13 Disinfection

Three basic strategies to keep microbiological contaminants out of drinking water:

1. Keeping microbiota out of water source
2. Treating water to remove contaminants
3. Maintaining safe water distribution system

Disinfection has two components:

1. Primary disinfection - inactivation of microorganisms in the water
2. Secondary disinfection - maintaining disinfecting residual in distribution system

History

Source water protection and filtration used in second half of 1800s

1880	Koch showed chlorine could inactivate bacteria
1902	First used of chlorination for disinfecting water in Belgium
1908	First use in US: Jersey City, NJ with calcium hypochlorite
1913	First use of chlorine gas - Philadelphia
1941	85% of public supplies chlorinated
mid-1970s	Formation of THMs demonstrated
1980s	Giardia identified as important pathogen Cryptosporium identified more recently

Disinfection methods

1 Free chlorine - most common
2 Combined chlorine (chloramines)
3 Ozone - strongest oxidant
4 Chlorine dioxide
5 UV light

} chemical disinfection

Chemical disinfection kinetics

Chick's Law - Harriet Chick, 1908

documented microorganism inactivation by phenol, mercuric chloride, silver nitrate

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

N = number of organisms per volume $[L^{-3}]$
k = Chick's Law constant $[T^{-1}]$

Integrate to get:

$$\ln\left(\frac{N}{N_o}\right) = -kt$$

N_o = starting number of organisms
N/N_o = "survival ratio"

Chick-Watson Model - Herbert Watson, 1908

$$C^n t = K$$

achieves particular level of disinfection (i.e. N/N_o)

C = concentration
n = empirical const called "coefficient of dilution"
K = constant (function of microorganisms)

If $n > 1$, disinfectant efficiency decreases with dilution – concentration is more important than time

$n < 1$, time is more important than conc.

$n = 1$, time and conc equally important

n is slope of log C vs log t plot (see pg 4)
by convention, 99% inactivation is plotted

If $n \approx 1$, then Chick-Watson model is:

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW}\, Ct$$

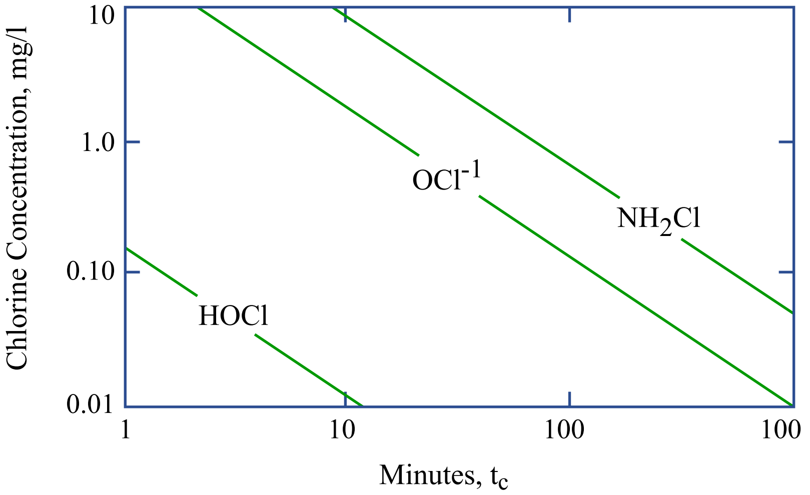
Λ_{CW} = Chick-Watson coefficient of specific lethality [L/mg·min]

Other models also exist – see MWH, 2005

Ct is specified by US EPA rules for Giardia and Cryptosporidium for different disinfectants and pH – unlike bacteria, no easy tests for Giardia and Crypto, so regulation focuses on technology (expressed as Ct) rather than monitoring

