The Fundamentals of Chlorine Chemistry and Disinfection

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George Bowman,
The Wisconsin State Lab of Hygiene
and
Rick Mealy,
The Wisconsin Dept. of Natural Resources

How do you respond to a water-related emergency?

…people reportedly becoming ill

…suspicion is it might be the water

…it could be a bacterial illness

…or it might be viral in nature

How do you respond?

“Nooooo!”

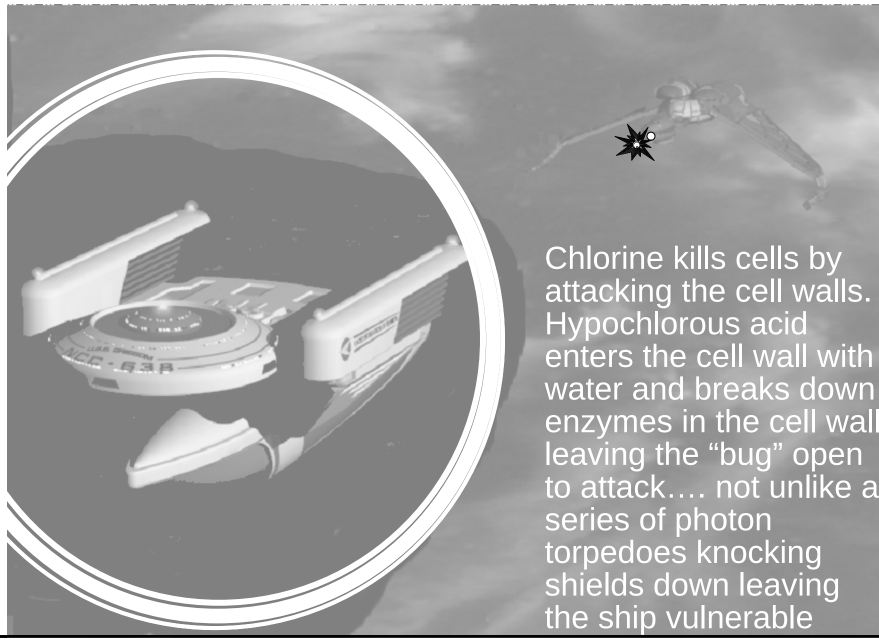
is NOT an acceptable response

"The best defense is a good offense."

– *heavyweight champion Jack Dempsey*

Kill the bugs ⇒ Disinfection **(Chlorination)**

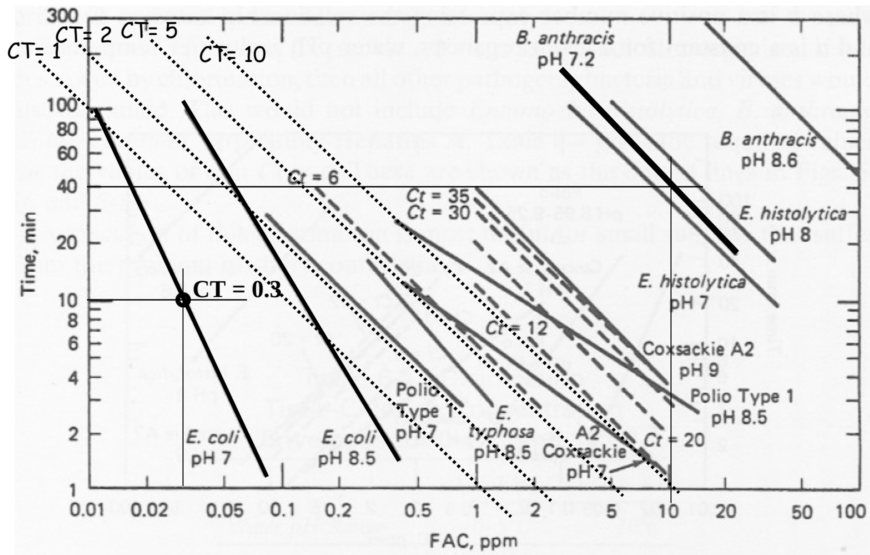
How does chlorine kill?



How effective is chlorine?

