DISINFECTION

- Why does getting this right matter?
- Disinfection Options
  - Chlorine
  - Ozone
  - Irradiation with Ultraviolet light
  - Iodine
  - Silver
- Disinfection mechanisms
  - Chicks law
  - CT
- Problems with Disinfection
  - Disinfection-by-products
  - Tastes and odors
  - Real pathogens
  - Getting the right dose
- Poisson Distribution of Pathogens
  - Probability of ingesting k pathogens
  - Implications for dose dependency
- WaterBorne Disease Outbreaks

Chlorine

- Chlorine sources
  - Gas
  - Bleach
  - Onsite production
- Chemistry
  - Metals
  - Water
  - Ammonia
  - Organics
- The case for Chlorine
  - It kills stuff
  - Residual
  - Recontamination
  - Regrowth
- Hypochlorinators
- Chlorine free
  - Some European cities

Chlorine saves lives…

- If you accept the "Chlorine eliminated Typhoid Line"
- 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

WHO on alternative disinfectants:

Iodine, silver, copper, quaternary ammonium compounds

- none of them are considered suitable for long-term use to disinfect drinking water
- Iodine is difficult to deliver to water and can cause adverse health effects
- However, iodine, either dissolved in water or in the form of an iodinated exchange resin, has been used for short-term water treatment
- Silver and copper are difficult to deliver to water and are only bacteriostatic.
- Quaternary ammonium compounds are limited in availability, costly and not effective against viruses and parasites.

Silver as a Disinfectant…

- Silver is used as a bacteriostatic agent for point-of-use or household water treatment by storing water in vessels composed of silver or passing water through porous or granular filter media impregnated with silver
- Many microbes including viruses, protozoan cysts, oocysts, and bacterial spores, are not inactivated at silver concentrations employed for point-of-use drinking water treatment
- Bacteria may develop silver resistance
- Therefore, silver is not recommended for routine disinfection of household water

Chlorine Disinfection Mechanisms*

- Oxidation of membrane-bound enzymes for transport and oxidative phosphorylation
- Oxidation of cytoplasmic enzymes
- Oxidation of cytoplasmic amino acids to nitrites and aldehydes
- Oxidation of nucleotide bases
- Chlorine substitution onto amino acids
- DNA mutations
- DNA lesions

(more likely)

*It is possible that none of these mechanisms have been documented

Chick's Law

- The death of microorganisms is first order with respect to time
- Thus, the remaining number of viable microorganisms, N, decreases with time, t, according to:

$$\frac{dN}{dt} = -kN$$

- where k is an empirical constant descriptive of the microorganism, pH and disinfectant used.
- Integrating with respect to time, and replacing limits ($N = N_o$ at $t = 0$) yields:

$$N = N_0 e^{-kt} \qquad \ln\frac{N}{N_0} = -kt \qquad pC^* = \frac{1}{\ln(10)}kt$$

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

Disinfectant Limitations

- Disinfection by products
- Tastes and Odors
- Real pathogens
- Getting the right dose

