119(a)(1)(I) compliance samples for bromate; and

§290.119(a)(1)(J) compliance samples for lead and copper.

§290.119(a)(2) Samples used to determine compliance with the treatment technique requirements and maximum residual disinfectant levels (MRDLs) of this subchapter must be analyzed by a laboratory approved by the executive director. These samples include:

§290.119(a)(2)(A) compliance samples for turbidity treatment technique requirements;

§290.119(a)(2)(B) compliance samples for the chlorine MRDL;

§290.119(a)(2)(C) compliance samples for the chlorine dioxide MRDL;

§290.119(a)(2)(D) compliance samples for the combined chlorine (chloramine) MRDL;

§290.119(a)(2)(E) compliance samples for the disinfection byproduct precursor treatment technique requirements, including alkalinity, total organic carbon, dissolved organic carbon analyses, and specific ultraviolet absorbance;

§290.119(a)(2)(F) samples used to monitor chlorite levels at the point of entry to the distribution system; and

§290.119(a)(2)(G) samples used to determine pH.

§290.119(a)(3) Non-compliance tests, such as control tests taken to operate the system, may be run in the plant or at a laboratory of the system's choice.

§290.119(b) Acceptable analytical methods. Methods of analysis shall be as specified in 40 Code of Federal Regulations (CFR) or by any alternative analytical technique as specified by the executive director and **approved** by the Administrator under 40 CFR §141.27. Copies are available for review in the Water Supply Division, MC 155, Texas Commission on Environmental Quality, P.O. Box 13087, Austin, Texas 78711-3087. The following National Primary Drinking Water Regulations set forth in Title 40 CFR are adopted by reference:

§290.119(b)(1) 40 CFR §141.852(a) and (c) for microbiological analyses;

§290.119(b)(2) 40 CFR §141.74(a)(1) for turbidity analyses;

§290.119(b)(3) 40 CFR §141.23(k) for inorganic analyses;

§290.119(b)(4) 40 CFR §141.24(e) - (g) for organic analyses;

§290.119(b)(5) 40 CFR §141.25 for radionuclide analyses;

§290.119(b)(6) 40 CFR §141.131(a) and (b) for disinfection byproduct methods and analyses;

§290.119(b)(7) 40 CFR §141.131(c) for disinfectant analyses other than ozone, and 40 CFR §141.74(b) for ozone disinfectant;

§290.119(b)(8) 40 CFR §141.131(d) for alkalinity analyses, bromide and magnesium, total organic carbon analyses, dissolved organic carbon analyses, specific ultraviolet absorbance analyses, and pH analyses;

§290.119(b)(9) 40 CFR §141.89 for lead and copper analyses and for water quality parameter analyses that are performed as part of the requirements for lead and copper;

§290.119(b)(10) 40 CFR §141.402(c) for groundwater source microbiological analyses; and

§290.119(b)(11) if a method is not contained in this section, a drinking water quality method can be approved for analysis if it is listed in 40 CFR Part 141, Subpart C, Appendix A.

§290.119(c) The definition of detection contained in 40 CFR §141.151(d) is adopted by reference.

Source Note: The provisions of this §290.119 adopted to be effective September 13, 2000, 25 TexReg 8880; amended to be effective May 16, 2002, 27 TexReg 4127; amended to be effective January 9, 2008, 33 TexReg 198; amended to be effective May 15, 2011, 36 TexReg 2860; amended to be effective November 8, 2012, 37 TexReg 8849; amended to be effective March 30, 2017, 42 TexReg 1466

§290.121 Monitoring Plans

§290.121(a) Applicability. All public water systems shall maintain an up-to-date chemical and microbiological monitoring plan. Monitoring plans are subject to the review and approval of the executive director. A copy of the monitoring plan must be maintained at each water treatment plant and at a central location.

§290.121(b) Monitoring plan requirements. The monitoring plan shall identify all sampling locations, describe the sampling frequency, and specify the analytical procedures and laboratories that the public water system will use to comply with the monitoring requirements of this subchapter.

§290.121(b)(1) The monitoring plan shall include information on the location of all required sampling points in the system. Required sampling locations for regulated chemicals are provided in §290.106 of this title (relating to Inorganic Contaminants), §290.107 of this title (relating to Organic Contaminants), §290.108 of this title (relating to Radionuclides Other than Radon), §290.109 of this title (relating to Microbial Contaminants), §290.110 of this title (relating to Disinfectant Residuals), §290.111 of this title (relating to Surface Water Treatment), §290.112 of this title (relating to Total Organic Carbon (TOC)), §290.113 of this title (relating to Stage 1 Disinfection Byproducts (TTHM and HAA5)), §290.114 of this title (relating to Other Disinfection Byproducts (Chlorite and Bromate)), §290.115 of this title (relating to Stage 2 Disinfection Byproducts (TTHM and HAA5)), §290.116 of this title (Relating to Groundwater Corrective Actions and Treatment Techniques), §290.117 of this title (relating to Regulation of Lead and Copper), and §290.118 of this title (relating to Secondary Constituent Levels).

