ENVR 133
Water and Wastewater Disinfection

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Disinfection

- Disinfection is any process to destroy or prevent the growth of microbes
- Many disinfection processes are intended to inactivate (destroy the infectivity of) the microbes by physical, chemical or biological processes
- Inactivation is achieved by altering or destroying essential structures or functions within the microbe
- Inactivation processes include denaturation of:
  - proteins (structural proteins, enzymes, transport proteins)
  - nucleic acids (genomic DNA or RNA, mRNA, tRNA, etc)
  - lipids (lipid bilayer membranes, other lipids)

Properties of an Ideal Disinfectant

- Broad spectrum: active against all microbes
- Fast acting: produces rapid inactivation
- Effective in the presence of organic matter, suspended solids and other matrix or sample constituents
- Nontoxic; soluble; non-flammable; non-explosive
- Compatible with various materials/surfaces
- Stable or persistent for the intended exposure period
- Provides a residual (sometimes this is undesirable)
- Easy to generate and apply
- Economical

Disinfectants in Water and Wastewater Treatment

- Free Chlorine
- Monochloramine
- Ozone
- Chlorine Dioxide
- Mixed Oxidants
  - Electrochemically generated from NaCl
- UV Light
  - Low pressure mercury lamp (monochromatic)
  - Medium pressure mercury lamp (polychromatic)
  - Pulsed broadband radiation

Summary of Disinfectants for Microbes in Water and Wastewater

- Historically, the essential barrier to prevention and control of waterborne microbial transmission and waterborne disease.
- Free chlorine: HOCl (hypochlorous) acid and OCl^- (hypochlorite ion)
  - HOCl at lower pH and OCl^- at higher pH; HOCl a more potent germicide than OCl^-
  - strong oxidant; relatively stable in water (provides a disinfectant residual)
- Chloramines: mostly NH_2Cl: weak oxidant; provides a stable residual
- ozone, O_3 , strong oxidant; provides no residual (too volatile and reactive)
- Chlorine dioxide, ClO_2,, strong oxidant; unstable residual (dissolved gas)
- Concerns due to health risks of chemical disinfectants and their by-products (DBPs), especially free chlorine and its DBPs
- UV radiation
  - low pressure mercury lamp: low intensity; monochromatic at 254 nm
  - medium pressure mercury lamp: higher intensity; polychromatic 220-280 nm)
  - reacts primarily with nucleic acids: pyrimidine dimers and other alterations

Factors Influencing Disinfection Efficacy and Microbial Inactivation

Least

- **Microbe type: Resistance to chemical disinfectants:**
  - **Vegetative bacteria: Salmonella, coliforms, etc.**
  - **Enteric viruses: coliphages, HAV, SRSVs, etc.**
  - **Protozoan (oo)cysts, spores, helminth ova, etc.**
    - ***Cryptosporidium parvum* oocysts**
    - ***Giardia lamblia* cysts**
    - ***Clostridium perfringens* spores**
    - ***Ascaris lumbricoides* ova**
    - **Acid-fast bacteria: *Mycobacterium* spp.**

Most

Factors Influencing Disinfection Efficacy and Microbial Inactivation (Continued)

Type of Disinfectant and Mode of Action

Free chlorine: strong oxidant; oxidizes various protein sulfhydryl groups; alters membrane permeability; also, oxidize/denature nucleic acid components, etc.

Ozone: strong oxidant; ditto free chlorine

Chlorine dioxide: strong oxidant; ditto free chlorine

Electrochemically generated mixed oxidants: strong oxidant; probably ditto free chlorine

Combined chlorine/chloramines: weak oxidant; denatures sulfhydryl groups of proteins

Ultraviolet radiation: nucleic acid damage: thymidine dimer formation, strand breaks, oxidation rxns.,etc.

Some Factors Influencing Disinfection Efficacy and Microbial Inactivation

Microbial strain differences and microbial selection:

- Disinfectant exposure may select for resistant strains

Physical protection:

- Aggregation
- particle-association
- protection within membranes and other solids

Chemical factors:

- pH
- Salts and ions
- Soluble organic matter
- Other chemical (depends on the disinfectant)

Some Factors Influencing Disinfection Efficacy and Microbial Inactivation - Bacteria

- <u>Surface properties conferring susceptibility or resistance</u>:
    - Resistance: Spore; acid fast (cell wall lipids); capsule; pili
    - Susceptibility: sulfhydryl (-SH) groups; phospholipids; enzymes; porins and other transport structures, etc.
- <u>Physiological state and resistance:</u>
    - Antecedent growth conditions: low-nutrient growth increases resistance to inactivation
    - Injury; resuscitation and injury repair;
    - disinfectant exposure may selection for resistant strains
- <u>Physical protection</u>:
    - Aggregation; particle-association; biofilms; occlusion (embedded within protective material), association with or inside eucaryotes; corrosion/tuberculation

