Disinfection

The Case for Chlorine

- It kills stuff (Revenge)
- Residual
  - It's the law... But is it a good idea?
  - Chlorine is the only available disinfectant that provides a residual
- Recontamination
  - Does a chlorine residual provide protection against recontamination?
  - How much chlorine would be required?
- Regrowth
  - Very few pathogens multiply in drinking water

Chlorine Based Disinfectants

Contaminant	MRDLG [1] (mg/L)[2]	MRDL[1] (mg/L) [2]	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Chloramines NH_2Cl (as Cl_2)	MRDLG =4[1]	MRDL =4.0[1]	Eye/nose irritation; stomach discomfort, anemia	Water additive used to control microbes
Chlorine (as Cl_2)	MRDLG =4[1]	MRDL =4.0[1]	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Chlorine dioxide (as ClO_2)	MRDLG =0.8[1]	MRDL =0.8[1]	Anemia; infants & young children: nervous system effects	Water additive used to control microbes

Maximum Residual Disinfectant Level (MRDL) - The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants. **Maximum Residual Disinfectant Level Goal (MRDLG)** - The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.

Chlorine is highly reactive

- First large-scale chlorination was in 1908 at the Boonton Reservoir of the Jersey City Water Works
- Typical dosage at the water treatment plant (1-5 mg/L)
  - variable, based on the chlorine demand
  - goal of 0.2 mg/L residual
- Trihalomethanes (EPA primary standard is 80 μg/L)1
- Chlorine concentration is reported as Cl_2 even when in the form of HOCl or OCl-

Chlorine oxidizes organic matter

1) http://water.epa.gov/lawsregs/rulesregs/sdwa/mdbp/mdbp.cfm#trihalomethanes

The EPA requires a chlorine residual

- Minimum free chlorine residual in a water distribution system should be 0.2 mg/L.[1]
- For all systems using surface water or groundwater under the influence of surface water for supply, a detectable disinfectant residual must be maintained within the distribution system in at least 95% of the samples collected (or heterotrophic bacteria counts must be less than or equal to 500 cfu/ml as an equivalent) and at least **0.2 mg/L concentration of residual disinfectant** (free or combined) entering the distribution system must be maintained.[2]

Chloramines are also known as combined chlorine

1) http://10statesstandards.com/waterstandards.html#4.3.3
2) http://www.epa.gov/ogwdw/disinfection/tcr/pdfs/issuepaper_effectiveness.pdf

Chorine isn't always required

- The European Union does not require disinfection. Of the 15 original European Union member states, only Spain and Portugal require disinfection in distribution systems.[1]
- Amsterdam stopped chlorinating in 1983
- Chlorine not required for groundwater!

1) http://www.epa.gov/ogwdw/disinfection/tcr/pdfs/issuepaper_effectiveness.pdf

Contamination on the way from the treatment plant to your house

- Necessary conditions:
  - Saturated contaminated soil
  - Leaky Pipe
  - Pressure outside pipe must exceed pressure inside pipe
- Potential Causes:
  - Negative pressure transients
  - Booster pumps

*Photo credits
Top: http://texas-slab-leak-repair.com/water_leak
Bottom: Emily Kumple

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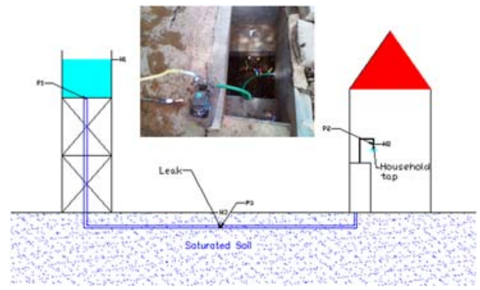
Flat terrain scenario for pipeline contamination



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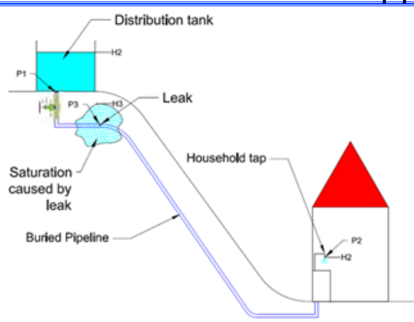
Recontamination is easy in hilly terrain with intermittent supply



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Cross Contamination is a

- Caused by:
  - Household booster pumps
  - Household taps at lower elevation than saturated ground
  - Pipeline pressure transients
- Prevented by:
  - 24/7 water supply
  - No household booster pumps
  - Float valves for household storage

Alicia Peters, David Gold, Weier Chen, Lucia Garcia-Iturri Gallego. Distribution System Contamination Prevention. 2014

Why is a Residual Required? Why is Chlorine the only option?

