

# Water quality I

# Water quality

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- Sources of water pollutants
- Types of water pollutants
- Oxygen demand: ThOD, COD, BOD
- Modeling BOD

# Sources of water pollutants

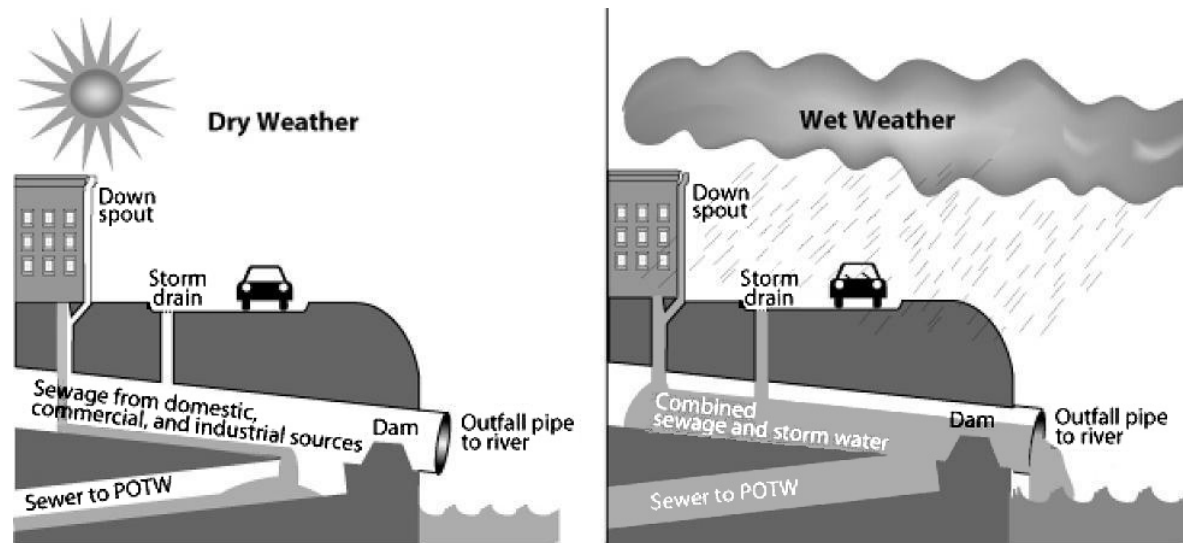
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- **Point sources:** collected by a network of pipes of channels and conveyed to a single point of discharge
  - ex: domestic sewage, industrial wastewater
- **Nonpoint sources:** have multiple and diffuse discharge points
  - ex: urban and agricultural runoff

# Combined sewer overflow (CSO)

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- A nonpoint pollution problem
- Combined sewer system ( $\leftrightarrow$  separate sewer system)
  - The sewage mixed with the storm water may go directly to the river (Combined Sewer Overflow)
  - Generally no longer constructed in the developed world, but old cities may still have the combined sewer



USEPA (2004)

# Types of water pollutants

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- **Oxygen-demanding material**
  - Any substances that can be oxidized in the water resulting in the consumption of dissolved molecular oxygen (DO)
  - Mostly biodegradable organic matter, but also includes inorganics (ex: ammonia)
  - Low DO poses a threat to fish and other higher forms of aquatic life that requires oxygen
  - Major source: human waste, food residue, industry (esp. food-processing & paper industries)

# Types of water pollutants

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- **Nutrients**

- Nitrogen & phosphorus
- Excessive nutrients → excessive algal growth
- Major source: agricultural runoff, human and animal excrement, P-based detergents, fertilizers, food-processing wastes
- Agricultural runoff may cause significant nutrient loadings to the water

# Types of water pollutants

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- **Pathogens**

- Bacteria, viruses, protozoa, and helminthes
- Excreted by diseased persons or animals
- Occurrence of pathogens in drinking water may cause outbreaks of gastrointestinal infections

# Types of water pollutants

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## 1993 Milwaukee Cryptosporidiosis outbreak

The 1993 Milwaukee Cryptosporidiosis outbreak was a significant distribution of the *Cryptosporidium* protozoan in Milwaukee, Wisconsin, and the largest waterborne disease outbreak in documented United States history. The Howard Avenue Water Purification Plant was contaminated, and treated water showed turbidity levels well above normal. It was one of two water treatment plants for Milwaukee. The root cause of epidemic was never officially identified; initially it was suspected to be caused by the cattle genotype due to runoff from pastures. It was also thought that melting ice and snowmelt carrying *Cryptosporidium* may have entered the water treatment plants through Lake Michigan. MacKenzie et al. and the CDC showed that this outbreak was caused by *Cryptosporidium* oocysts that passed through the filtration system of one of the city's water-treatment plants, arising from a sewage treatment plant's outlet 2 miles upstream in Lake Michigan.