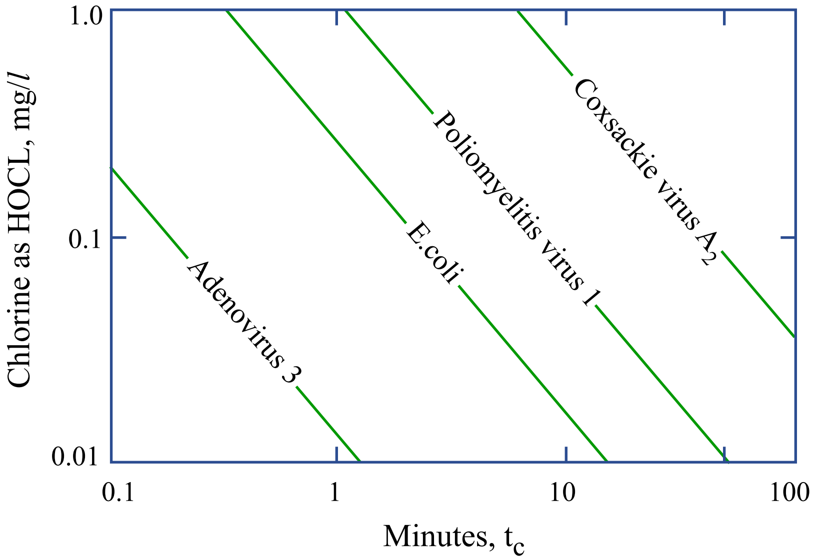
Page 5 (from MWH, 2005, p. 1063) shows Ct to achieve 99% removal by various technologies

Note: chlorine is relatively ineffective against Cryptosporidium (C. Parvum)
UV is particularly effective against Giadia and Crypto.



Concentration versus contact time for 99% kill of E. coil by various forms of chlorine at 2°C to 6°C.

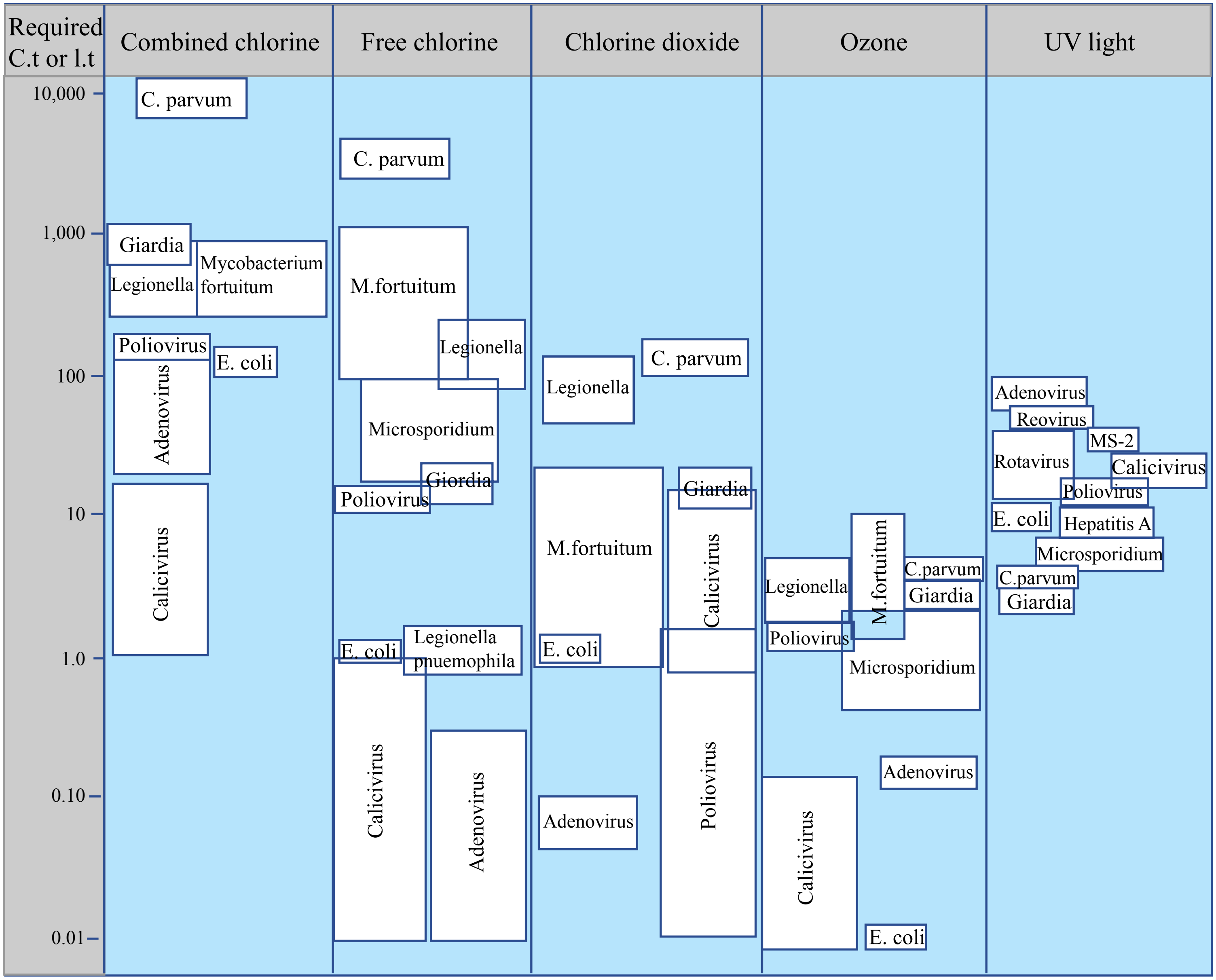
Figure by MIT OCW.