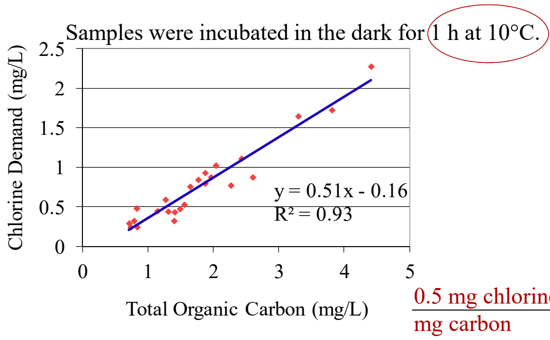
- Inactivating microorganisms in the distribution system
  - Treatment breakthrough
  - Leaking pipes, valves, and joint seals
  - Cross-connection and backflow
  - Finished water storage vessels
  - Improper treatment of equipment or materials before and during main repair
  - Intentional introduction of contaminants into distribution system
- Indicating distribution system contamination (If residual chlorine is monitored continuously it might be possible to detect an increase in contamination from a decrease in chlorine.)
- Controlling biofilm growth

Chlorine is assumed to protect against recontamination

- Proponents of maintaining a disinfectant residual point to situations where residuals were not maintained and preventable waterborne disease outbreaks occurred.
- Haas (1999) argues that both a 1993 Salmonella outbreak caused by animal waste introduced to a distribution system reservoir and a 1989 E. coli O157:H7 outbreak could have been prevented if distribution system chlorination had been in effect.
- Both of these outbreaks were due to bacterial pathogens that are sensitive to chlorine and could have been at least partially inactivated.[1]

1) http://www.epa.gov/ogwdw/disinfection/tcr/pdfs/issuepaper_effectiveness.pdf

Chlorine Demand vs. Total Organic Carbon

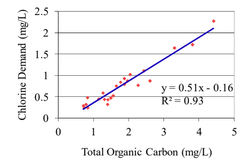


$\frac{0.5 \text{ mg chlorine}}{\text{mg carbon}}$

Chlorine Protection against Recontamination?

- How much sewage would residual chlorine at 0.2 to - 0.5 mg/L protect you from?

0.4 to 1.0 mg/L of organic carbon



How much organic matter could be treated by residual Cl_2?

- Take a town of 5000 people
- Flow rate per person is about 3 mL/s
- Average flow rate is 15 L/s
- Assume storage tank is half full when contamination event occurs
- Small town storage tanks typically provides 1/3 day of storage – 432,000 L
- Assume 0.2 mg/L Cl_2 residual – 0.4 mg/L C
- 173 gm of organic carbon (distributed uniformly throughout the entire storage tank…)

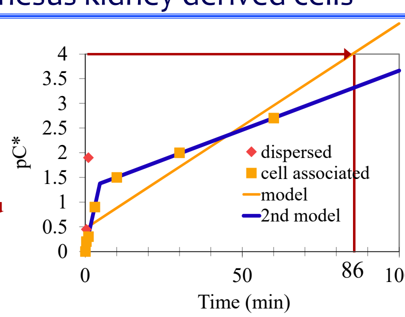
Inactivation of Shielded Pathogens

- Many of the studies measuring inactivation of pathogens by disinfectants were conducted using dispersed pathogens
- What happens if the pathogens are embedded in an organic particle?
- Fecal contamination potentially contains pathogens embedded in protective organic matter

Cell Associated virus was inside fetal rhesus kidney derived cells

0.36 mg/L average free Cl_2 at pH 6

What do you conclude?

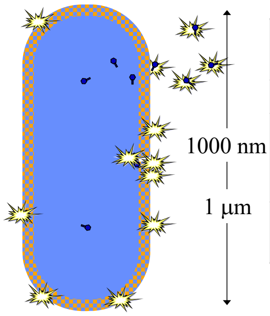


$C_{Cl} \cdot t$ to get pC* of 4 is (86 min)*(0.36 mg/L)=31 (min mg/L)

Embedded virus particles are protected from chlorine

- The rate of virus deactivation dropped significantly when the virus particles were inside kidney cells
- The deactivation of embedded virus particles can not be described by a single first order reaction (Chicks Law is violated)
- What is controlling the rate of virus deactivation?