# Types of water pollutants

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## **1993 Milwaukee Cryptosporidiosis outbreak (continued)**

This abnormal condition at the water purification plant lasted from March 23 through April 8, after which, the plant was shut down. Over the span of approximately two weeks, 403,000 of an estimated 1.61 million residents in the Milwaukee area (of which 880,000 were served by the malfunctioning treatment plant) became ill with the stomach cramps, fever, diarrhea and dehydration caused by the pathogen. At least 104 deaths have been attributed to this outbreak, mostly among the elderly and immunocompromised people, such as AIDS patients.

*(Wikipedia, 2014)*

# Types of water pollutants

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- **Suspended solids (SS)**
  - Particles carried by water
  - When the water flow slows down, most SS settle down, but colloidal particles do not settle readily
  - Cause turbidity in water and may destroy habitat for benthic organisms

# Types of water pollutants

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- **Salts**

- Often measured as total dissolved solids (TDS): measure the weight remaining after evaporating a filtered water sample
- Evaporation of water from reservoirs, canals, and during application to plants increases salinity
- Increased salinity causes reduction in crop yield & threats to aquatic life

# Types of water pollutants

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- **Pesticides**

- Herbicides, insecticides, fungicides, ...
- Kills herbs, insects, fungi, ... → why not toxic to humans?
- Migrates to surface water by runoff; to groundwater by infiltration

# Types of water pollutants

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- **Pharmaceuticals and personal care products (PPCP)**
  - Of recent interest
  - Substances used by humans and pets for health or cosmetic reasons and the products used to boost growth or health of livestock
  - Sources: human activity, residues from manufacturing, residues from hospitals, illegal drugs, drug use to animals (antibiotics and steroids)

# Types of water pollutants

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- **Endocrine disrupting chemicals (EDCs)**

- Compounds mimicking hormones

- example:

- polychlorinated biphenyls (PCBs): coolant, insulator, plasticizer
- atrazine: pesticide
- phthalates: plasticizer
- bisphenol A (BPA): making plastics
- natural and synthetic estrogen
  - contraceptive pills:  $17\alpha$ -ethynylestradiol (EE2)

- May cause adverse effects at relatively low concentrations

- Can interfere with the regulation of reproductive and developmental processes or alter the normal physiological function of the endocrine system



<http://shopping.naver.com>

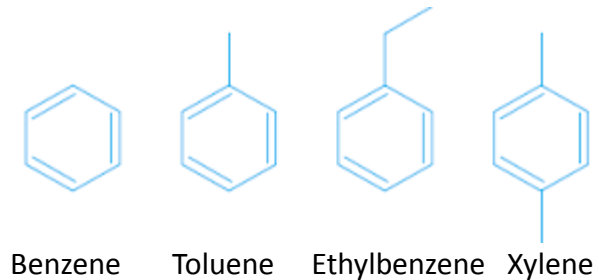
# Types of water pollutants

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- Other toxic organic chemicals

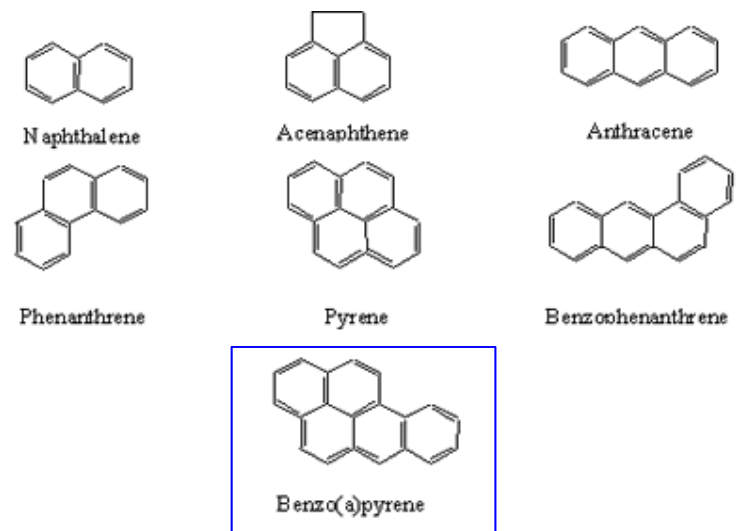
- **BTEX**

- Benzene, Toluene, Ethylbenzene, Xylene
    - Spills from gasoline and other petroleum products