- ❑ We need a measure to gauge the killing power
- ❑ The measure commonly used is the “CT” value for any particular agent
- ❑ “**CT**” stands for **C**oncentration x **T**ime
- ❑ Concentration is in ppm (parts per million)
- ❑ Time is in minutes
- ❑ A CT value of 10 could mean
  - Exposure to 10 ppm for 1.0 minute (10 x 1 = 10)
  - Exposure to 1.0 ppm for 10 minutes (1 x 10 = 10)
  - Exposure to 2.0 ppm for 5 minutes (2 x 5 = 10)
- ❑ **The lower the CT value, the more effective the killing agent is**

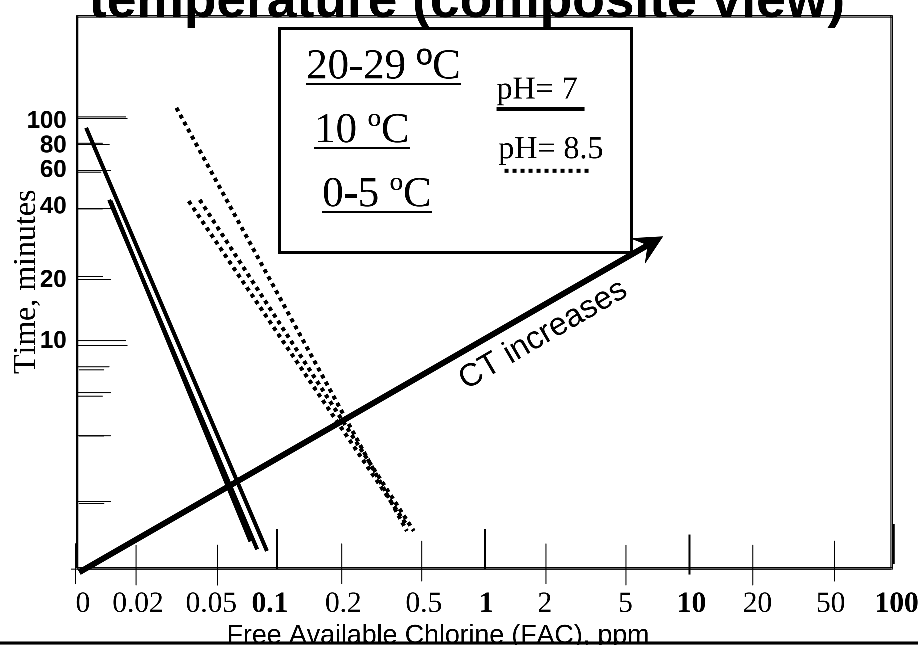
Chlorine effectiveness at 0-5° C (3 log)



Reprinted from *Journal American Water Works Association* **54**, 1379, Nov.1962,

CT values less than 1 for chlorine against E. coli show high effectiveness
Even a CT value of 400 means the resilient anthrax can be handled.

Chlorine effectiveness with temperature (composite view)



Effect of Cl_2 on E.coli

- Recent study on effect of chlorine on E. coli
- Tested 6 strains of O157:H7 at 4 Cl_2 levels
  - ☠ 0.25 mg/L
  - ☠ 0.5 mg/L
  - ☠ 1.0 mg/L
  - ☠ 2.0 mg/L

X **0 0.5 1** **and 2 mins**

contact time

- 5/6 isolates + E. coli control strain were highly susceptible to chlorine
- >7 log10 reduction of each of these strains by 0.25 mg/L free chlorine within 1 min (CT value = 0.25)

Each "log_{10}" = 90% reduction; 4 log_{10} = 99.99% reduction
SDWA requires 4 log reduction

OK, chlorine works, but how? and why?

Chlorine gas rapidly hydrolyzes to hypochlorous acid **:**

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Aqueous solutions of sodium or calcium hypochlorite hydrolyze :

$$Ca(OCl)_2 + 2H_2O \rightarrow Ca^{2+} + 2HOCl + 2OH^-$$

$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^-$$

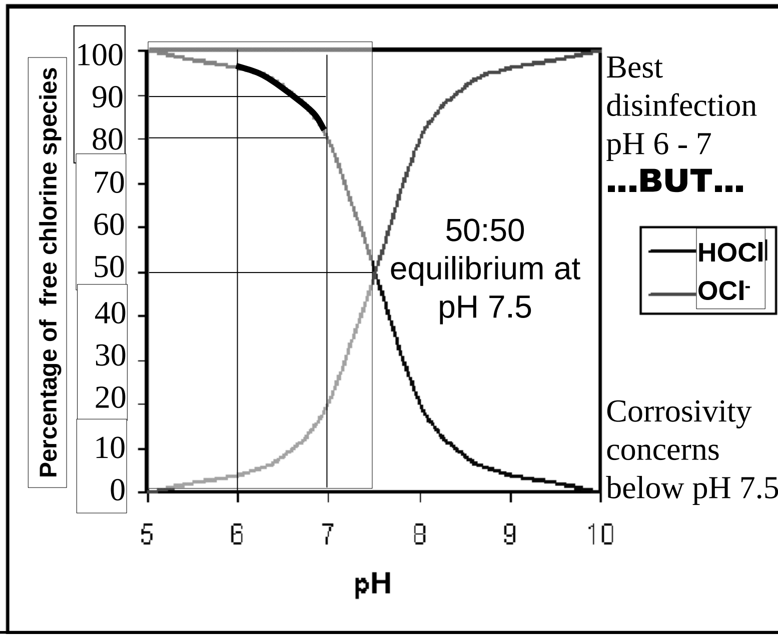
The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl –) are commonly referred to as **"free" or "available"**