§290.121(b)(1)(A) The location of each sampling site at a treatment plant or pump station must be designated on a plant schematic. The plant schematic must show all water pumps, flow meters, unit processes, chemical feed points, and chemical monitoring points. The plant schematic must also show the origin of any flow stream that is recycled at the treatment plant, any pretreatment that occurs before the recycle stream is returned to the primary treatment process, and the location where the recycle stream is reintroduced to the primary treatment process.

§290.121(b)(1)(B) Each entry point to the distribution system shall be identified in the monitoring plan as follows:

§290.121(b)(1)(B)(i) a written description of the physical location of each entry point to the distribution system shall be provided; or

§290.121(b)(1)(B)(ii) the location of each entry point shall be indicated clearly on a distribution system or treatment plant schematic.

§290.121(b)(1)(C) The address of each sampling site in the distribution system shall be included in the monitoring plan or the location of each distribution system sampling site shall be designated on a distribution system schematic. The distribution system schematic shall clearly indicate the following:

§290.121(b)(1)(C)(i) the location of all pump stations in the distribution system;

§290.121(b)(1)(C)(ii) the location of all ground and elevated storage tanks in the distribution system; and

§290.121(b)(1)(C)(iii) the location of all chemical feed points in the distribution system.

§290.121(b)(1)(D) The system must revise its monitoring plan if changes to a plant or distribution system require changes to the sampling locations.

§290.121(b)(2) The monitoring plan must include a written description of sampling frequency and schedule.

§290.121(b)(2)(A) The monitoring plan must include a list of all routine samples required on a daily, weekly, monthly, quarterly, annual, or less frequent basis and identify the sampling location where the samples will be collected.

§290.121(b)(2)(B) The system must maintain a current record of the sampling schedule.

§290.121(b)(3) The monitoring plan shall include the public water system's Sample Siting Plan as required by §290.109(d)(1) - (6) of this title. The public water system's Sample Siting Plan shall include a list of all microbial distribution compliance monitoring sites as required by §290.109(d) of this title, including all routine and repeat microbial sample sites. As required by §290.109(d)(2)(G) of this title, a public water system that collects more than the minimum number of required routine microbial samples shall include the additional routine sample sites in the public water system's Sample Siting Plan. In addition, a public water system that is required to collect any associated raw groundwater source(s) compliance samples, as required by §290.109(d)(4) of this title, shall include the microbial raw groundwater well compliance sites in the public water system's Sample Siting Plan. The repeat sample sites, as required by §290.109(d)(3) of this title, shall be associated to their originating routine microbial sample sites. The Sample Siting Plan shall include all groundwater sources and any associated sampling points necessary to meet the requirements of §290.109(d) of this title.

§290.121(b)(4) The monitoring plan must identify the analytical procedures that will be used to perform each of the required analyses.

§290.121(b)(5) The monitoring plan must identify all laboratory facilities that may be used to analyze samples required by this chapter.

§290.121(b)(6) The monitoring plan shall include a written description of the methods used to calculate compliance with all maximum contaminant levels, maximum residual disinfectant levels, and treatment techniques that apply to the system.

§290.121(b)(7) The monitoring plan shall include any groundwater source water monitoring plan developed under §290.109(d)(4) of this title to specify well sampling for triggered coliform monitoring.

§290.121(b)(8) The monitoring plan shall include any initial distribution system evaluation compliance documentation required by §290.115(c)(5) of this title. The monitoring plan must be revised to show Stage 2 sample sites by the date shown in Figure: 30 TAC §290.115(a)(2) titled "Date to Start Stage 2 Compliance."

§290.121(b)(9) The monitoring plan shall include any raw surface water monitoring plan required under §290.111 of this title.

§290.121(c) Reporting requirements. All public water systems shall maintain a copy of the current monitoring plan at each treatment plant and at a central location. The water system must update the monitoring plan when the water system's sampling requirements or protocols change.

§290.121(c)(1) Public water systems that treat surface water or groundwater under the direct influence of surface water must submit a copy of the monitoring plan to the executive director upon development and revision.

§290.121(c)(2) Public water systems that treat groundwater that is not under the direct influence of surface water or purchase treated water from a wholesaler must develop a monitoring plan and submit a copy of the monitoring plan to the executive director upon request.