Scales of the Embedded Virus

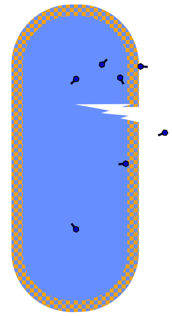


Location	Deactivation rate
Dispersed	Very fast
Inside cell with disrupted cell wall	Slow
Inside intact cell	Very slow

Virus particles are about 20 nm

HOCl are about 0.2 nm

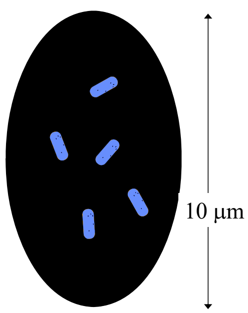
Mass Transport and Chlorine Protection



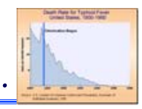
- Chlorine must diffuse through cell contents to reach virus
- Organic material inside the cell reacts with chlorine before it gets to the virus

Larger particle aggregates provide long term protection from chlorine

- Turbid water could easily have organic particles that are 10 or even 100 µm in diameter
- The amount of organic matter in a small particle and the slow diffusion would provide long term protection for embedded pathogens



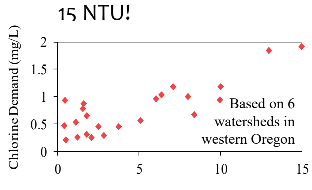
Chlorine save lives…



- If you accept the "Chlorine eliminated Typhoid Myth"
- Then you will likely recommend chlorination as the first line of defense in the Global South-
- But in small systems (in the Global South)
  - Chlorine dose is generally not controlled based on a target residual dose
  - Surface water may currently be untreated and hence have high turbidity
    - that correlates with high chlorine demand
    - that contains pathogens embedded in organic particles

Chlorine demand is positively correlated with turbidity

- Disclaimer – There is no solid connection between chlorine demand and turbidity
- But – organic matter is often associated with particulate matter
- If using a chlorine dose of 2 mg/L, then no residual chlorine would be maintained above 15 NTU!



Turbidity and Chlorine

- Chlorine test showing no residual after exposure to turbid tap water (left)

Chlorine Sources

- On Site Production (electrolysis)
- Chlorine gas (Cl_2)
- Liquid Bleach (NaOCl)
- Calcium hypochlorite (1 mg $Ca(OCl)_2$ is equivalent to 0.65 mg of Cl_2)

Bleach Concentration in terms of sodium hypochlorite (NaOCL)			Bleach concentration in terms of Available Chlorine (As Cl_2)			Additional Information (estimated)	
Wt. %	Trade %	Grams per liter	Wt. %	Trade %	Grams per liter	Density of the solution (lb/U.S. gal)	Specific gravity of the solution
5	5.4	53.9	4.8	5.1	51.4	9.0	1.08
10	11.6	115.8	9.5	11.0	110.4	9.7	1.16
15	18.6	185.7	14.3	17.7	177.0	10.3	1.24

How much Clorox should you add to a 5 gallon bucket or a 1L bottle?

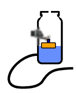
$$\text{Stock} := 51400\frac{\text{mg}}{\text{L}} \qquad \text{Stock} := 51400\frac{\text{mg}}{\text{L}}$$

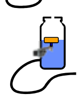
$$\text{Dose} := 2\frac{\text{mg}}{\text{L}} \qquad \text{Dose} := 2\frac{\text{mg}}{\text{L}}$$

$$20\text{L}\cdot\frac{\text{Dose}}{\text{Stock}} = 0.78\text{mL} \qquad 1\text{L}\cdot\frac{\text{Dose}}{\text{Stock}} = 39\mu\text{L}$$

Calcium hypochlorite is cheaper to transport

- Relatively inexpensive ($3 per kg)
- Easy to transport (high equivalent moles of Cl_2 per unit mass)
- Less dangerous than chlorine gas
- High calcium concentration results in insoluble calcium carbonate from exposure to the atmospheric CO_2 or dissolved carbonates.
- Clogs tubing and float valves (submerged orifice works better to avoid contact with atmospheric CO_2)





Chlorine Reactions

Charges 0 +1 -2 +1 -1

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

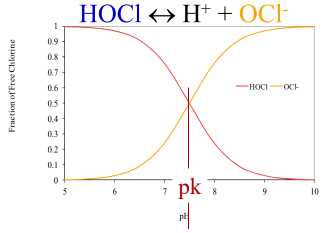
Hypochlorous acid $HOCl \leftrightarrow H^+ + OCl^-$ Hypochlorite ion

- The sum of HOCl and OCl^- is called the free chlorine residual

Chlorine and pH

- HOCl is the more effective disinfectant
- Therefore chlorine disinfection is more effective at low pH
- Dissociation constant is $10^{-7.5}$
- HOCl and OCl^- are in equilibrium at pH 7.5

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



$$pC^* = \frac{t_{contact}\cdot C_{Cl}^{0.85}}{0.2828\left(pH^{2.69}\right)\left(0.933^{(T-5)}\right)}$$

EPA Pathogen Inactivation Requirements

Safe Drinking Water Act

- SDWA requires 99.9% inactivation for *Giardia* and 99.99% inactivation of viruses
- *Giardia* is more difficult to kill with chlorine than viruses and thus *Giardia* inactivation determines the CT