Some Factors Influencing Disinfection Efficacy and Inactivation - Viruses

Virus type, structure and composition:

- Envelope (lipids): typically labile to disinfectants
- Capsid structures and capsid proteins (change in conformation state)
- Nucleic acids: genomic DNA, RNA; # strands
- Glycoproteins: often on virus outer surface; typically labile to disinfectants

Physical state of the virus(es):

- Aggregated
- Particle-associated
- Embedded within other materia (within membranes)

Factors Influencing Disinfection Efficacy and Microbial Inactivation - Parasites

Parasite type, structure and composition:

Protozoan cysts, oocysts and spores

Some are very resistant to chemical disinfectants

Helminth ova: some are very resistant to chemical disinfection, drying and heat.

- **Strain differences and selection:**

Disinfectant exposure may select for resistant strains

- **Physical protection:**

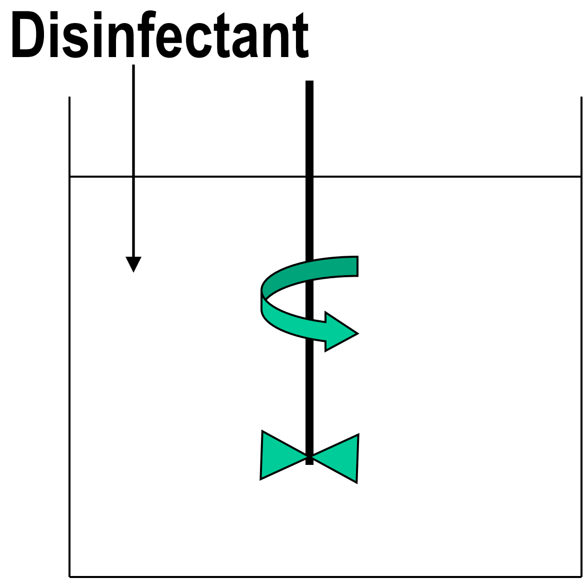
Aggregation; particle-association; protection within other solids

Factors Influencing Disinfection Efficacy and Microbial Inactivation - Water Quality

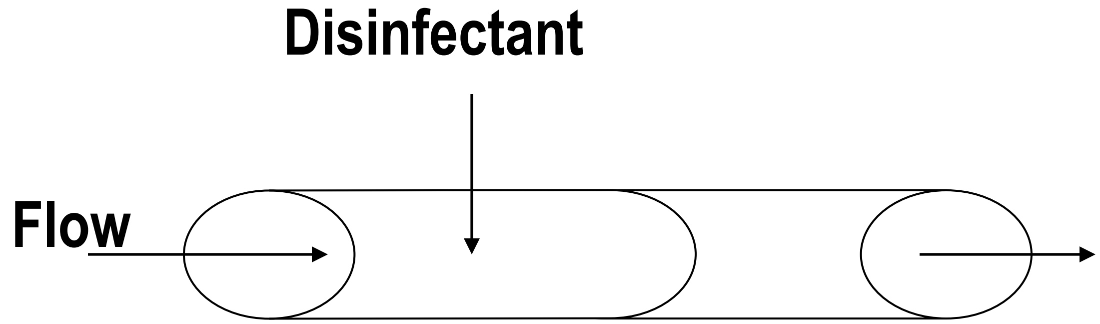
- Particulates: protect microbes from inactivation;
  consume disinfectant
- Dissolved organics: protect microbes from inactivation; consumes or absorbs (for UV radiation) disinfectant; Coat microbe (deposit on surface)
- pH: influences microbe inactivation by some agents
  - free chlorine more effective at low pH where HOCl predominates
    - neutral HOCL species more easily reaches microbe surface and penetrates)
    - negative charged OCl^- has a harder time reaching negatively charged microbe surface
  - chlorine dioxide is more effective at high pH
- Inorganic compounds and ions: influences microbe inactivation by some disinfectants; depends on disinfectant

Factors Influencing Disinfection Efficacy and Microbial Inactivation - Reactor Design, Mixing & Hydraulic Conditions

Disinfection kinetics are better in plug-flow (pipe) reactors than in batch (back-mixed) reactors



Batch or Back-mixed Reactor



Plug-flow or Pipe Reactor

Disinfection Kinetics: Chick's Law
First-Order or Exponential Kinetics

Assumes:

- all organisms are identical
- death (inactivation) results from a first-order or "single-hit" or exponential reaction.