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

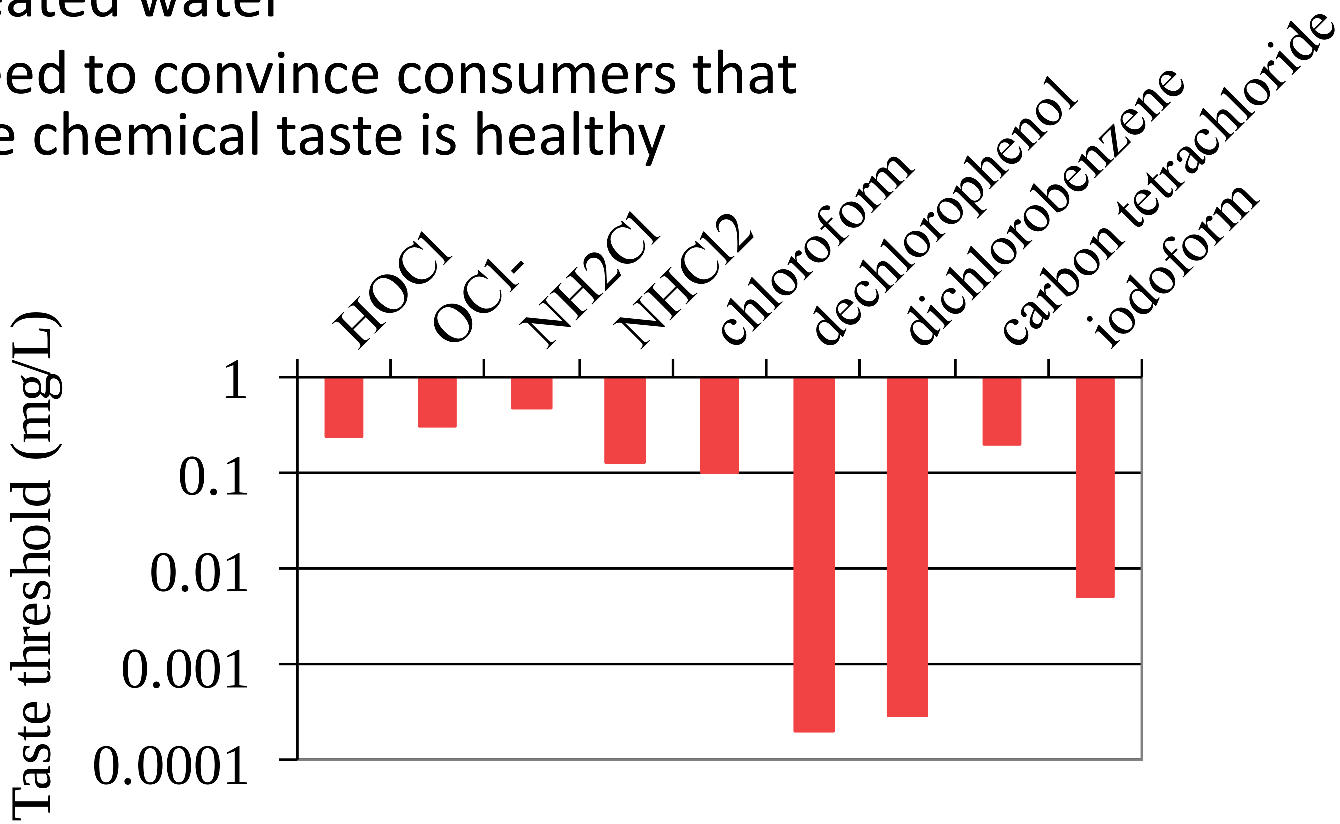
Disinfectants

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 (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.

Tastes and Odors: Taste Thresholds

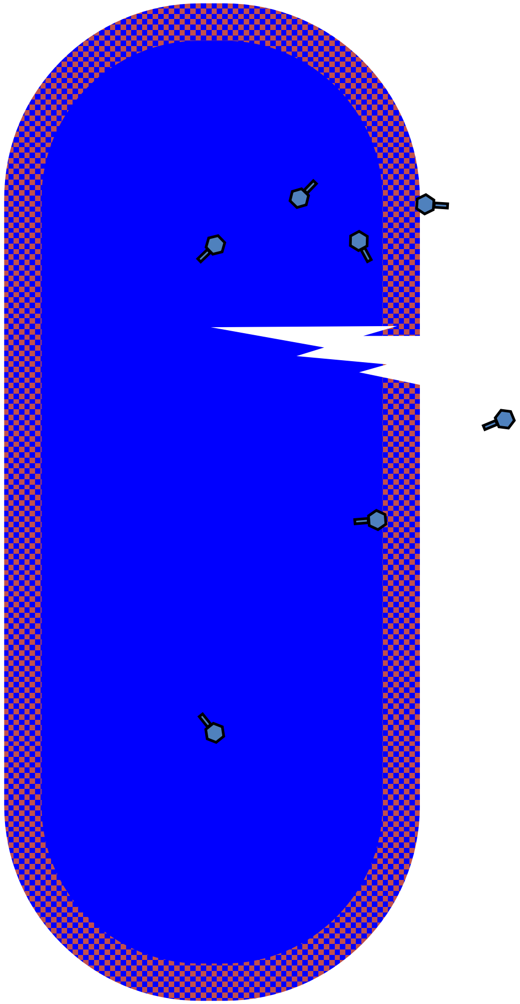
- Complaints of the chlorine taste should not be discounted
- Chlorine taste may prevent some consumers from using treated water
- Need to convince consumers that the chemical taste is healthy