Hypochlorous acid is a weak acid and will disassociate:

$$HOCl \Leftrightarrow H^+ + OCl^-$$

In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl –) will be present.
Hypochlorous acid (HOCl) is the more (20x) germicidal form.

Free Chlorine Distribution with pH



Reaction of chlorine/hypochlorite on addition to water

Gas chlorine

$Cl_2 + H_2O$ ➔

$HOCl + H^+ + Cl^-$

↓

$HOCl \Leftrightarrow H^+ + OCl^-$

The generation of free H^+ ions help to lower pH.

Hypochlorite

$Ca(OCl)_2 + 2H_2O$ ➔

$2HOCl + Ca^{++} + 2OH^-$

↓

$HOCl \Leftrightarrow H^+ + OCl^-$

$NaOH \Rightarrow Na^+ + OH^-$

$NaOCl + H_2O$ ➔

$HOCl + Na^+ + OH^-$

↓

$HOCl \Leftrightarrow H^+ + OCl^-$

$NaOH \Rightarrow Na^+ + OH^-$

NOTE: Sodium hydroxide (NaOH) is used as a stabilizing agent. On reaction with water, NaOH ionizes to Na^+ and OH^-, thereby adding to the available OH^- ions and further raising the pH.

Free OH^- ions means pH is raised

Lower pH ➔ better disinfection (HOCl is predominant)

Effect of increasing bleach* concentration on pH of typical southwest WI well.

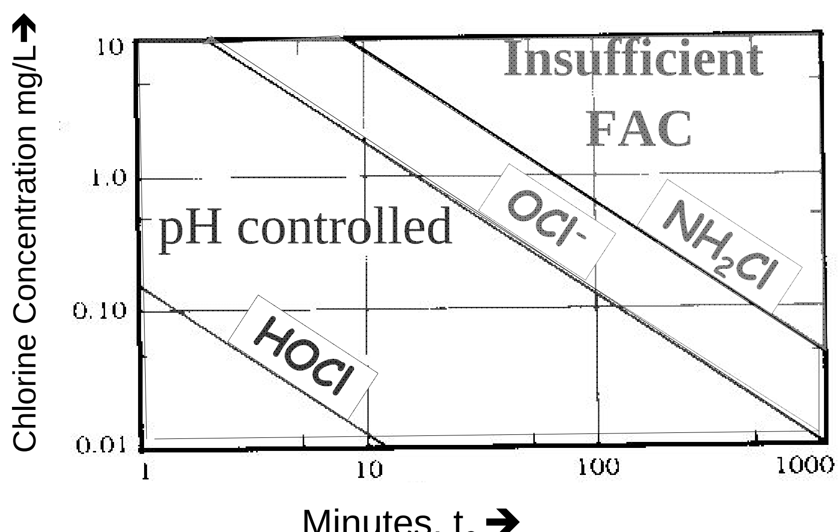
Free Cl_2 ppm	pH	% HOCl	% OCl-
100	**7.83**	**30%**	**70%**
200	8.33	10%	90%
500	8.73	5%	95%
1000	9.24	3%	97%
2000	9.57	2%	98%

Use of household bleach:
= ↑ pH,
= ↑ OCl-, ↓ HOCl
= ↓ effectiveness of FAC
= **Chlorine gas is the best option**

Data from State Laboratory of Hygiene
*Household bleach = 5.25% available chlorine

Effectiveness of chlorine forms vs. E. coli 2-6 °C, 99% reduction

From: Reynolds & Richards, 1996. Unit Processes in Environmental Engineering.