§290.121(c)(3) All water systems must provide the executive director with any revisions to the plan upon request.

§290.121(d) Compliance determination. Compliance with the requirements of this section shall be determined using the following criteria.

§290.121(d)(1) A public water system that fails to submit an administratively complete monitoring plan by the required date documented in a request from the executive director or fails to submit updates to a plan when changes are made to a system's surface water treatment commits a reporting violation.

§290.121(d)(2) A public water system that fails to maintain an up-to-date monitoring plan commits a monitoring violation.

§290.121(e) Public notification. A community system that commits a violation described in subsection (d) of this section shall notify its customers of the violation in the next Consumer Confidence Report that is issued by the system.

Source Note: The provisions of this §290.121 adopted to be effective September 13, 2000, 25 TexReg 8880; amended to be effective May 16, 2002, 27 TexReg 4127; amended to be effective February 19, 2004, 29 TexReg 1373; amended to be effective December 23, 2004, 29 TexReg 11729; amended to be effective January 9, 2008, 33 TexReg 198; amended to be effective May 15, 2011, 36 TexReg 2860; amended to be effective March 30, 2017, 42 TexReg 1466

Attachment 4: Hydrant sampler

Hydrant sampler and tap sampler

This section shows how to make a hydrant sampler or tap sampler to help with sampling. It is provided here to help PWS staff provide some tools that can be used to make sure that coliform samples are collected from the distribution main—not from stagnant water in the sample line.

The US EPA Technical Support Center (TSC) has developed some tools to help systems perform more consistent sampling for distribution system studies. These devices control the flow but they also have other features that can be useful.

The hydrant sampler has

- a pressure gauge,
- a temperature probe,
- a flush line to which one can attach a hose to direct the water flow, and
- a side-stream valve that can be used to collect a sample at a lower rate.

The tap sampler is fitted with

- a hose to direct the flush-water in the direction you choose and
- a temperature probe.

The other features fitted to the hydrant sampler would not be useful when collecting a sample from the customer's tap.

All these procedures are designed to ensure that you can collect a representative sample and obtain accurate information about your distribution system

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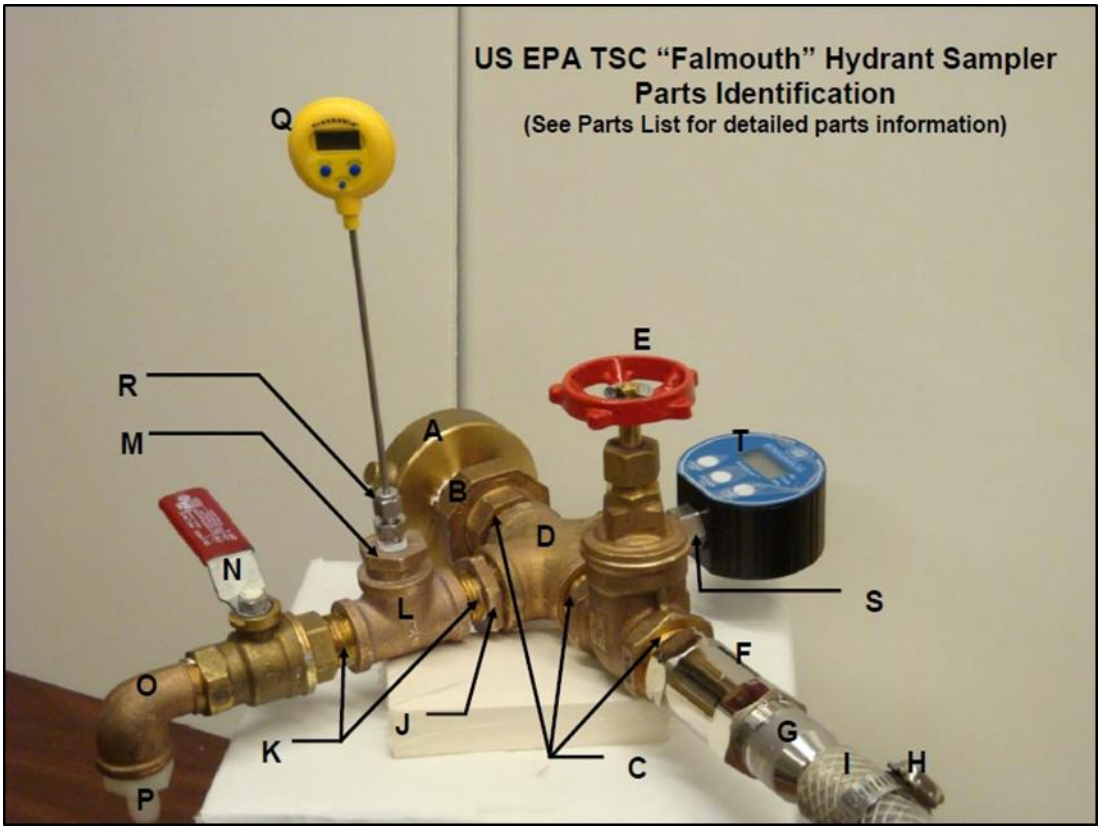
The EPA's Technical Support Center (TSC) helps PWSs and states (like Texas) with strategies for successful operation. This procedure and description are adapted from EPA TSC documents.