Chick's law:

$- dN/dT = kN$

where:

N = number (concentration) of organisms

T = time

$\ln N_t/N_o = -kT$

where N_o = initial number of organisms

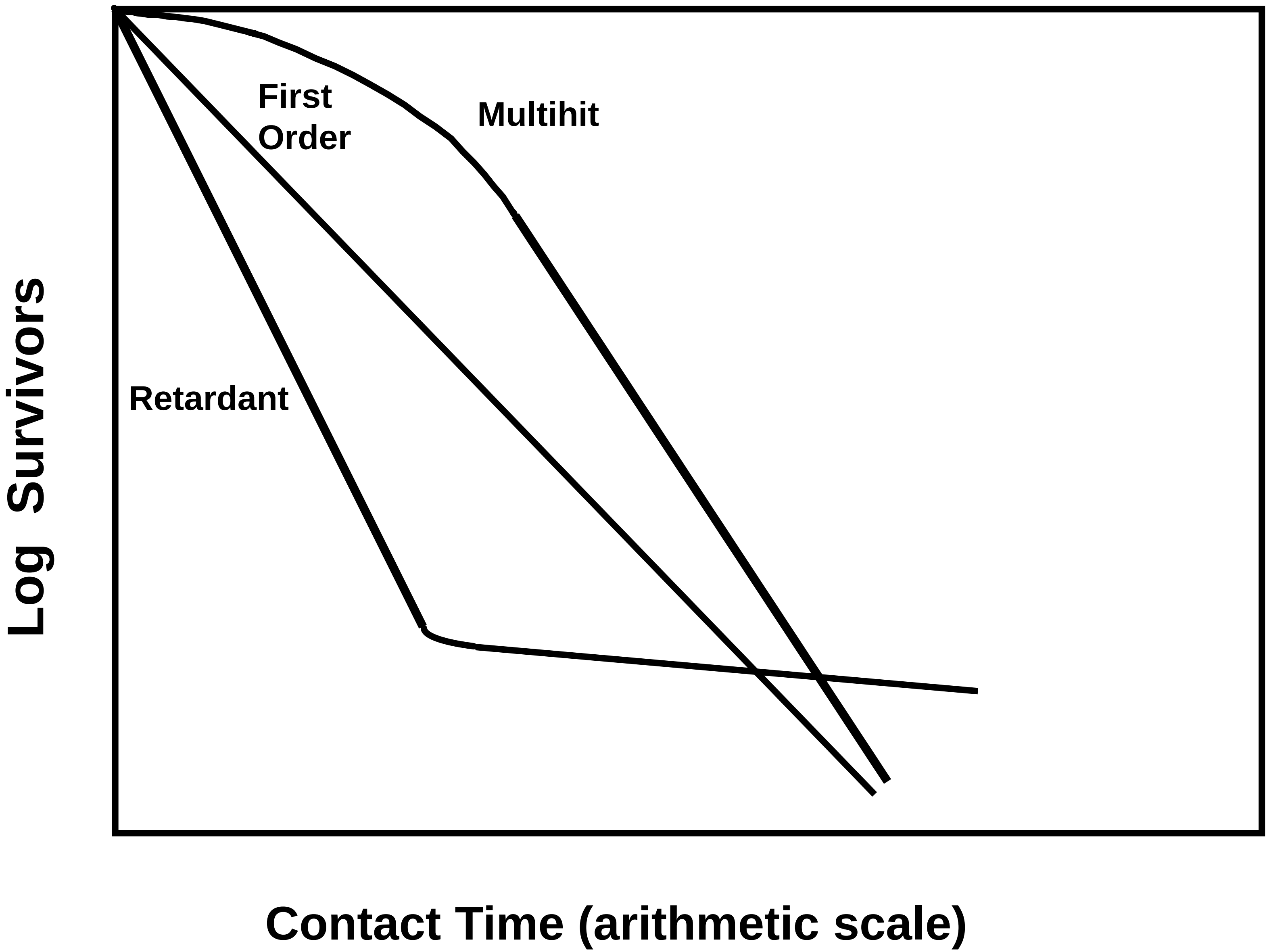
N_t = number of organisms remaining at time = T

No = initial number of organisms (T = 0)

Also:

$N/N_o = e^{-kT}$

DISINFECTION AND MICROBIAL INACTIVATION KINETICS



Microbial Inactivation Kinetics

First-order or exponential kinetics assumed

- Chick's Law and Chick-Watson Model
- Assumption is often not met in practice
- CT concept wrongly assumes 1st-order kinetics always occur

Departures from 1st-order kinetics are common

- Retardant curves: "persistent fraction"; mixed populations; aggregation
- Declining rate: decline in disinfectant concentration over time.
- "Shoulder" curves: multihit kinetics; aggregation