Hypochlorous acid >> Hypochlorite >> Chloramines

What are chloramines?
How do they affect disinfection?

a) At pHs < 8, significant levels of HOCl are present-

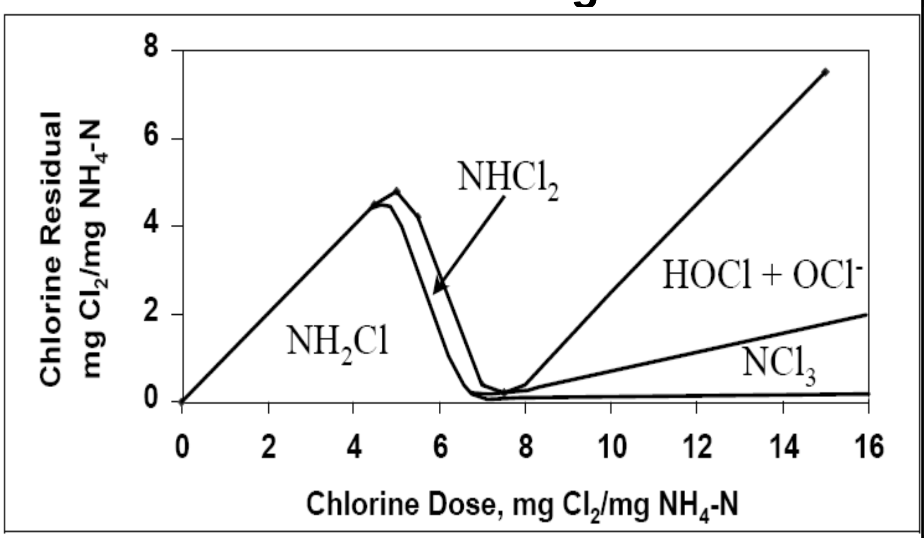
b) If NH_3 is present, HOCl will react to form one of 3 chloramines depending on pH, temperature, & reaction time.

Monochloramine: (stinky)
$2NH_3 + 2HOCl \downarrow 2NH_2Cl + 2H_2O$
Dichloramine: (stinkier)
$2NH_2Cl + 2HOCl \downarrow 2NHCl_2 + 2H_2O$
Trichloramine: (stinkiest!)
$NHCl_2 + 3HOCl \downarrow NCl_3 + 3H_2O$

c) additional free chlorine + chloramine ⇨ H^+, H_2O , and N_2 gas which will come out of solution.

Chloramines: effective vs. bacteria but NOT viruses.

Chloramine Formation with Chlorine Dosage



Source: EPA 815-R-99-014, April 1999
Alternative Disinfectants and Oxidants Guidance Manual

Chlorine Disinfection: other concerns

Free Available Chlorine (FAC) is the major (disinfection agent)

"Demands" on chlorine

Instantaneous

- If the water contains iron (Fe^{+2}) and manganese (Mn^{+2}), insoluble oxides are formed on introduction of chlorine

Intermediate

- Reaction of chlorine with ammonia to form chloramines. This "combined chlorine" offers limited disinfection

Longer Term

- Organic matter- chlorine is consumed during the oxidation process

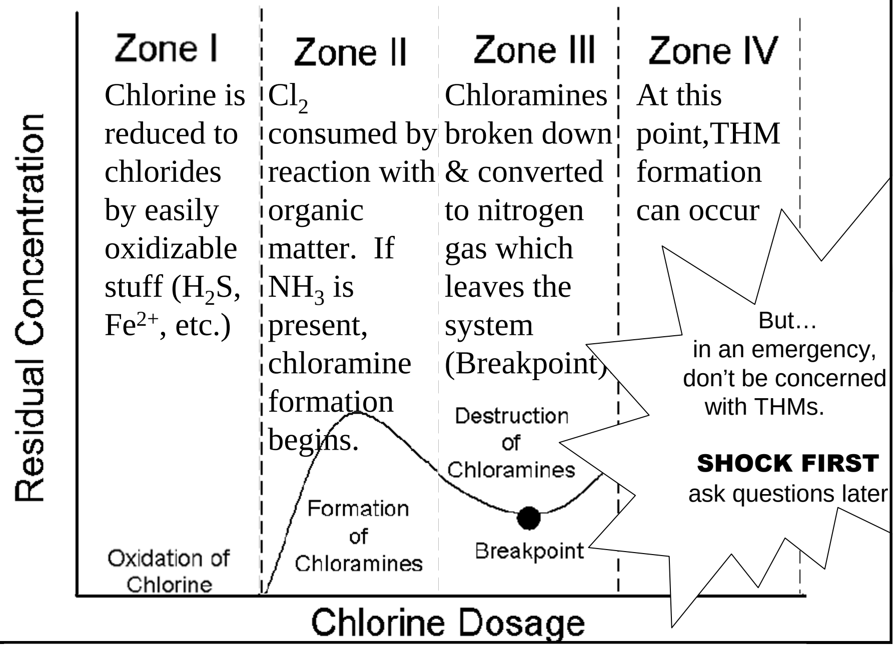
BOTTOM LINE

Disinfection cannot proceed until the oxidant demand has been destroyed.