Chlorine Taste Acceptance

- The introduction of chlorine into a community that has always drunk water without the addition of chemicals can be difficult.
- Reducing the amount of chlorine added might increase the social acceptance of chlorination.
- With less chlorine, there is less breakthrough of chlorinated compounds into the finished water, and therefore less of a chemical taste.
- If the water doesn’t taste strongly like chemicals, more people are likely to subscribe to the use of chlorine for disinfection.

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

Getting the Right Dose: WHO on Chlorination

- Chlorine compounds usually destroy 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. [handwritten above "pathogens": exposed]
- 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.
- The amount of chlorine that will be needed to kill the pathogens will be affected by the quality of the untreated water and by the strength of the chlorine compound used.
- If the water is excessively turbid, it should be filtered or allowed to settle before chlorinating it (_Remove particles first!_____)

Effect of Pathogen Dose

$$\text{For CV} = 0.001,\ P_{k>0} = 0.001$$

- What happens if the pathogen dose is 10 rather than 1?
- Let's assume that the concentration of this new pathogen is 10 times as great (CV=0.01)
- What is the probability that you ingest 10 or more? For CV = 0.01, $P_{k\geq 10} = 3\text{x}10^{-27}$
- Pathogens with an infectious dose of 1 are potentially quite harmful even at very low concentrations!
- Pathogens with an infectious dose>1 are not dangerous at low concentration!

Chlorine Sources

- On Site Production (electrolysis)
- Chlorine gas (Cl_2)
- Liquid Bleach (NaOCl)
- Calcium hypochlorite (Contains 65% available chlorine) $Ca(OCl)_2$

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

Chlorine

- First large-scale chlorination was in 1908 at the Boonton Reservoir of the Jersey City Water Works in the United States
- Widely used in the US
- Typical dosage (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)
- Chlorine concentration is measured as Cl_2 even when in the form of HOCl or OCl^-

Chlorine oxidizes organic matter

Chlorine Reactions

Charges: Cl_2 → 0; in HOCl: H → +1, O → -2, Cl → +1; Cl^- → -1

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

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

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

Ammonia Reactions

-3 +1 -3 +1 +1

$$NH_{3(aq)} + HOCl \rightarrow NH_2Cl + H_2O$$

Combined chlorine

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$$

- Substitution reactions…
- The combined chlorine maintains its oxidizing potential

Breakpoint Chlorination

- Removal of ammonia by chlorination

$$\overset{-3}{2NH_{3(aq)}} + \overset{+1}{3HOCl} \rightarrow \overset{0}{N_2} + \overset{-1}{3Cl^-} + 3H_2O$$