- **Polycyclic aromatic hydrocarbons (PAHs)**

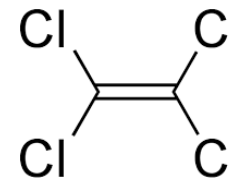
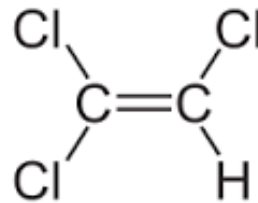
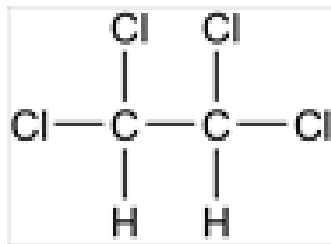
- Compounds with two or more fused benzene rings
    - Some are carcinogenic
    - Incomplete combustion, petroleum



# Types of water pollutants

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- Other toxic organic chemicals
  - Chlorinated ethenes and ethanes
    - Tetrachloroethane (**TCA**), trichloroethylene (**TCE**), tetrachloroethylene (**PCE**)
    - Solvents for dry cleaning and metal washing



***per**chloroethylene*



# Types of water pollutants

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- **Arsenic**

- Neither metal nor non-metal, but metalloid
- Source: mineral dissolution from weathered rocks and soils, mainly from iron oxides or sulfide minerals → arsenic contamination is often a naturally occurring problem
- Human carcinogen
- Significant groundwater contaminant in many regions of the world (ex: 33-77 million of Bangladesh's 125 million people are at risk of As poisoning from groundwater)
- Exist in quite high levels in Korea as well!

# Types of water pollutants

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- **Toxic metals**

- Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Mercury (Hg)
- Sources: industrial waste, wastewater treatment plants, stormwater runoff, mining operations, smokestack emissions, etc.
- Some heavy metals bioaccumulate and biomagnify (ex: mercury in tuna)

# Types of water pollutants

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- **Toxic metals**
  - **Acid mine drainage (AMD)**
    - Water in mine operations gets acidic by a series of geochemical and microbial reactions
    - Generally metal solubility increases as pH lowers
    - Water contamination, ecosystem destruction, corrosion of infrastructure
  - **Outbreaks: recall from your middle school class!**
    - Minamata, Japan – mercury
    - Toyoma, Japan – cadmium (itai-itai disease)

# Types of water pollutants

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- **Heat**

- Water used as coolants is discharged to the receiving waters
- May destroy the aquatic ecosystem
- Temperature increases → decrease in oxygen solubility and enhanced microbiological activity → oxygen depletion in rivers

# Types of water pollutants

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- **Nanoparticles**

- Particles having a dimension  $< 100$  nm
- Naturally occurring humic material;  $\text{TiO}_2$  particles in paints, varnishes, paper, plastics, creams, etc.; carbon nanoparticles in tires, tennis rackets, video screens, etc.; protein-based nanomaterials in the production of soaps, shampoos, and detergents
- Rapidly increasing production
- Toxicity and fate not well known



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# Oxygen demand

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- Indicators needed to predict the extent of oxygen depletion and to maintain sufficient levels of DO in rivers and streams
- **Theoretical oxygen demand (ThOD)**
  - the amount of oxygen required to oxidize a substance to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  calculated by stoichiometry
  - the chemical composition of the substance should be known

# Oxygen demand

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**Q:** Compute the ThOD of 108.75 mg/L of glucose ( $C_6H_{12}O_6$ ).

# Oxygen demand

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- **Chemical oxygen demand (COD)**
  - A measured quantity – does not depend on the knowledge of the chemical composition of the substances in the water
  - The organic compounds in a water is oxidized by a strong oxidizing agent such as potassium dichromate ( $K_2CrO_7$ ) or potassium permanganate ( $KMnO_4$ )
  - The difference between the amount of oxidizing agent at the beginning and the end of the test is used to calculate COD



# Oxygen demand

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- Biochemical oxygen demand (BOD)
  - The oxygen demand is measured by a bioassay
  - The water sample is inoculated with bacteria that degrade organic matter in water
  - The difference in DO in the water sample at the beginning and end of the test is used to calculate BOD



# BOD Measurement

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**Step 1.** Take the wastewater sample and dilute if needed. Fill the test bottle (usually 300 mL) with the (diluted) sample and a suspension of microorganisms (seed) if needed. Seal the bottle to prevent air intrusion/water evaporation.

$$\text{Dilution factor} = P = \frac{\text{volume of wastewater sample}}{\text{volume of wastewater} + \text{dilution water}}$$

*The expected BOD of the diluted sample should be 2-6 mg/L.*

*\* saturation DO concentration at 20 °C: 9.17 mg/L*

# BOD Measurement

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**Step 2.** Prepare blank samples (control) containing only the dilution water and the seed.