Concentration versus contact time for 99% kill of E. coil and three enteric viruses by HOCl at 0°C to 6°C.

Figure by MIT OCW.

Adapted from: Reynolds, T. D., and P. A. Richards. *Unit Operations and Processes in Environmental Engineering*. 2nd ed. Boston, MA: PWS Publishing Company, 1996, pp. 742-743.



Overview of disinfection requirements for 99 percent inactivation.

Figure by MIT OCW.

Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. *Water Treatment: Principles and Design*. 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, p. 1063.

Chlorine disinfection

Most widely used - effective at low conc., inexpensive, forms residual

Drawback: forms THMs

Applied as chlorine gas or hypochlorite

Acts by oxidizing enzymes of cells, preventing essential metabolic processes

Chlorine gas: $Cl_2 + H_2O \rightarrow HOCl + HCl$

↑

hypochlorous acid

$HOCL \rightleftharpoons H^+ + OCL^-$

↑ favored below pH 7.5

↑ hypochlorite ion (favored above pH 7.5)

Hypochlorite: $\underset{\text{solid}}{Ca(OCl)_2} \xrightarrow{H_2O} Ca^{+2} + 2OCl^-$

$\underset{\text{liquid}}{NaOCl} \longrightarrow Na^{+1} + OCl^-$

↑

equilibrates with HOCl

chlorox is 5.25% NaOCl

HOCl is more effective disinfectant than OCl^- but both are excellent

HOCl reacts with ammonia:

$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$
monochloramine favored at pH > 6

$NH_2Cl + 2HOCl \rightarrow NHCl_2 + 2H_2O$
dichloramine favored at pH ≈ 5

$NHCl_2 + 3HOCl \rightarrow NCl_3 + 3H_2O$
nitrogen trichloride (trichloramine)

chloramines are effective against bacteria (e.g. pipe growth)
much less effective against viruses

chloramine contributes to chlorine residual
along with residual free chlorine ($HOCl$ & OCl^-)
chloramines are longer lasting

Chlorine also reacts with organics

With phenol to form chlorophenols - strong taste and odor

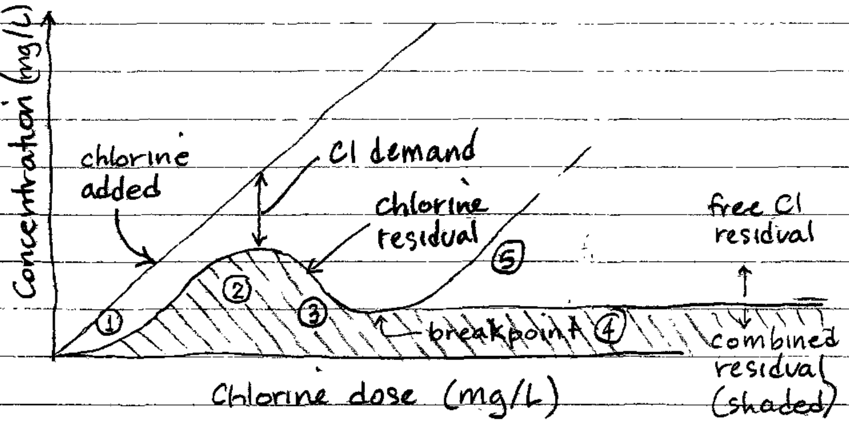
With NOM (natural organic matter, e.g. humic acids) to form tri-halo methanes (THMs)