Hydrant sampling device

In distribution system sampling, oftentimes residential or business taps are not available to sample at (especially in remote areas of the system), so hydrants are used. Since hydrants are designed to be fully open, a device is needed to keep the hydrant open, but allow the sampler to sample the water in controlled, safe manner. See details provided below.



Picture of EPA TSC "Falmouth" Hydrant Sampler

Procedure for Using Hydrant Sampler

This is a generic procedure you can follow. For your system, you may want to update this to add any steps or processes unique to your system.

1. Make sure you have a data sheet to record your results.
2. Make sure you have the list of sites with their calculated flush time (CFT).
3. Close all valves on sampler and connect to hydrant.
4. Open hydrant (**slowly**) until fully open.
5. Open main valve on sampler, start the timer. The flowrate is set to 20 gpm by the orifice on the flow control valve.
6. At the CFT or time designated by the rule of thumb close the main valve, open the side-stream sample valve, and collect the water sample(s). If multiple samples are collected over a significant span of time relative to the flushing time, turn off the tap in between samples.
7. Take water temperature reading at time of sample. If CFT is unknown track temperature stabilization along with CFT to estimate adequate flush.
8. Take water pressure reading at time of sample (if desired).
9. When sampling is completed shut off all valves and slowly close hydrant.
10. Make sure you wrote: Location, Date, Time start/time end, Temperature, and all analytical results on your data sheet.

Hydrant Sampler Parts Lists

Main Section of Sampler

Item	**Photo Letter**	**# Per Sampler**
Hydrant Adapter/Reducer (2½" FNST Inlet by 1" MNPT Outlet)B	A	1
1" FNPT Brass, Water Pressure Reducing Valve		1
1" FNPT Brass Union	B	1
1" MNPT Red Brass Nipple, Closed Threaded	C	3
1" FNPT Red Brass Cross	D	1
1" FNPT Brass Gate Valve	E	1
Dole Flow Control Valve, 20.0 GPM, 1" FNPT Inlet/Outlet	F	1
1" MNPT X 1" ID Red Brass Hose Adapter	G	1
#16 Hose Clamp for 1" ID Hose	H	1
Thread Sealant Tape, PTFE, 3/4" × 520"	-	1
1" ID Hose (Reinforced PVC), 50 ft	I	5 ft

Sampling Section

Item	**Photo Letter**	**# Per Sampler**
1" MNPT X 3/4" FNPT Red Brass Reducing Bushing	J	1
3/4 " MNPT Red Brass Nipple, Closed Threaded, pk/5	K	2
3/4" FNPT Brass Tee	L	1
3/4"MNPT X 1/4" FNPT Red Brass Reducing Bushing	M	1
3/4" FNPT Brass Ball Valve	N	1
3/4" NPT 90° Red Brass Street Elbow	O	1
3/4" MNPT X 1/4 " ID Nylon Hose Adapter	P	1

Temperature Probe

Item	**Photo Letter**	**# Per Sampler**
Temperature probe with X" probe diameter (Must have accurate measurement of probe diameter)	Q	1
X" X 1/4" NPT Male Connector, Bored Through with Teflon Ferrule C	-	1
PTFE Front Ferrule, 3 mm	-	1

PTFE Back Ferrule, 3 mm	R	1

Pressure Gauge

Item	Photo Letter	# Per Sampler
1" MNPT x 1/4" FNPT Chrome Plated-Brass Reducing Bushing	S	1
SSI 300 PSI Digital Pressure Gauge, 1/4"MNPT Connector	T	1

Footnotes for the parts tables

A--Fittings are rated for maximum of 150 psi, sampler may not be safe when system pressures exceed this value. Sampler could be modified to include a pressure reducing valve (PRV).

B--Some systems have special hydrant threads specific to their system, however the majority of systems use FNST.