**Step 3.** Incubate the samples and blanks at 20°C in the dark. Usually the incubation time is 5 days.

**Step 4.** Measure the DO after incubation.

***The BOD of the wastewater sample can be calculated as:***

$$BOD_t = \frac{DO_{b,t} - DO_{s,t}}{P}$$

$DO_{b,t}$  = DO concentration in blank after  $t$  days of incubation

$DO_{s,t}$  = DO concentration in sample after  $t$  days of incubation

# Oxygen demand

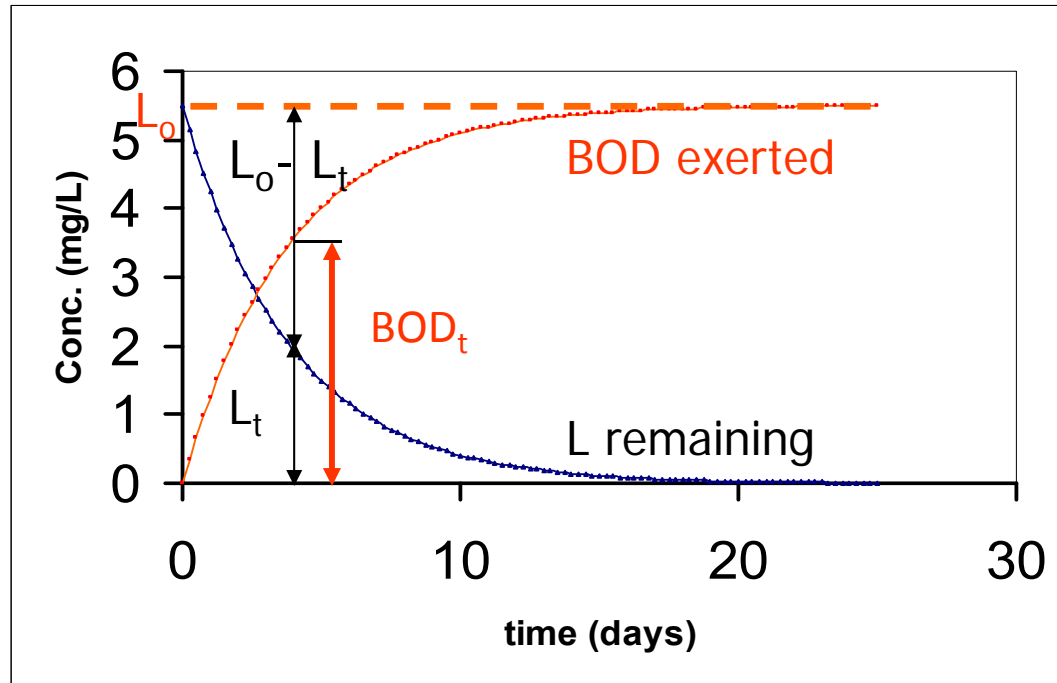
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## **ThOD $\geq$ COD $>$ BOD**

- Some organic compounds may not be oxidized even with a strong oxidizing agent (ThOD  $\geq$  COD)
- Some carbon is used for bacterial growth; some organic compounds are not biodegradable; some organic matter is converted to non-biodegradable materials (COD  $>$  BOD)

# Modeling BOD

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$L$  = oxygen demand of remaining biodegradable organic chemicals (mg/L)

- $L_t$  decreases with time and  $BOD_t$  increases with time
- $L_0 = L_t + BOD_t$
- $L_0 (= BOD_\infty)$ : ultimate BOD

# Modeling BOD

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The degradation of organic compounds by microorganisms is modeled as a first-order reaction:

$$\frac{dL}{dt} = -kL \quad k = \text{first-order reaction constant (day}^{-1}\text{)}$$

Integration of the equation gives:

$$L_t = L_0 e^{-kt}$$

As  $BOD_t = L_0 - L_t$ ,

$$BOD_t = L_0(1 - e^{-kt})$$

# Modeling BOD

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The magnitude of the BOD rate constant,  $k$  depends on:

1. Nature of waste: whether the waste is easily biodegradable or not
2. Ability of organisms to use waste: the microorganisms in the test bottle may not be ready to degrade the waste! (recall the “lag phase”)
3. Temperature

$$k_T = k_{20}\theta^{T-20}$$

$k_T$  = BOD rate constant at temperature T (day<sup>-1</sup>)

$k_{20}$  = BOD rate constant at 20°C (day<sup>-1</sup>)

$\theta$  = temperature coefficient

(use 1.135 for 4-20°C and 1.056 for 20-30°C)

# Modeling BOD

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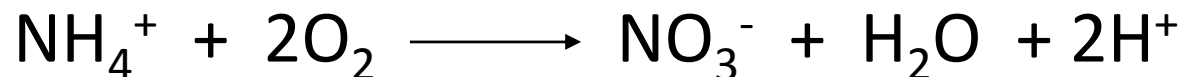
**Q:** The  $BOD_5$  of a wastewater is 120 mg/L and the BOD rate constant is  $0.115 \text{ day}^{-1}$  at  $20^\circ\text{C}$ . What is the ultimate BOD? If the wastewater is incubated at  $15^\circ\text{C}$  with a supply of oxygen, how much oxygen will be used by microorganisms in three days?



# Nitrogenous BOD

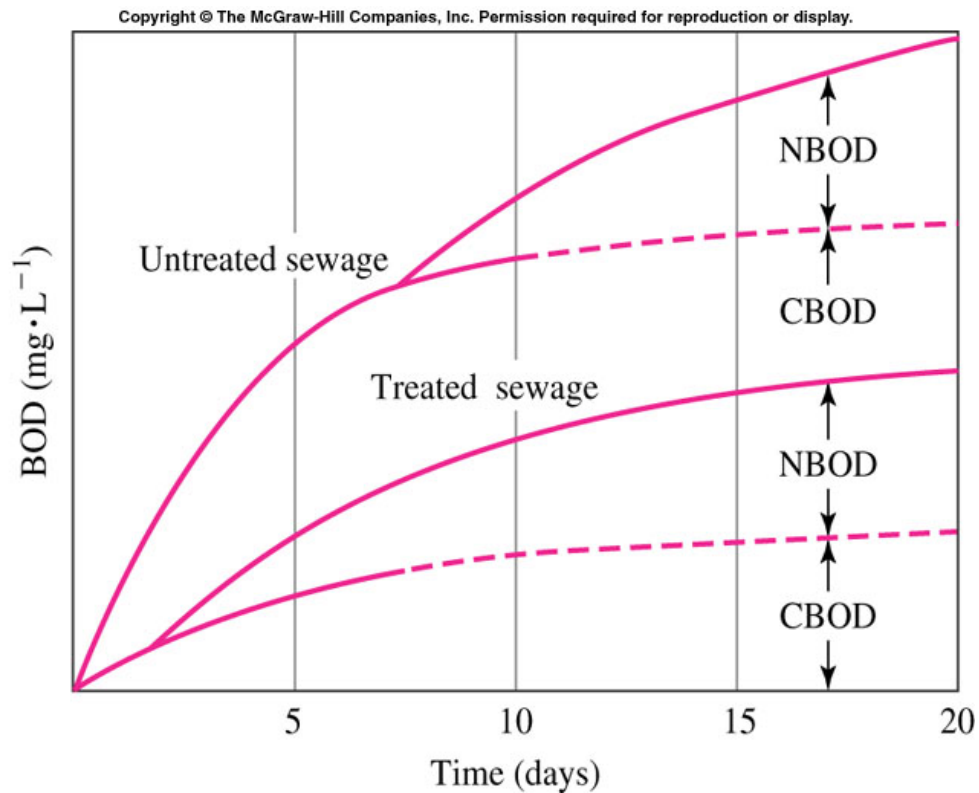
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- So far, our assumption was that the oxygen demand is due to carbon oxidation only
- Organic compounds also contain reduced nitrogen
- The reduced nitrogen is released to form ammonium ion ( $\text{NH}_4^+$ )
- This may contribute significantly to overall oxygen demand by:



# Nitrogenous BOD

The BOD curve when NBOD is significant



- Lag time exists because carbon-utilizing bacteria carbon is more prevalent at the beginning
- As CBOD goes down, the population of ammonia-utilizing bacteria increases, leading to NBOD consumption
- For treated sewage, the lag time is shorter, because there's not much food for carbon-utilizing bacteria

# Reading assignment

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Textbook Ch 9 p. 378-403