How do I know if I have "free" chlorine (FAC) needed for best disinfection?

- ❑ To have free available chlorine for disinfection you must be past the "breakpoint"
- ❑ Before the breakpoint, chlorine is used up by inorganics (oxidizing Fe, Mn to chloride) and organics (chloramine formation) in the system
- ❑ Beyond breakpoint, every ppm of chlorine added to the system is measured as FREE chlorine
- ❑ "Shock" chlorination is another rapid way to ensure the presence of significant FAC.

Chlorination & Breakpoint



Ensuring you are at Breakpoint

- **Measure Free <u>and</u> Total chlorine**
- **Bump up chlorinator to increase chlorine dose a certain known amount**
- **On the following day, re-test Free and Total chlorine.**
- **If Total increases but Free does not, you are NOT at breakpoint.**
- **Repeat process until both Total and Free chlorine increase similarly upon adjustment**

Breakpoint Flowchart

Day 1:
Chlorine applied: 1.5 mg/L
FAC: 0.0 mg/L
Total Residual: 0.8 mg/L

→ **Bump up the chlorinator**

+ 0.2 ppm Cl_2 ⇨

Day 2:
Chlorine applied: 1.7 mg/L
FAC: 0.1 mg/L
Total Residual: 1.0 mg/L

→ **Free ⇧ 0.1 ppm; Total ⇧ 0.2 ppm**
Bump up the chlorinator

+ 0.3 ppm Cl_2 ⇨

Almost there! **Day 3:**
Chlorine applied: 2.0 mg/L
FAC: 0.3 mg/L
Total Residual: 0.7 mg/L

→ **Free ⇧ 0.2 ppm; Total ⇩ 0.3 ppm**
Bump up the chlorinator

+ 0.2 ppm Cl_2 ⇨

We're there! **Day 4:**
Chlorine applied: 2.2 mg/L
FAC: 0.5 mg/L
Total Residual: 0.7 mg/L

→ **Free ⇧ 0.2 ppm; Total no change**
Breakpoint!!!!!

Why Breakpoint Chlorination?

- **Recommended deterrent to bioterrorism**
  - ☞ 2 of the DNR's "16 recommendations" for reducing risk relate to chlorination
  - ☞ Many biotoxins can be inactivated by proper disinfection with "free" chlorine.
- **Public protection**
  - ☞ Remember the Walkerton, Ontario outbreak (May 2000) of E. coli O157:H7
- **Liability protection for your water utility.**
  - ☞ illnesses… loss of life➔ attorneys… litigation…

Can you have too much chlorine?

Chlorine is a health concern at certain levels of exposure. Drinking water containing chlorine in excess of standards:

- *potential for irritating effects to eyes and nasal passages.*
- *potential for stomach discomfort.*

Disinfection ByProducts Rule (FR 12/16/98)
Maximum Residual Disinfection Level (MRDL): **4.0 mg/L**
Compliance is based on an annual average.

(this allows the residual to be substantially increased on a short term basis such as would be required to deal with a known or suspected act of chemical/ bio-terrorism)

Little or no risk with drinking water that meets the USEPA MRDL and should be considered safe with respect to chlorine.

pH & disinfection (chlorine):
What you need to know

1. The best disinfection occurs at lower pH.
2. If you have high alkalinity and high pH (> 8) consider longer chlorine contact time due to reduced efficiency of the hypochlorite form.
3. Chlorine (hypochlorite) is a strong base. Therefore, in a low alkalinity system, be wary of pH changes with chlorination.

Chlorination Alternatives

- Chloramination
- UV
- Ozone
- Chlorine Dioxide
- Bromination

Chloramines as a disinfectant

- Addition of ammonia (NH_3) and chlorine (Cl_2) compounds separately. Compounds typically used:
  - Anhydrous ammonia
  - Hypochlorous acid (HOCl)
- Ammonia is applied first because it tends to prevent formation of trichloramine (chlorinous odor and taste)
- Adding ammonia first also prevents the formation of THMs.
- Target ratio: 3:1 HOCl to NH_3 produces the best tasting water