C--Size of male connector (X) depends on probe diameter of temperature probe used

Possible Sources for Parts

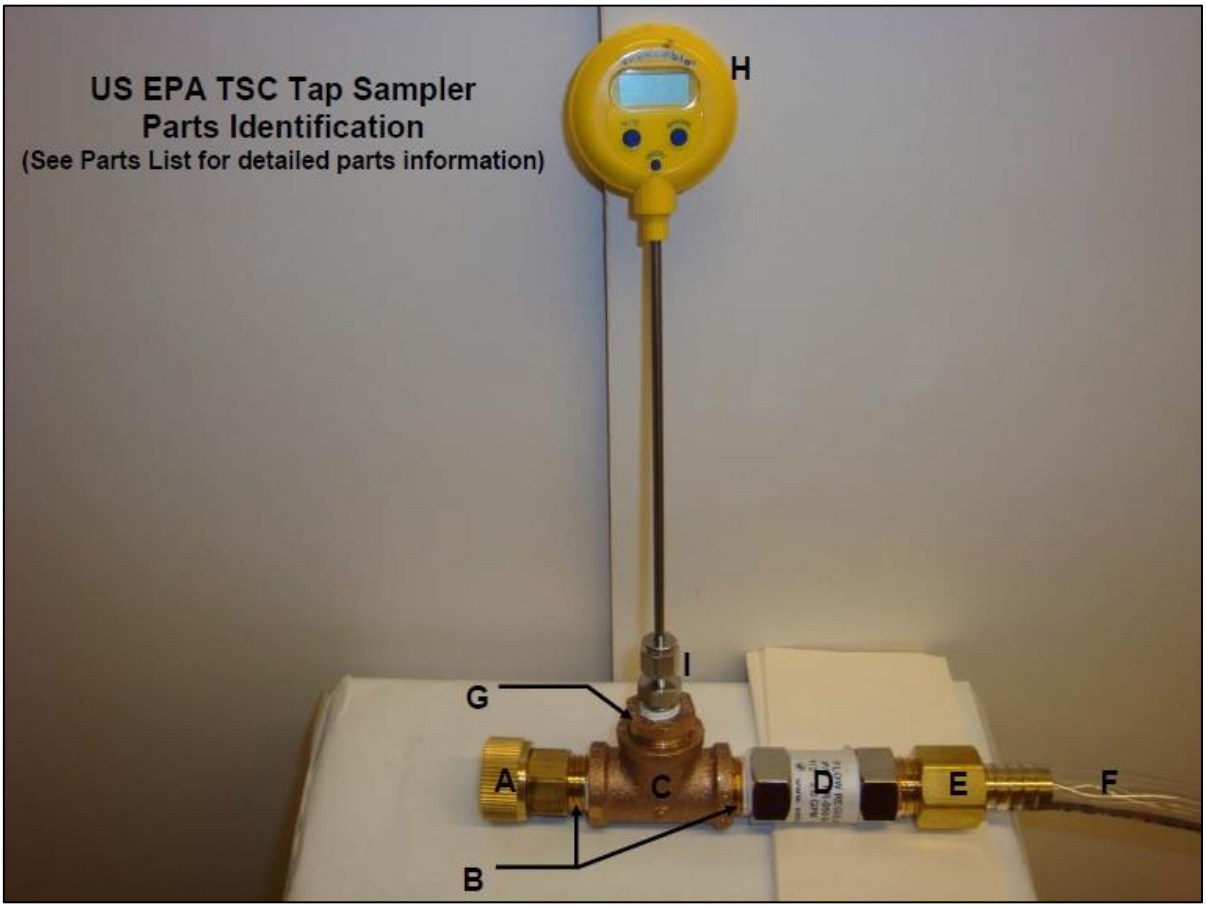
- Pollard Water - www.Pollardwater.com, or 800/437-1146
- Grainger - www.grainger.com, stores nationwide
- Home Depot
- Swaqelock - Check at swagelock.com for local supplier
- Eddington Industries, LLC - www.eddington-ind.com
- Fisher Scientific - www.fishersci.com

Hose-bibb tap sampler

After the hydrant sampler was designed and constructed, a tap sampler was later designed for sampling at residential and business hose bibbs or other taps that would allow the sampling team to measure an accurate calculated flush time at the desired 2 gpm flowrate.

Procedure for Using the Tap Sampler

1. Make sure you have a data sheet to record your results.
2. Make sure you have the list of sites with their calculated flush time (CFT).
3. Remove aerator and connect sampler to faucet.
4. Turn on cold water tap fully and start the timer. The flowrate should be set to 2 gpm based on the flow control valve
5. At 2xCFT or time designated by the rule of thumb turn off the tap and collect the water sample(s). If multiple samples are collected over a significant span of time relative to the flushing time, turn off the tap in between samples.
6. Take water temperature reading at time of sample. If CFT is unknown track and record temperature stabilization along with CFT to estimate adequate flush.
7. When sampling is completed disconnect from faucet.