$CHCl_3$ chloroform
$CHCl_2Br$ bromodichloromethane
$CHClBr_2$ dibromochloromethane
$CHBr_3$ bromoform

Known as DBP - disinfection by-products
Problematic because THMs are suspected human carcinogens

Chlorine dosage is determined so as to ensure adequate residual - known as breakpoint chlorination

Determined by lab experiments in which chlorine is added and residual is measured:



Chlorine demands:

① At first, inorganic reducing chems NO_3, H_2S, Fe^{2+} $Cl_2 \rightarrow 2Cl^-$
② After satisfaction of initial demand, chloramines formed, creating combined residual
③ With increasing Cl dosage, formation favors dichloramine over monochloramine, then trichloramine over dichloramine. Trichloramine is unstable, breaks down to N_2 and reduces chlorine residual
④ Low point of chlorine residual is "breakpoint"
⑤ Further increase in Cl adds free residual

Desired dosage for water treatment is beyond the breakpoint
Actual breakpoint concentration varies with the water quality of the raw water - typically 4-10 mg/L
Desired residual = 0.2 mg/L at furthest point in distribution system
(Note 0.5 mg/L is generally objectionable to consumers)

Dechlorination

Chlorination is also used as a final step in wastewater treatment but here residual chlorine has adverse effects on aquatic life and is not desired

Sulfur dioxide used to remove residual Cl =

$$SO_2(g) + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$\rightleftharpoons 2H^+ + SO_3^=$$

$$SO_3^{2-} + HOCl \rightarrow SO_4^{-2} + Cl^- + H^+$$

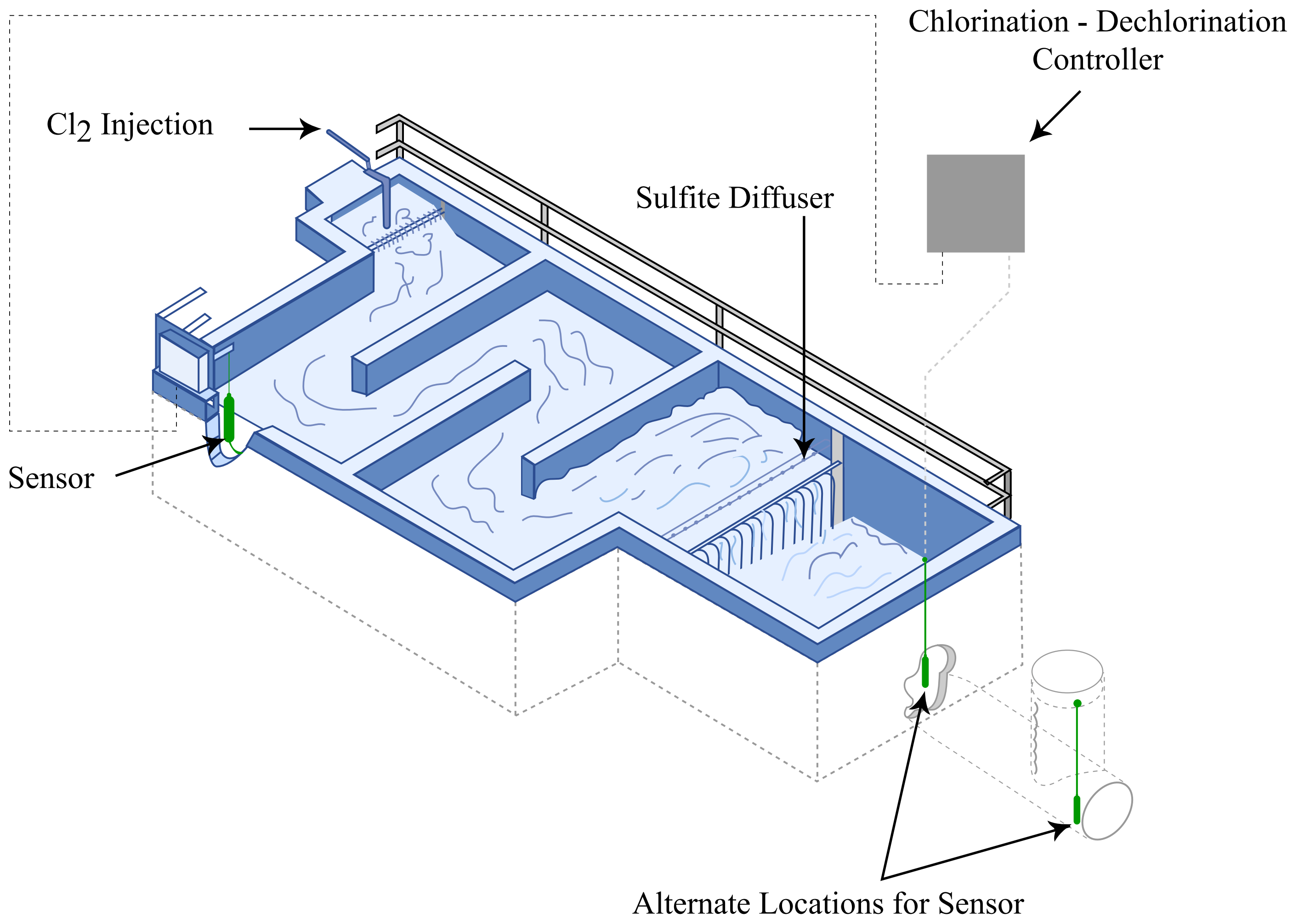
$$SO_3^{2+} + NH_2Cl + H_2O \rightarrow SO_4^{-2} + Cl^- + NH_4^+$$