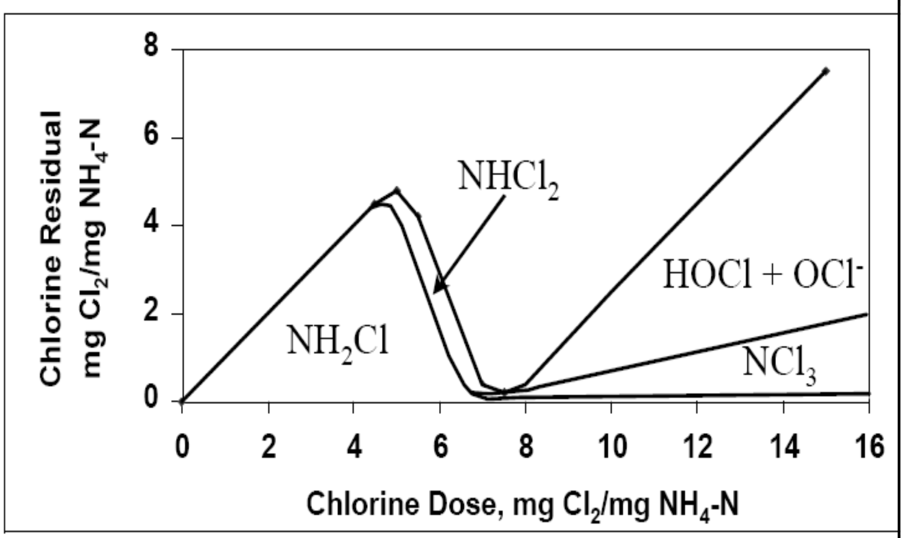
Chloramines as a disinfectant

- Reactions
  - Monochloramine: $NH_3 + Cl_2 = NH_2Cl + HCl$
  - Dichloramine: $NH_3 + 2Cl_2 = NHCl_2 + 2HCl$
  - Trichloramine: $NH_3 + 3Cl_2 = NCl_3 + 3HCl$

  pH control is key to successful chloramination in PWS

  (Note for breakpoint chlorination): *To eliminate NH_3 in drinking water using the breakpoint process, (e.g., surface water supply) chlorine is fed at a ratio of 10-12 to 1 to the ammonia level.*
- When chloramines are used, the distribution system must be continually monitored for mono- and dichloramine residuals and DO. Total chlorine is not enough.

Chloramine Formation



Source: EPA 815-R-99-014, April 1999
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Chloramination: potential problems

- Adding NH_3 may compromise water quality at the tap
- Should the residual chloramine be depleted in the distribution system, serious dead-end problems can result.
- Nitrification can occur.
- Residual chloramines can pass through RO membranes on dialysis machines which can cause damage to red blood cells.
- Chloramines are toxic to aquatic life in aquariums.
- Requires longer contact time to be an effective germicidal agent.
- The process is complex, requires careful control and continual monitoring.
- Taste and odor problems can occur

Chloramines as a disinfectant

Taste and odor threshold concentrations:

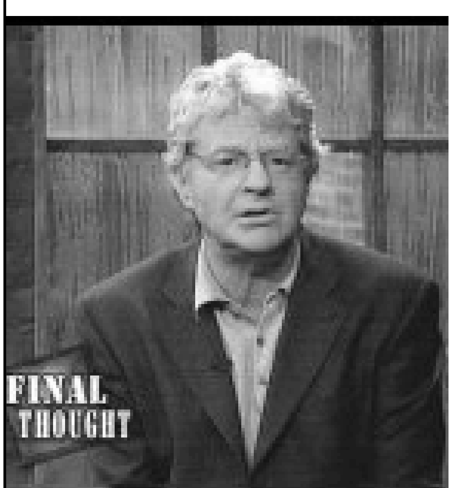
- Free chlorine (HOCl): 20 mg/L
- Monochloramine (NH_2Cl): 5.0 mg/L
- Dichloramine ($NHCl_2$): 0.8 mg/L
- Trichloramine (NCl_3): 0.02 mg/L

Disinfection Techniques Summary

- Chlorine in very low doses and minimal contact time can easily kill even the most heinous of bacteria (E. coli O157:H7)
- Some of the alternative disnfection techniques CAN provide superior disinfection to chlorine, but there are cost and maintenance issues to consider
- Many alternative techniques still require post-chlorination to meet NR 809 requirements.

Final Thoughts

The best defense to provide continual protection of public health...



- …if possible, practice breakpoint chlorination
- …test for and maintain a FAC residual of 0.5 ppm <u>throughout</u> the system
- …remember that disinfection is based on "CT" …
  Concentration (ppm)
  × Contact Time (minutes)
- …regardless of whether you use chlorine or chloramination, control of pH is absolutely critical

Questions?