Types of Disinfection Kinetics

- **Disinfection is a kinetic process**
- **Increased inactivation with increased exposure or contact time.**
  - **Chick's Law: disinfection is a first-order reaction. (NOT!)**
  - **Multihit-hit or concave up kinetics: initial slow rate; multiple targets to be "hit"; diffusion-limitions in reaching "targets"**
  - **Concave down or retardant kinetics: initial fast rate that decreases over time**
    - **Different susceptibilities of microbes to inactivation; heterogeneous population**
    - **Decline of of disinfectant concentration over time**

Disinfection Activity and the CT Concept

- Disinfection activity can be expressed as the product of disinfection concentration (C) and contact time (T) Assumes first order kinetics (Chick's Law) such that disinfectant concentration and contact time have the same "weight" or contribution in disinfection activity and in contributiong to CT
- Example: If CT = 100 mg/l-minutes, then
  - If C = 10 mg/l, T must = 10 min. in order to get CT = 100 mg/l-min.
  - If C = 1 mg/l, then T must = 100 min. to get CT = 100 mg/l-min.
  - If C = 50 mg/l, then T must = 2 min. to get CT = 100 mg/l-min.
  - So, any combinationof C and T giving a product of 100 is acceptable because C and T are interchangable
- The CT concept fails if disinfection kinetics do not follow Chick's Law (are not first-order or exponential)

Factors Influencing Disinfection of Microbes

- **Microbe type: disinfection resistance from least to most: vegetative bacteria $\rightarrow$viruses $\rightarrow$ protozoan cysts, spores and eggs**
- **Type of disinfectant: order of efficacy against *Giardia* from best to worst**
  - **Best: $O_3 \leftarrow ClO_2 \leftarrow$ iodine/free chlorine $\leftarrow$ chloramines: Worst**
  - **BUT, order of effectiveness varies with type of microbe**
- **Microbial aggregation:**
  - **protects microbes from inactivation**
  - **microbes within aggregates can not be readily reached by the disinfectant**

Inactivation of *Cryptosporidium* Oocysts in Water by Disinfectants

Disinfectant	CT_{99} (mg-min/L)	Reference
Free Chlorine	7,200+	Korich et al., 1990
Monochloramine	7,200+	Korich et al., 1990
Chlorine Dioxide	>78	Korich et al., 1990
Mixed oxidants	<120	Venczel et al., 1997
Ozone	~3-18	Finch et al., 1994 Korich et al., 1990 Owens et al., 1994
UV radiation	IT: <10 mJ/cm^2	Hijnan et al, 2006

(*C. parvum* oocysts inactivated by low doses of UV radiation: <10 $mJoules/cm^2$)

Free Chlorine - Background and History

- Considered to be first used in 1905 in London
  - But, electrochemically generated chlorine from brine (NaCl) was first used in water treatment the late 1800s
- Reactions for free chlorine formation:

  Cl_2 (g) + H2O <=> HOCl + H+ + Cl-

  HOCl <=> $H^+ + OCl^-$
- Chemical forms of free chlorine: Cl_2 (gas), NaOCl (liquid), or $Ca(OCl)_2$ (solid)
- Has been the “disinfectant of choice” in US until recently.
- recommended maximum residual concentration of free chlorine < 5 mg/L (by US EPA)
- Concerns about the toxicity of free chlorine disinfection by-products (trihalomethanes and other chlorinated organics)