Chlorination

Cl_2 added with proprietary chlorinators (see Fig 11.17 in VH text)

Desired Ct is best achieved in plug flow (or nearly plug flow) reactors

Typical chlorine contact chamber is serpentine chamber with baffles - see pg 10 - Figure from Droste, 1997, p. 522



Typical contact chamber for chlorination. Baffles are provided to promote plug flow. When chlorine has been applied at elevated concentrations, sulfite is added to reduce chlorine to levels that will not cause consumer reaction to chlorine taste and odor.

Figure by MIT OCW.

Adapted from: Binnie, C., M. Kimber, and G. Smethurst. *Basic Water Treatment*. 3rd ed. Cambridge, UK: Royal Society of Chemistry, 2002.

Ozonation

Ozone (O_3) is more powerful oxidant than HOCl

Ozone inactivates microorganisms by
1. Direct oxidation
2. Decomposition into hydroxyl radicals HO·
   which are also strong reactants

Widely used in Europe, increasingly used in US

Advantages: excellent disinfectant (including for
Gardia and Cryptosporidium)
does not form THMs, chlorophenols
effective against taste and odor
requires short contact time

Disadvantages: short contact-time reactors prone
to short-circuiting
more costly than Cl_2
does not create disinfecting residual
may produce harmful by-products
ozone gas is potentially explosive

Ozone treatment design based on Ct, with consideration of ozone decay over time

Ozone is sparingly soluble – usually introduced as gas by fine-bubble porous diffusers in deep basins

Ozone consumption by specific water to be treated measured in lab (analogous to determining chlorine demand) $C_{residual} = C_{dose} - C_{demand}$

Decay of $C_{residual}$ over time measured in lab reactors pulsed with ozone → C vs. t

Integrate C vs. t to get Ct

Ozone contactors usually introduce O_3 and get water contact in same tank (pg 13 from MWH pg 1121)

Ozone bubbled into chamber creates fully-mixed conditions

But desire plug flow to ensure Ct is achieved

Solution is to create tanks-in-series to approximate PFR

Some designs seek counter-current flow to achieve better O_3 transfer (bubble rise is slowed by counterflow of water)

Ozone is generated on-site in a corona discharge - electric arc generated by high voltage between two plates separated by air gap