Rick Mealy
(608) 264-6006
richard.mealy@Wisconsin.gov

Wisconsin DNR
PO Box 7921
Madison, WI 53707

George Bowman
(608) 224-6279
gtb@mail.slh.wisc.edu

State Laboratory of Hygiene
2601 Agriculture Drive
Madison, WI 53718

State Lab web address:
http://www.slh.wisc.edu/outreach/
LabCert web address:
http://www.dnr.state.wi.us/org/es/science/lc/

Periodic Table - Halogen sequence

					helium 2 He 4.0026
boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]

Those elements in the same column share similar properties, thus we can expect Bromine and Iodine to have some disinfectant capability.

As one moves downward through a column, molecular weight increases increasing toxicity potential.

[*Notice the proximity of Iodine (I)to toxic heavy metals such as antimony (Sb) and lead (Pb*)]

Bromine & Iodine Disinfection

Bromine

$H_2O + Br_2 \Rightarrow H^+ + Br^- + HOBr$

- Major difference (vs. Cl2): effectiveness starts dropping at pH 8.5
- Does form bromamines…as effective as HOBr
- Bromine is relatively scarce, making it more expensive choice
- Bromine is more physiologically active thus its use is limited.

Iodine

$H_2O + I_2 \Rightarrow H^+ I^- + HOI$

- Effectiveness NOT affected by pH
- Does NOT react with ammonia (no Iodamines)
- Iodine is very scarce, making it a very expensive choice
- Iodine is extremely physiologically active (i.e., thyroid gland)…thus its use is limited.

Chlorine Dioxide Disinfection

Initially used at Niagara Falls water utility (ca. 1944) for taste & odor control.

Produced by reacting sodium chlorite with chlorine or an acid.

Advantages

- Strong disinfectant
- Does NOT produce THMs
- effective vs. Cryptosporidium & Giardia
- weakens organism allowing chlorine to work

DIS-Advantages

- Relatively expensive to generate; explosive above 10%
- Unstable--reverts to chlorite & chlorate (other DBPs)

Ozone Disinfection

- $3\ O_2 \Leftarrow\Rightarrow 2\ O_3$ (ozone)
- $O_3 \rightarrow O_2 + O\bullet$ (oxygen radical)
- Bugs killed immediately upon contact (cell rupture)
- Oxygen radical apparently is the actual cause
- strongest disinfectant used in water treatment
- effectiveness unimpaired by NH_3 or pH
- leaves DO in its wake

- Must be generated on-site
- no residual
- difficult to adjust to differing demand
- expensive

Ozone - Advantages & Disadvantages

ADVANTAGES

- Strong oxidizing power + short contact time = effective kill of bugs & viruses in seconds;
- Produces no taste or odor;
- Provides oxygen to the water after disinfecting;
- Requires no chemicals;
- Oxidizes iron and manganese;
- Destroys and removes algae;
- Reacts with and removes all organic matter;
- Decays rapidly in water, avoiding any undesirable residual effects;
- Removes color, taste, and odor;
- Aids coagulation.

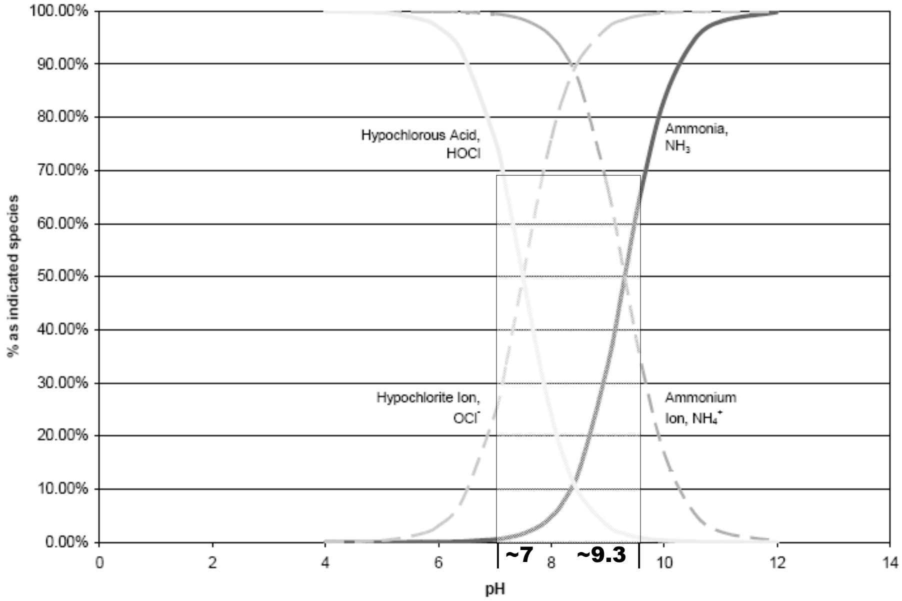
DIS-ADVANTAGES

- Toxicity ↑ with concentration and exposure time;
- Cost is > chlorination;
- Installation can be complicated;
- Ozone-destroying device is required at the exhaust
- May produce undesirable aldehydes and ketones by reacting with certain organics;
- No residual in distribution system, ∴ post-chlorination is required;
- Much less soluble in water than chlorine; thus special mixing devices are necessary; and
- Oxidizes some refractory organics either too slowly or not at all to be of practical significance.