Effect of pH on Percentages of HOCl and OCl⁻

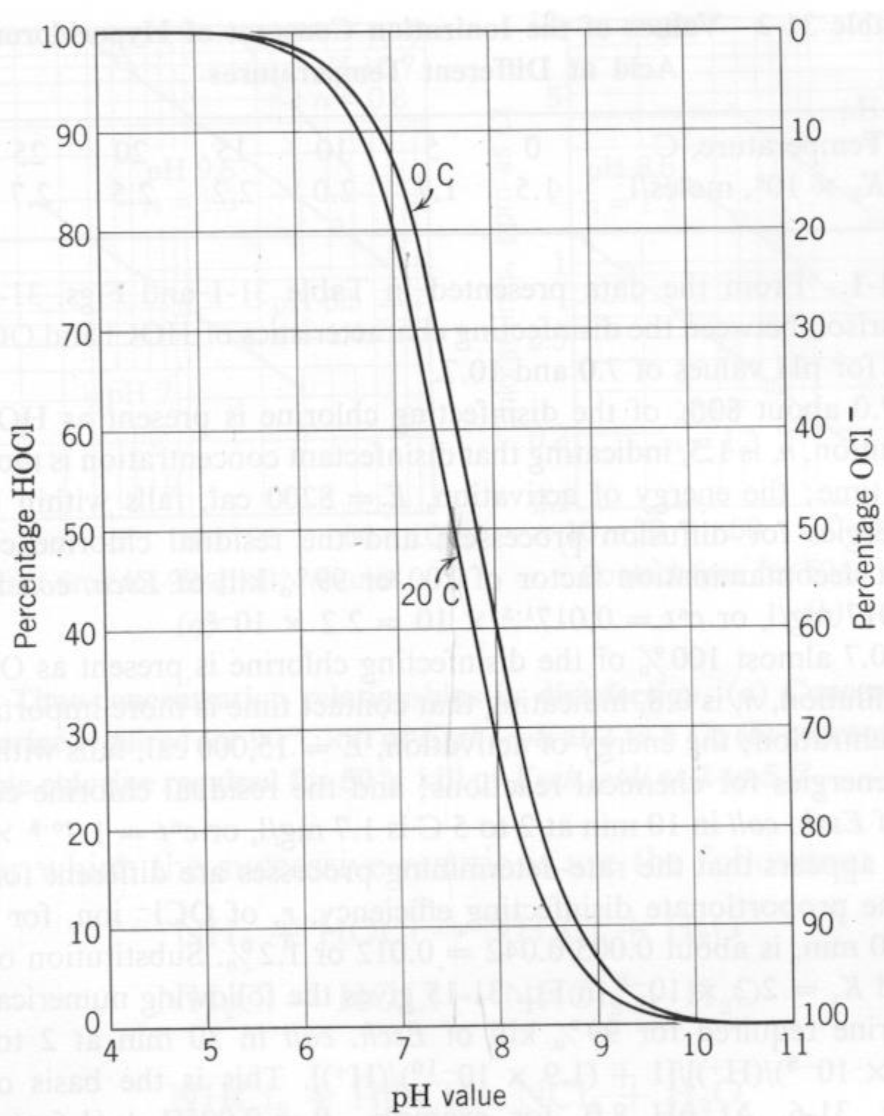


Fig. 31-5. Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures. (After Morris, Sec. 31–11, footnote 14.)

Free Chlorine and Microbial Inactivation

- Greater microbial inactivation at lower pH (HOCl) than at high pH (OCl^-)
  - Probably due to greater reactivity of the neutral chemical species with the microbes and its constituents
- Main functional targets of inactivation:
  - Bacteria: respiratory activities, transport activities, nucleic acid synthesis.
  - Viruses: reaction with both protein coat (capsid) and nucleic acid genome
  - Parasites: mode of action is uncertain
- Resistance of *Cryptosporidium* to free chlorine (and monochloramine) has been a problem in drinking water supplies
  - Free chlorine (bleach) is actually used to excyst *C. parvum* oocysts!

Monochloramine - History and Background

- first used in Ottawa, Canada and Denver, Co. (1917)
- became popular to maintain a more stable chlorine residual and to control taste and odor problems and bacterial re-growth in distribution system in 1930’s
- decreased usage due to ammonia shortage during World War II
- increased interest in monochloramine:
  - alternative disinfectant to free chlorine due to low THM potentials
  - more stable disinfectant residual; persists in distribution system
  - secondary disinfectant to ozone and chlorine dioxide disinfection to provide long-lasting residuals

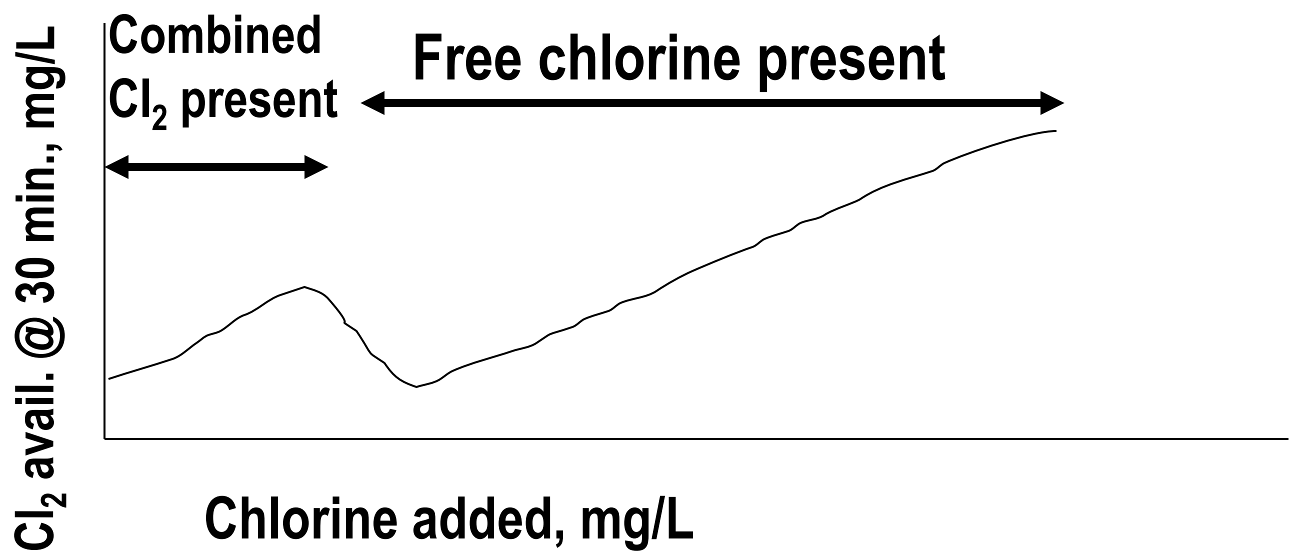
Monochloramine: Chemistry and Generation)