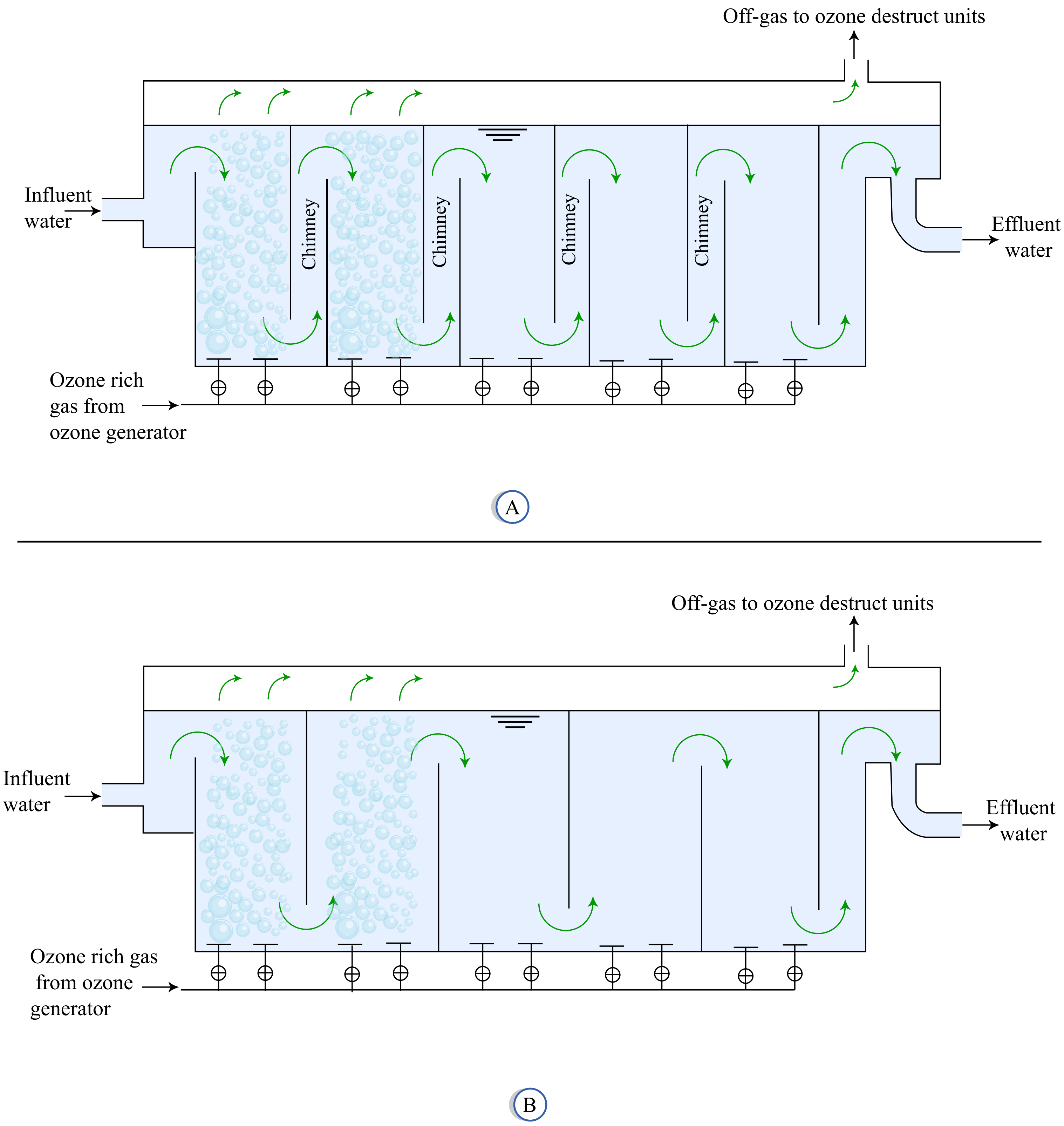
$$O_2 \xrightarrow{\not\!\!\;} 2O\cdot$$

$$O\cdot + O_2 \rightarrow O_3$$

(same effect as lightning storm)

Chlorine Dioxide ClO_2

- stronger oxidant than Cl_2
- creates long-lasting residual
- effective against taste and odor
- produces few by-products, however chlorate and chlorite ions are produced but limited by regulations to non-toxic conc.
- Widely used in Europe, less common in U.S.
- More expensive than Cl_2



Schematics cross-sectional views of two alternate designs for five-chamber, over-under ozone contact chamber: (a) with chimneys and (b) without chimneys.

Figure by MIT OCW.

Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. *Water Treatment: Principles and Design*. 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, p. 1121.