Picture of EPA TSC Tap Sampler

Parts List for Main Section of Tap Sampler

Item	**Photo Letter**	**Quantity Per Sampler**	**Potential Source**
Garden hose coupling, 1/2" FNPT outlet	A	1	1,5
1/2" NPT close nipple	B	2	1,5
1/2" NPT Tee	C	1	1,5
Dole Flow Control Valve - 2.0 gpm, model 2GB, 1/2" FNPT inlet/outlet	D	1	1,5
1/2" MNPT X 1/2" ID hose adapter	E	1	1,5
1/2 " ID hose	F	2 ft	2

Parts List for Temperature Probe Section of Tap Sampler

Item	Photo Letter	Quantity Per Sampler	Potential Source
Reducing bushing 1/2" NPT X 1/4" NPT	G	1	1,5
Temperature probe with X" probe diameter (must have accurate measurement of the probe diameter)	H	1	6
X" X 1/4" NPT male connector, bored through with Teflon ferrule (Size of the male connector (X") depends on the probe diameter of the temperature probe used.)			3

Potential sources

1--Pipe fittings are available at plumbing supply and hardware stores

2--Hose, fittings and hardware available at Lowes and Home Depot

3--Swagelock - Check at swagelock.com for local supplier

4--Eddington Industries, LLC (888) 813-9900

5--Grainger - www.grainger.com, stores nationwide

6--Scientific equipment suppliers

Attachment 5. Nitrification introduction

Nitrification in drinking water distribution systems with chloramines can cause rapid decreases in disinfectant residuals, which in turn can cause TC+.

Nitrification is outside the scope of this DAM. Instead, it is a topic for another one-day training: "DAM 8: HOW TO DEVELOP A NITRIFICATION ACTION PLAN (NAP) FOR A PUBLIC WATER SYSTEM (PWS) USING CHLORAMINES" (the NAP DAM). It is highly recommended that PWSs with chloramines take advantage of that training, which is provided through the TCEQ's Financial, Managerial, and Technical (FMT) Assistance Program. Call TCEQ at 512-239-4691 to seek this training.

Documents and data

A PWS that has the potential to have chloramines present is required to have:

- Minimum residual compliance data for total chlorine;
- Chloramine-effectiveness monitoring data for total chlorine, monochloramine, and free available ammonia;
- Nitrification-detection data for (at least) nitrite and nitrate; and
- A Nitrification Action Plan.

Additional process management data may also be available.

Resources

Twenty years ago, as more systems turned to chloramines to solve disinfection byproducts issues, the unintentional consequence of nitrification became a challenge. Since that time, numerous resources have become available.

EPA

EPA Distribution System Issue Paper (DSIP) "NITRIFICATION"

www.epa.gov/sites/production/files/2015-09/documents/nitrification_1.pdf

Web site: Basic Information about Chloramines and Drinking Water Disinfection

www.epa.gov/dwreginfo/
basic-information-about-chloramines-and-drinking-water-disinfection

TCEQ

The TCEQ provides free, on-site training. Directed Assistance Module (DAM) 8 can be requested by contacting the TCEQ Financial, Managerial, and Technical (FMT) program at 512-239-4691, or visiting the web at:

www.tceq.texas.gov/drinkingwater/fmt

Nitrification Control

- At the treatment plant
  - Increasing chloramine dose or residual
  - Using chlorine-to-ammonia application ratios closer to 5 mg Cl_2:1 mg NH_3-N
  - Removing chloramine-demanding substances like natural organic matter
  - pH control
  - Chlorite addition

- In the distribution system
  - Decreasing distribution system residence times
  - Periodic changes to free chlorine
  - Flushing programs
  - Booster stations designed to increase chloramine residual and decrease free ammonia concentration

Biocide-to-Food Ratio

- Biocide: Food Ratio = $\frac{\text{Total Chlorine Concentration}}{\text{Free Ammonia Concentration}}$

- Nitrification observed in tanks where
  Biocide: Food Ratio = 0.3 to 1.4 mg Cl_2/mg N

- Nitrification <u>not</u> observed in tanks where
  Biocide: Food Ratio = 2 to 5 mg Cl_2/mg N

Attachment 6: Training Evaluation Form

To be completed by trainees who participated in Directed Assistance Module (DAM) 5: Process Management for PWSs Using Chloramines".