Monochloramine formation:

- $HOCl + NH_3 \Leftrightarrow NH_2Cl + H_2O$
- Stable at pH 7 - 9, moderate oxidation potential
- Generation
  - pre-formed monochloramine:
    mix hypochlorite and ammonium chloride (NH_4Cl) solution at Cl_2 : N ratio at 4:1 by weight, 10:1 on a molar ratio at pH 7-9
  - dynamic or forming monochloramination:
  - initial free chlorine residual, folloowed by ammonia addition to produce monochloramine
    - greater initial disinfection efficacy due to free chlorine
- Dosed at several mg/L

Reaction of Ammonia with Chlorine: Breakpoint Chlorination

- **Presence of ammonia in water or wastewater and the addition of free chlorine results in an available chlorine curve with a "hump"**



- **At chlorine doses between the hump and the dip, chloramines are being oxidatively destroyed and nitrogen is lost (between pH 6.5-8.5).**

Ozone

- first used in 1893 at Oudshoon
- used in 40 WTPs in US in 1990 (growing use since then), but more than 1000WTPs in European countries
- increased interest as an alternative to free chlorine (strong oxidant; strong microbiocidal activity; perhaps less toxic DBPs)
  - A secondary disinfectant giving a stable residual may be needed to protect water after ozonation, due to short-lasting ozone residual.
- Colorless gas; relatively unstable; reacts with itself and with OH^- in water; less stable at higher pH
- Formed by passing dry air (or oxygen) through high voltage electrodes to produce gaseous ozone that is bubbled into the water to be treated.

Chlorine Dioxide

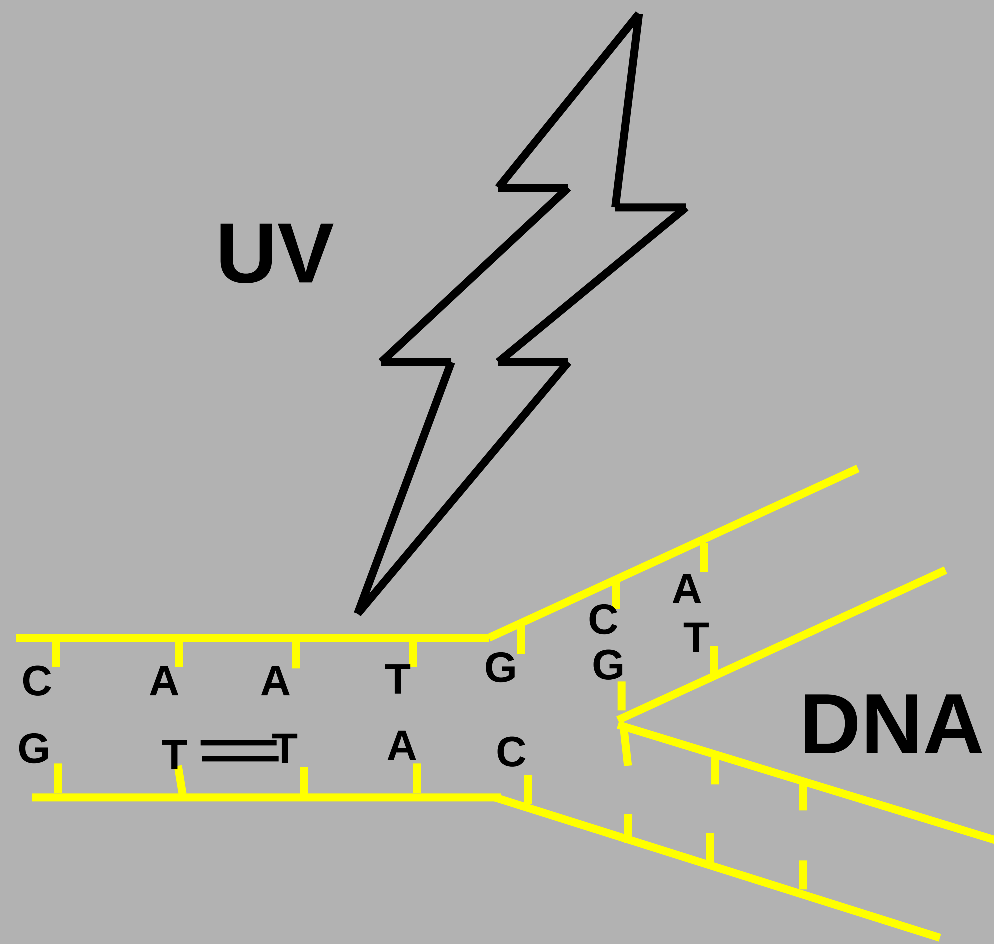
- **first used in Niagara Fall, NY in 1944 to control phenolic tastes and algae problems**
- **used in 600 WTP (84 in the US) in 1970's as primary disinfectant and for taste and odor control**
- **very soluble in water; generated as a gas or a liquid on-site, usually by reaction of Cl_2 gas with $NaClO_2$:**
  - **$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$**
- **usage became limited after discovery of it's toxicity in 1970's & 1980's**
  - **thyroid, neurological disorders and anemia in experimental animals by chlorate**
- **recommended maximum combined concentration of chlorine dioxide and it's by-products < 0.5 mg/L (by US EPA in 1990's)**