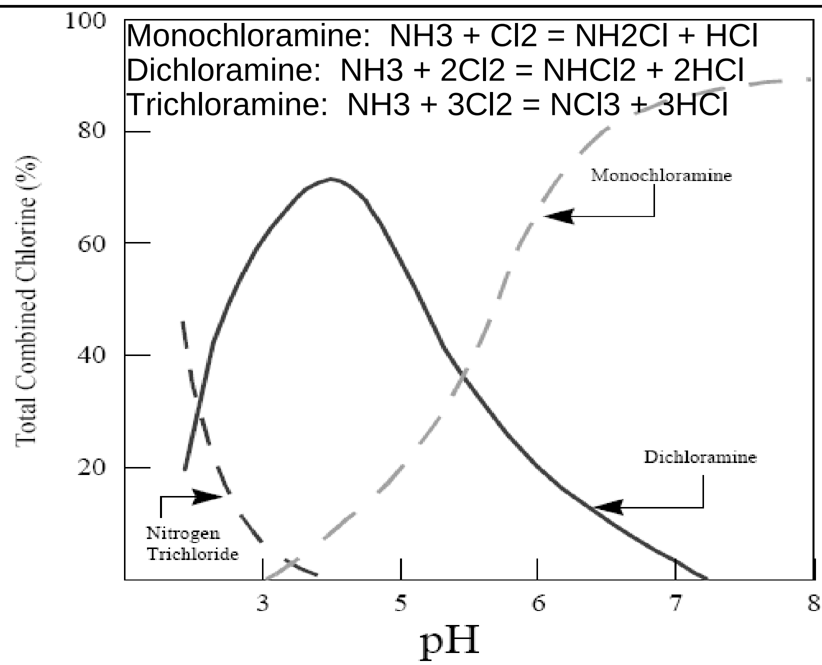
UV Disinfection

- Kill bugs by oxidizing their enzymes and destroying genetic material
- Most effective wavelength is 2,650 Angstroms(Å) (anything less than 3,100 is effective)
- Mercury vapor lamp is economical, produces 2,537 Å
- Water needs to be clear/colorless and shallow (3-5” deep)
- No residual effect
- Cost is high

Ammonia vs. Chlorine



Source: Freese and Nichols, Inc , 2006.
The ties that bind: forming chloramines that last



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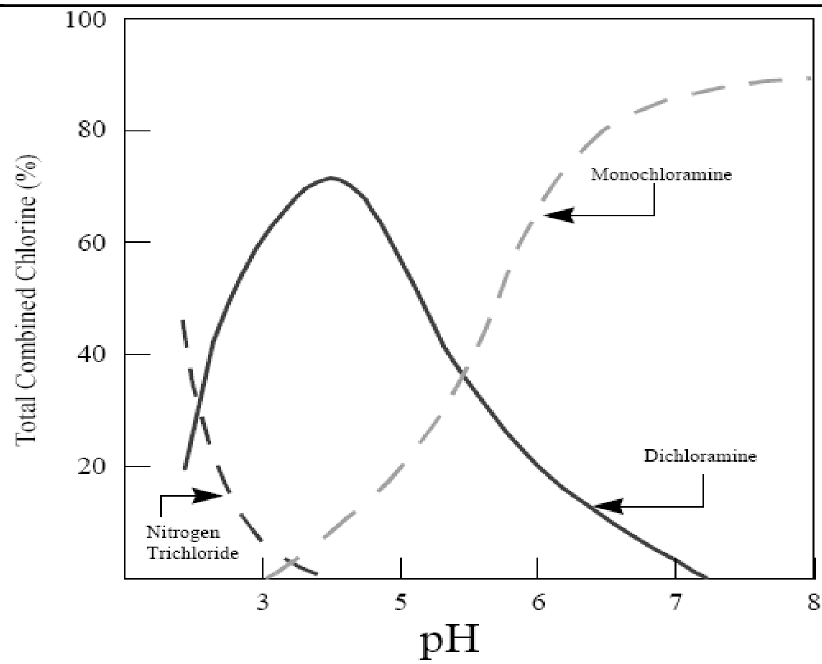

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