Training location: _____ Date: _____

Instructor Name: _____

Overall Evaluation:

① Strongly Agree ② Agree ③ No Opinion ④ Disagree ⑤ Strongly Disagree

	←Agree Disagree→
1. The DAM agenda accurately described the training.	① ② ③ ④ ⑤
2. The training was TOO technical and complicated.	① ② ③ ④ ⑤
3. The training was TOO simple and basic.	① ② ③ ④ ⑤
4. The schedule was reasonable.	① ② ③ ④ ⑤
5. The handouts and Student Guide were understandable and helpful.	① ② ③ ④ ⑤
6. The materials will be useful for future reference and training others.	① ② ③ ④ ⑤
7. The graphics in this DAM helped me understand the subjects covered.	① ② ③ ④ ⑤
9. Chapter 1 adequately explained the breakpoint curve.	① ② ③ ④ ⑤
10. Chapter 2 adequately explained the sample analysis process.	① ② ③ ④ ⑤
11. Chapter 2 helped me be able to fill out the LAM.	① ② ③ ④ ⑤
12. Chapter 3 adequately explained distribution sample sites and schedules	① ② ③ ④ ⑤
13. Chapter 4 adequately explained the importance of mixing.	① ② ③ ④ ⑤
14. Chapter 4 adequately explained dosing calculations.	① ② ③ ④ ⑤
15. Chapter 5 adequately explained treatment plant considerations.	① ② ③ ④ ⑤
16. After this training, it will be easier to manage chloramination.	① ② ③ ④ ⑤

Training location: _____ Date: _____

Specific Suggestions:

What could we change to improve this Directed Assistance Module?

What did we not explain well enough for you to understand?

What areas did we spend too much time on?

What areas did we spend too little time on?

What are some other issues where you feel more training is needed?

What other comments or suggestions do you have?

Note: TCEQ may contact PWS participants to follow up for quality assurance.

Attachment 7a: Pre-Test

Instructions: The Pre- and Post-Tests are intended to help you evaluate your learning. All staff who participate in this training event should complete this Pre-Test. Answer all questions to the best of your ability. After the Post-Test is done, the Instructor will go over the correct answers.

Training location: _____ Date: _____

If you turn in the Pre- and Post-test, please keep them together so that the instructor can see where learning was successful.

Position—check all that apply

○ Operator ○ Student ○ Administrator ○ Assistance provider

○ Engineer ○ Consultant ○ Regulator ○ Other _____

Pre-test: Mark ALL answers that apply.

1. The family of chloramines includes these species:

   ① Free chlorine.
   ② Monochloramine.
   ③ Dichloramine.
   ④ Trichloramine.
   ⑤ Free ammonia.

2. The chemicals that have regulatory maximum and/or minimum compliance levels include:

   ① Total chlorine.
   ② Monochloramine.
   ③ Dichloramine.
   ④ Trichloramine.
   ⑤ Free ammonia.

3. Free chlorine can exist in the presence of free ammonia.

   ① True.
   ② False

4. The breakpoint curve:

   ① Is the same for every type of water.
   ② Has a 'peak' at the optimum chlorine-to-ammonia-nitrogen (or chlorine-to-ammonia) ratio.
   ③ X axis is time, and Y axis is space.
   ④ Shows the point at which it is most appropriate to take a break.
   ⑤ Can be used to diagnose and visualize issues with chloramine residuals.

5. Sample sites for total chlorine, monochloramine, and ammonia:

   ① Must be at all hydrants and dead-end mains.
   ② Must be representative of the entire distribution system.
   ③ Must include all pressure planes.
   ④ Must be located before and after chlorine and/or ammonia injection points.
   ⑤ Are not required for purchased-water systems.
   ⑥ Must be at coliform sites.

6. How frequently must monochloramine and free ammonia samples be collected?

   ① At least weekly, at representative sites.
   ② Often enough to figure out whether anything bad is happening to the residual (like nitrification or unstable residuals).
   ③ Continuously.
   ④ At a different time than total chlorine.

7. What is the purpose of maintaining a disinfectant residual?

   ① To make the water smell funny.
   ② To kill or sterilize (inactivate) pathogens.
   ③ To cause beneficial nitrification.
   ④ To track water age in the distribution system.

8. Sample sites representative of the distribution system…

   ① Should include all pressure planes.
   ② Should be located at the entry point(s).
   ③ Should include areas of high water-age.
   ④ Should be sampled less frequently than quarterly for nitrite and nitrate
   ⑤ Should not be at dedicated sample stations.