UV radiation

Disinfects by:
- damaging nucleic acids - DNA, RNA
- forms hydroxyl radicals - strong oxidant

200-300 nm wavelength is absorbed by DNA → disinfecting range for UV (also range likely to cause skin cancer)

Very effective against cryptosporidium

Radiation produced by lamps
- Low-pressure UV lamp - 254 nm only
- Medum-pressure UV lamp - 210-300 nm range

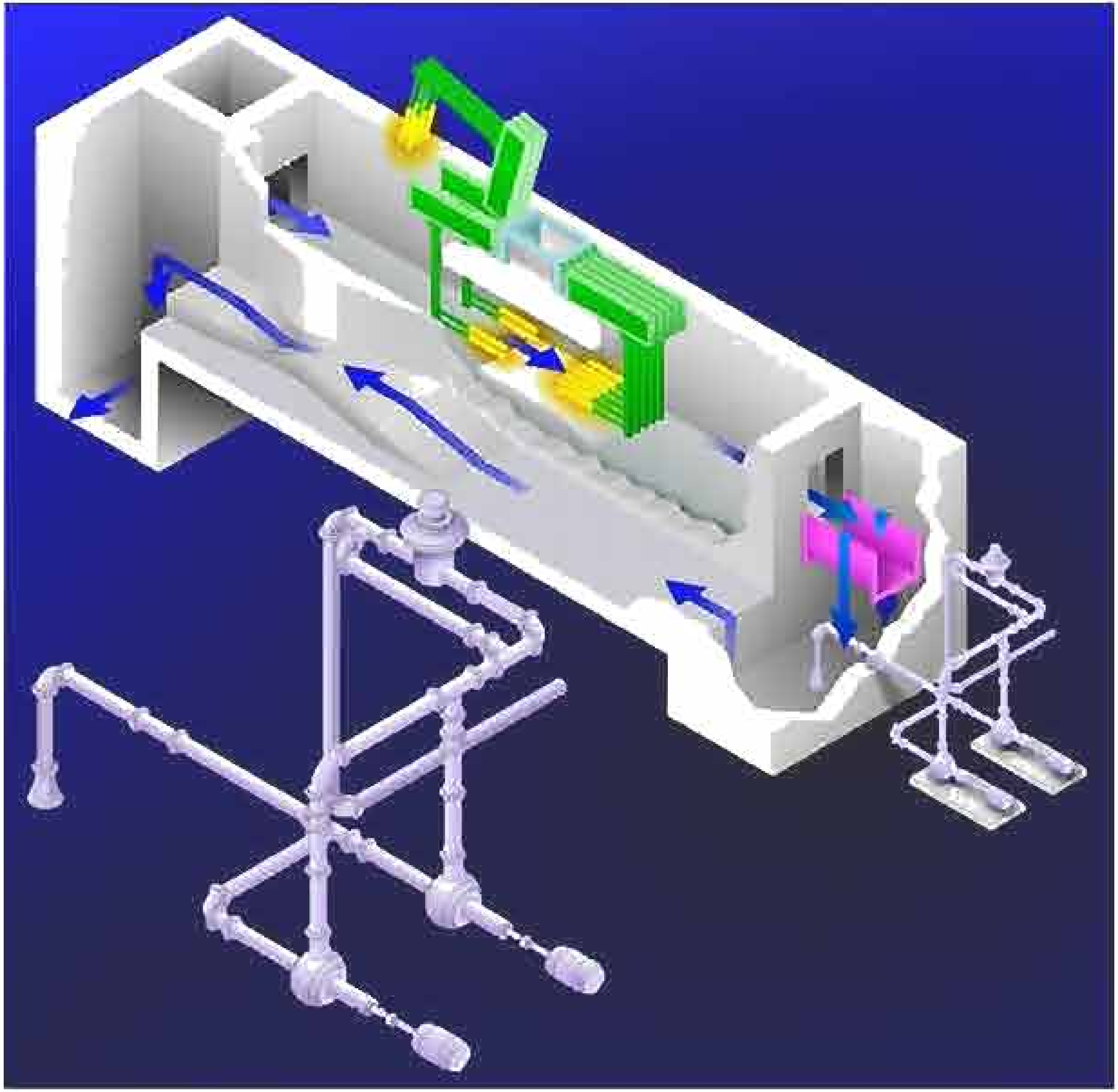
Interferences due to
- Absorption by dissolved substances in water
- Shading of organisms by particulates

UV contactors have very short residence times - seconds to minutes
Short-circuiting is a potential problem

Treatment equipment consists of array of electricity-powered lamps suspended in water flow - see picture pg. 15

Or, pipe with long lamp down the middle

SODIS - solar disinfection - is low-tech solution that uses sunlight to disinfect water