Concentration x Time

EPA Credits for *Giardia* Inactivation

Treatment type	Credit
Conventional Filtration	99.7%
Direct Filtration*	99%
Disinfection	f(time, conc., pH, Temp.)

$$pC^* = \frac{t_{contact} \cdot C_{Cl}^{0.85}}{0.2828\left(pH^{2.69}\right)\left(0.933^{(T-5)}\right)}$$

* No sedimentation tanks

EPA Disinfection CT Credits

To get credit for 99.9% inactivation of *Giardia*:

Contact time (min)

chlorine (mg/L)	pH 6.5 2°C	pH 6.5 10°C	pH 7.5 2°C	pH 7.5 10°C
0.5	300	178	430	254
1	159	94	228	134

Inactivation is a function of time, concentration, pH, and temperature.

Where did these numbers (to 3 significant digits) come from?

CT equation for Giardia

$$C_{Cl} \cdot t_{contact} = 0.2828\left(pH^{2.69}\right)\left(C_{Cl}^{0.15}\right)\left(0.933^{(T-5)}\right)pC^*$$

$$t_{contact} = 0.2828\left(pH^{2.69}\right)\left(C_{Cl}^{-0.85}\right)\left(0.933^{(T-5)}\right)pC^*$$

$$pC^* = \frac{t_{contact} \cdot C_{Cl}^{0.85}}{0.2828\left(pH^{2.69}\right)\left(0.933^{(T-5)}\right)}$$

- C_{Cl} = Free Cl_2 Residual [mg/L]
- $t_{contact}$ = Time required [min]
- pH = pH of water
- T = Temperature, degrees C
- pC* = -[Log(fraction remaining)]

Note: These equations are NOT dimensionally correct!

Disinfection Byproducts

Contaminant	MCLG[1] (mg/L)[2]	MCL (mg/L)[2]	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Bromate	zero	0.010	Increased risk of cancer	Byproduct of drinking water disinfection (plants that use **ozone**)
Chlorite	0.8	1.0	Anemia; infants & young children: nervous system effects	Byproduct of drinking water disinfection (plants that use **chlorine dioxide**)
Haloacetic acids (HAA5)	n/a[6]	0.060	Increased risk of cancer	Byproduct of drinking water disinfection
Total Trihalomethanes (TTHMs)	none[7] ---------- n/a[6]	0.10 ---------- 0.080	Liver, kidney or central nervous system problems; increased risk of cancer	Byproduct of drinking water disinfection

What happens to residual chlorine when you drink it?

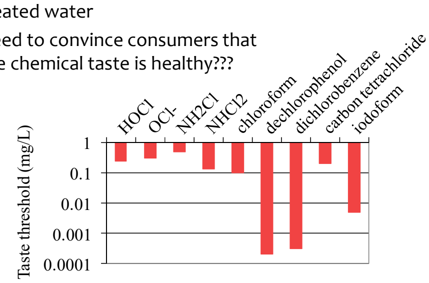
Dark side of chlorine

- Bladder cancer in the US in 2011 - New cases: 69,250 - Deaths: 14,990 (http://www.cancer.gov/cancertopics/types/bladder)
- 15% attributable to exposure to chlorination by-products (http://www.ncbi.nlm.nih.gov/pubmed/8932920)
- 1/139,000 people may die from bladder cancer from exposure to chlorination by-products

$$\frac{1}{14990\,\frac{0.15}{312640961}} = 139044$$

Tastes and Odors: Taste Thresholds

- Complaints of the chlorine taste should not be discounted
- Chlorine taste may prevent some consumers from using treated water
- Need to convince consumers that the chemical taste is healthy???



Getting the Right Dose: WHO on Chlorination

- Chlorine compounds usually destroy exposed pathogens after 30 minutes of contact time, and free residual chlorine (0.2–0.5 mg per liter of treated water) can be maintained in the water supply to provide ongoing disinfection.
- Several chlorine compounds, such as sodium hypochlorite and calcium hypochlorite, can be used domestically, but the active chlorine concentrations of such sources can be different and this should be taken into account when calculating the amount of chlorine to add to the water. Remove particles first!

Conclusions

- Chlorine can inactivate many types of pathogens with inactivation efficiency a function of pathogen type, embedded protection, contact time, pH, dose…
- Chlorination cannot replace particle removal for surface waters
- If you can see cloudiness in a glass of water it is too dirty for chlorine!
- Chlorine cannot make water contaminated with feces safe to drink
- Efforts to prevent contamination of treated water all the way to the consumer's mouth are very important!

Confusions

- The importance of chlorine residual for protection against recontamination is unclear
- There are negative health effects to chlorination
- Chlorine dosages should be kept as low as possible
- Removal of dissolved organics is important to reduce disinfection byproduct formation