- Oxidizing equivalents of chlorine are consumed

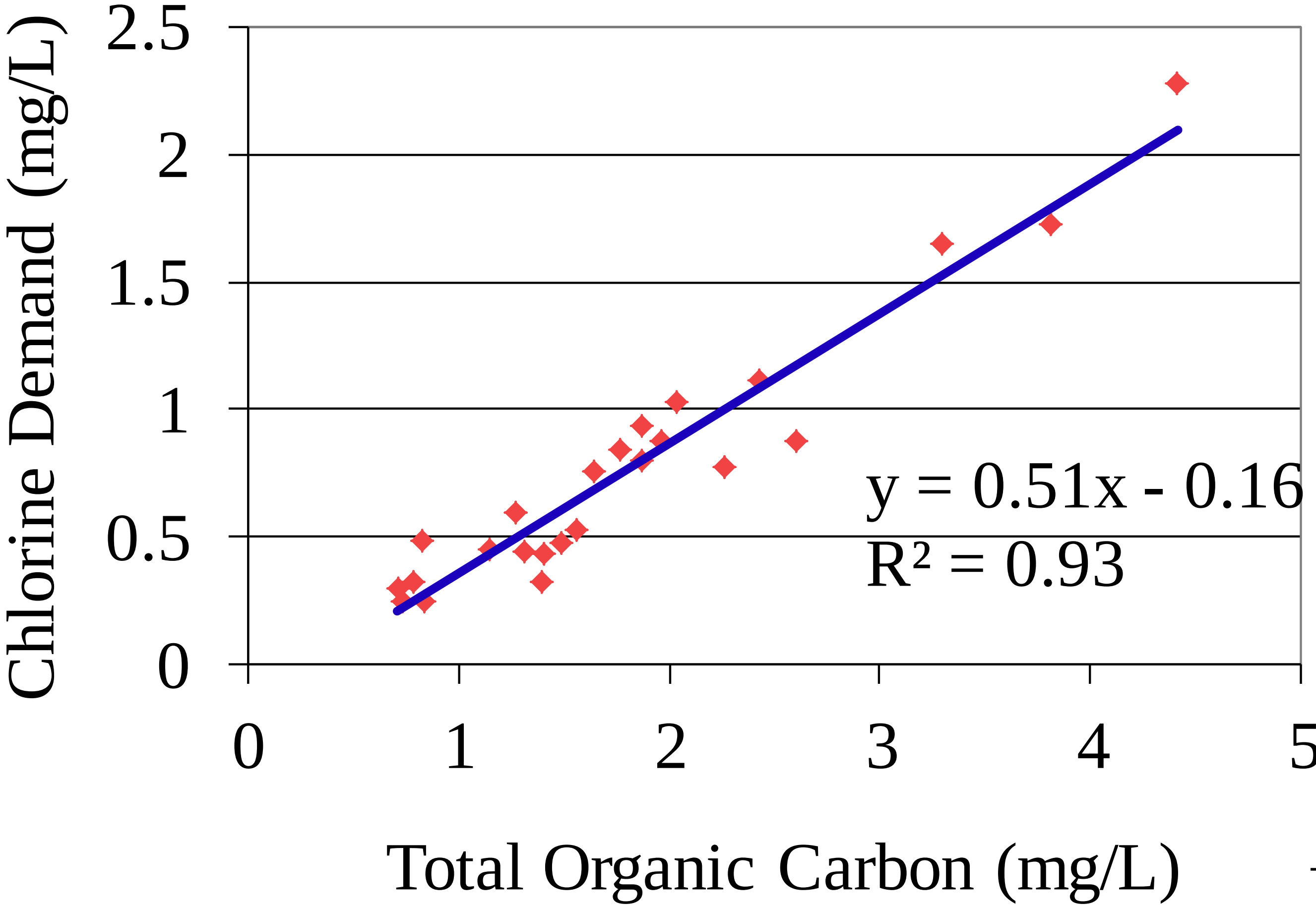
Does Chlorine Completely oxidize organic matter?

NO!

~~$4HOCl + CH_4 \rightarrow CO_2 + 2H_2O + 4Cl^- + 4H^+$~~

- Oxidation states
  - Carbon in organic matter (-4)
  - Carbon in carbon dioxide (+4)
  - Chlorine in HOCl (+1)
  - Chloride (-1)
- Therefore should take 4 moles of chlorine (Cl_2) per mole of organic carbon
- 23.6 g chlorine/g organic carbon

Chlorine Demand vs. Total Organic Carbon



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

Reaction with organic compounds with unsaturated linkages

$$\begin{array}{ccccccc} & & & & & \text{Cl} & \text{OH} \\ -\text{C}=\text{C}- & + & \text{HOCl} & \rightarrow & - & \text{C} - & \text{C} - \\ \text{H}\quad\;\text{H} & & & & & \text{H} & \text{H} \end{array}$$

- Chlorine doesn’t oxidize the organic carbon
- Chlorine maintains its oxidation number

$$\frac{0.5\ mg\ Cl_2}{mg\ C} \square \frac{mole\ Cl_2}{70.9\ g\ Cl_2} \square \frac{mole\ Cl^{+1}}{mole\ Cl_2} \square \frac{12\ g\ C}{mole\ C} \approx \frac{mole\ Cl^{+1}}{12\ mole\ C}$$