Chlorine Dioxide

- High solubility in water
  - 5 times greater than free chlorine
- Strong Oxidant; high oxidative potentials;
  - 2.63 times greater than free chlorine, but only 20 % available at neutral pH
- neutral compound of chlorine in the +IV oxidation state; stable free radical
  - Degrades in alkaline water by disproportionating to chlorate and chlorite.
- Generation: On-site by acid activation of chlorite or reaction of chlorine gas with chlorite
- About 0.5 mg/L doses in drinking water
  - toxicity of its by-products discourages higher doses

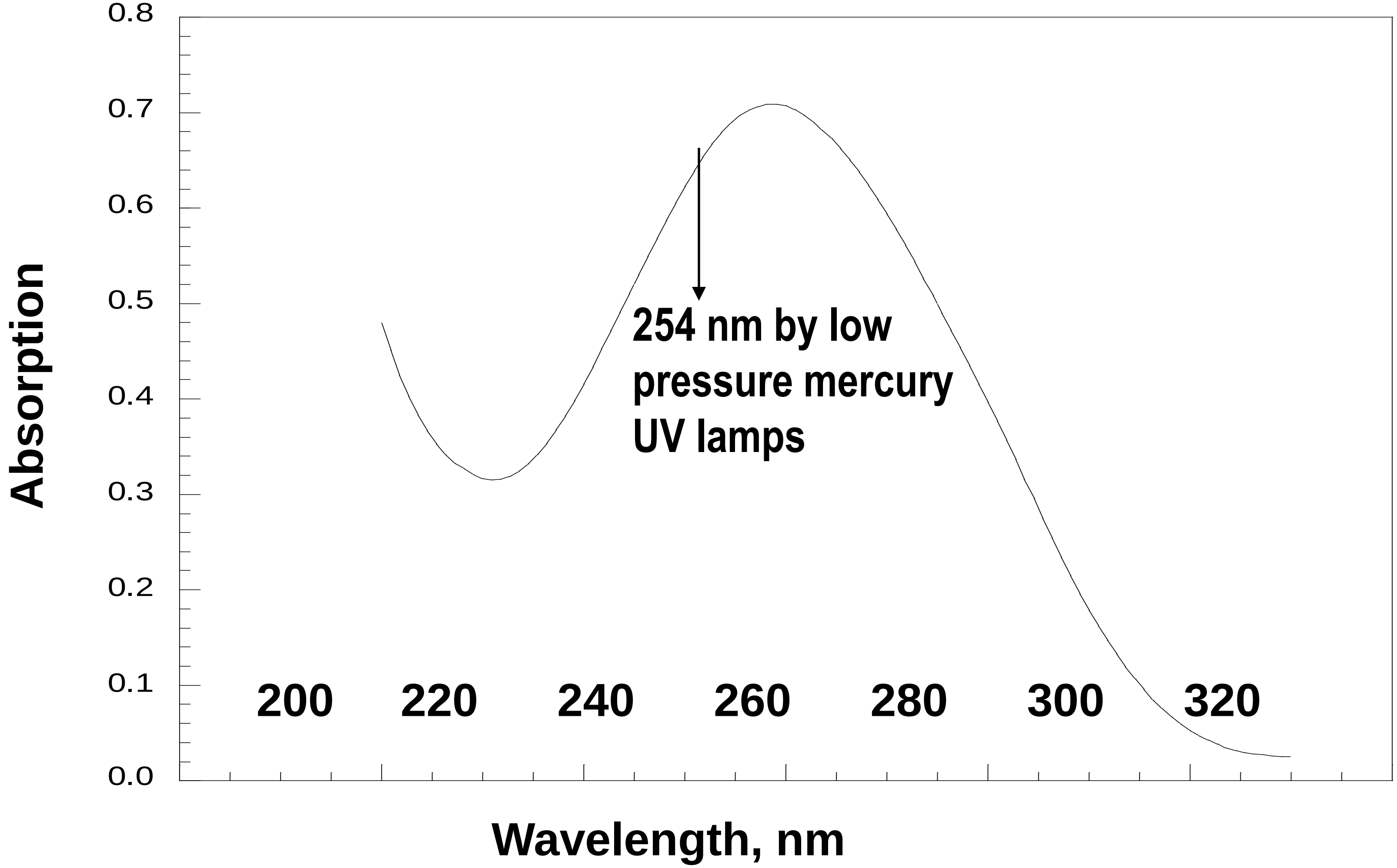
Ultraviolet Radiation and Effects

- Physical process
- Energy absorbed by DNA
- Inhibits replication
- Pyrimidine Dimers
- Strand Breaks
- Other Damage

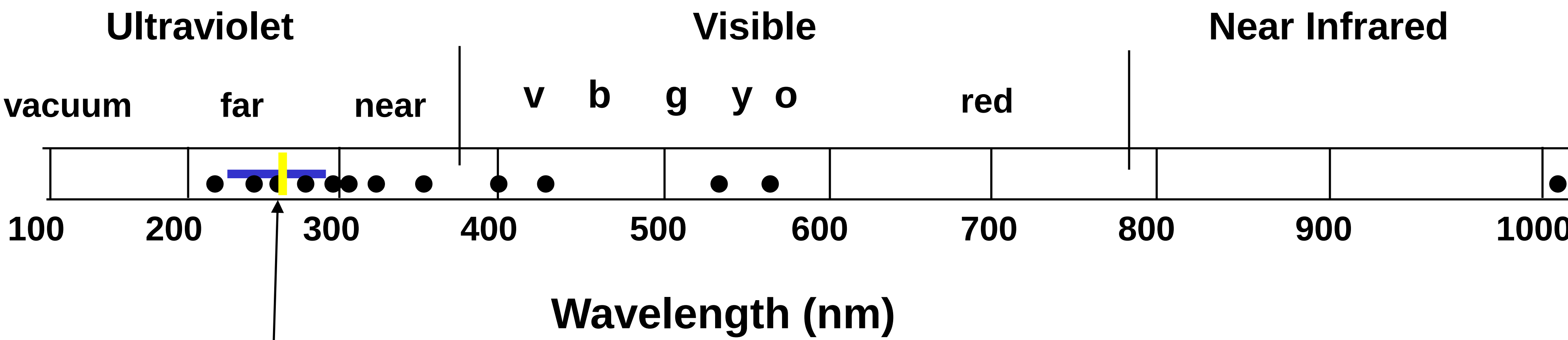


UV Absorption Spectra of DNA: Basis for Microbial Activity

(pH 7 in 0.1M phosphate buffer)



Low and Medium Pressure UV Technologies



Low Pressure UV

- **monochromatic (254 nm)**
- **temp: 40 - 60 °C**
- **88-95% output at 254nm**
- **low intensity output**

Medium Pressure/Pulsed UV

- **polychromatic**
- **temp: 400-600/15,000 °C**
- **output over germicidal range**
- **high intensity output**

UV Disinfection Effectiveness

Microbe	
vegetative bacteria	least resistant
Giardia lamblia cysts	
C. parvum oocysts	
Viruses (esp. adenoviruses)	
bacterial spores	most resistant

UV is effective against *Cryptosporidium* and *Giardia* at low doses (few mJ/cm^2)

Disinfection:
A Key Barrier Against Microbes in Water and Wastewater

- Free chlorine and chloramines are the most commonly used disinfectants
- Maintaining disinfectant residual during treated water storage and distribution is essential.
  - A problem for O_3 and ClO_2, which do not remain in water for very long and for UV, which produces no disinfectant residual
  - A secondary disinfectant may be needed to provide a stable residual
- UV radiation is a promising disinfectant because it inactivates Cryptosporidium at low doses; it is less effective against viruses
  - UV may have to be used with a chemical disinfectant to protect the water with a residual through distribution and storage (EPA's Coliform Rule)
- Sequential disinfection with a strong oxidant (HOCl, O_3 or ClO_2) followed by UV irradiation may provide complimentary efficacy
  - Oxidants effective against viruses and bacteria