Clements, John, 2004. Ultraviolet Disinfection. Brown and Caldwell Engineers. February 2004. http://www.xaraxone.com/FeaturedArt/jc/html/08.htm Accessed 3/13/05

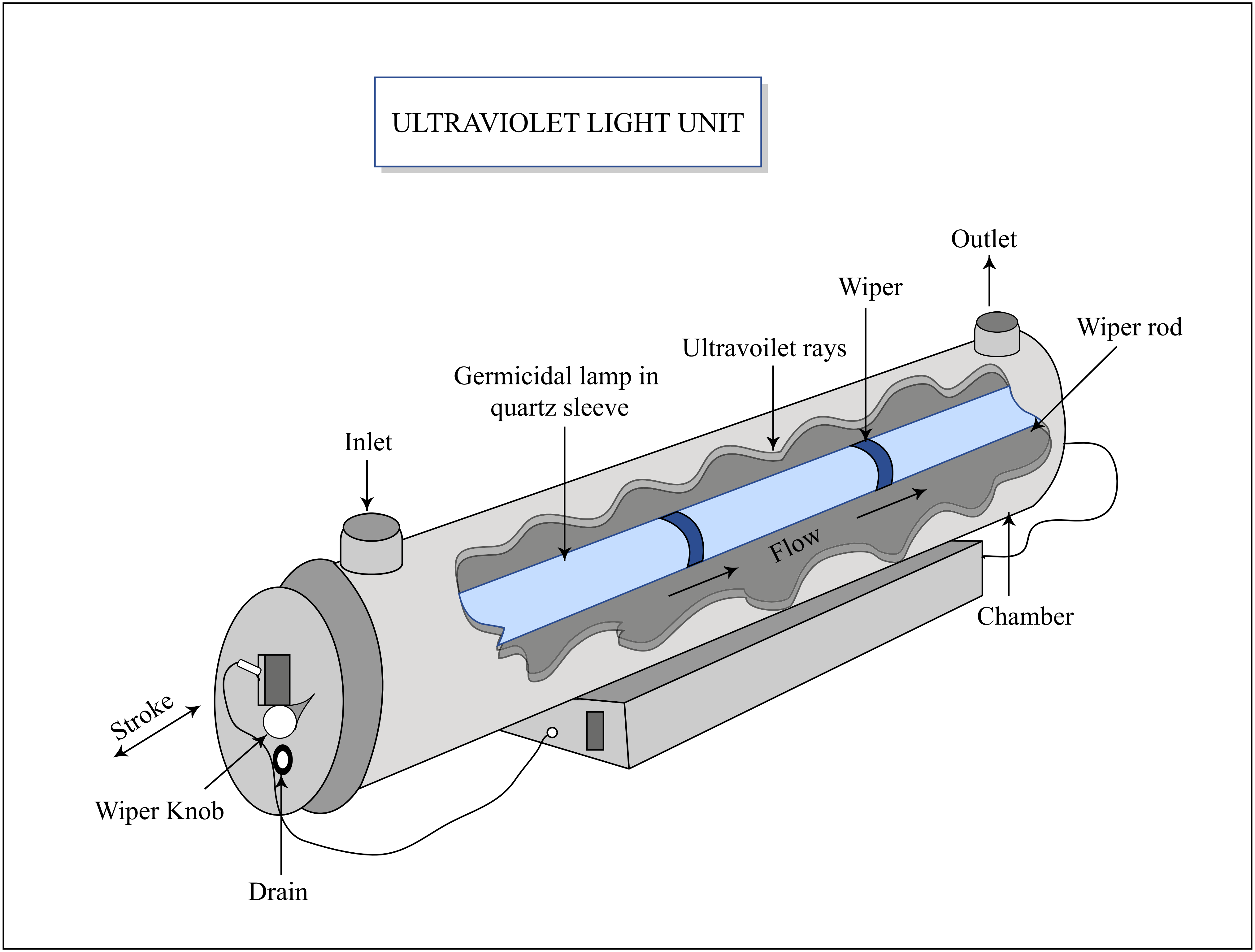


Figure by MIT OCW. Adapted from: Mancl, Karen M.. "Bacteria in Drinking Water." The Ohio State University Extension Bulletin. *Bulletin* 795 (1989).