9. An SOP for disinfectant residual collection and analysis:

   ① Should not be used.
   ② Should be given to all new staff.
   ③ Should include instructions for diluting over-range ammonia samples.
   ④ Will help ensure that results are precise and correct.

10. Which of these statements are true?

   ① Monochloramine is the disinfecting member of the chloramine family.
   ② Trichloramine is three times better than monochloramine.
   ③ Free chlorine lasts longer than monochloramine.

Attachment 7b: Post-Test

Instructions: The Pre- and Post-Tests are intended to help you evaluate your learning. All staff who participate in this training event should complete this Pre-Test. Answer all questions to the best of your ability. After the Post-Test is done, the Instructor will go over the correct answers.

Training location: _____ Date: _____

If you turn in the Pre- and Post-test, please keep them together so that the instructor can see where learning was successful.

Position—check all that apply

○ Operator ○ Student ○ Administrator ○ Assistance provider

○ Engineer ○ Consultant ○ Regulator ○ Other _____

Pre-test: Mark ALL answers that apply.

1. The family of chloramines includes these species:

   ① Free chlorine.
   ② Monochloramine.
   ③ Dichloramine.
   ④ Trichloramine.
   ⑤ Free ammonia.

2. The chemicals that have regulatory maximum and/or minimum compliance levels include:

   ① Total chlorine.
   ② Monochloramine.
   ③ Dichloramine.
   ④ Trichloramine.
   ⑤ Free ammonia.

3. Free chlorine can exist in the presence of free ammonia.

   ① True.
   ② False

4. The breakpoint curve:

   ① Is the same for every type of water.
   ② Has a 'peak' at the optimum chlorine-to-ammonia-nitrogen (or chlorine-to-ammonia) ratio.
   ③ X axis is time, and Y axis is space.
   ④ Shows the point at which it is most appropriate to take a break.
   ⑤ Can be used to diagnose and visualize issues with chloramine residuals.

5. Sample sites for total chlorine, monochloramine, and ammonia:

   ① Must be at all hydrants and dead-end mains.
   ② Must be representative of the entire distribution system.
   ③ Must include all pressure planes.
   ④ Must be located before and after chlorine and/or ammonia injection points.
   ⑤ Are not required for purchased-water systems.
   ⑥ Must be at coliform sites.

6. How frequently must monochloramine and free ammonia samples be collected?

   ① At least weekly, at representative sites.
   ② Often enough to figure out whether anything bad is happening to the residual (like nitrification or unstable residuals).
   ③ Continuously.
   ④ At a different time than total chlorine.

7. What is the purpose of maintaining a disinfectant residual?
   ① To make the water smell funny.
   ② To kill or sterilize (inactivate) pathogens.
   ③ To cause beneficial nitrification.
   ④ To track water age in the distribution system.

8. Sample sites representative of the distribution system…

   ① Should include all pressure planes.
   ② Should be located at the entry point(s).
   ③ Should include areas of high water-age.
   ④ Should be sampled less frequently than quarterly for nitrite and nitrate
   ⑤ Should not be at dedicated sample stations.

9. An SOP for disinfectant residual collection and analysis:

   ① Should not be used.
   ② Should be given to all new staff.
   ③ Should include instructions for diluting over-range ammonia samples.
   ④ Will help ensure that results are precise and correct.

10. Which of these statements are true?

   ① Monochloramine is the disinfecting member of the chloramine family.
   ② Trichloramine is three times better than monochloramine.
   ③ Free chlorine lasts longer than monochloramine.

Attachment 8. Plan of Action

This form is intended to help you follow up on any items that you did not finish during the DAM itself. **Detach this from the Student Guide first thing** in the day. During the day, jot down items that you need to follow up on from each workshop.

- Document what needs to be done, who needs to get it done, and when it needs to be done. Every action item should have a person assigned, and a deadline.
- For large items, consider the first step, second step, and so on. It is okay if the first step is to "Make a timeline on completing the new pipeline" or something like that.

After the NAP DAM, copy all of the Action Items on to your normal calendar or task list—or communicate the tasks to the people who will be assigned to them.

Plan of Action!

ACTION ITEM	PERSON TO ACT	DEADLINE

Note: Use additional paper if needed.

Notes

Revision table

Action	Date	Comment
Created	May 15, 2007	Pre-QC first draft created
Revised	August 13, 2007	Updated based on QC
Revised	October 8, 2007	To include a cover page, incorporate a course description and agenda and add chapter headings
Revised	May 14, 2008	Updated
Revised	September 29, 2010	Updated
Version 2	July 7, 2018	To place in accessible format, update to describe current rule requirements, and correct minor typographical errors.

Thank you for participating in this Directed Assistance Module.