# Water quality II

# Today's lecture

- Biochemical oxygen demand (BOD)
  - Concept
  - Measurement
  - Modeling
  - Nitrogenous BOD
- DO dynamics in river
  - DO sag curve
  - Modeling DO in the river
  - Solution: Streeter-Phelps equation

**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.

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

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

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

**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:

$$BOD_t = \frac{DO_{b,t} - DO_{s,t}}{P}$$
  $DO_{b,t} = DO \text{ concent}$  days of incubation

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

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

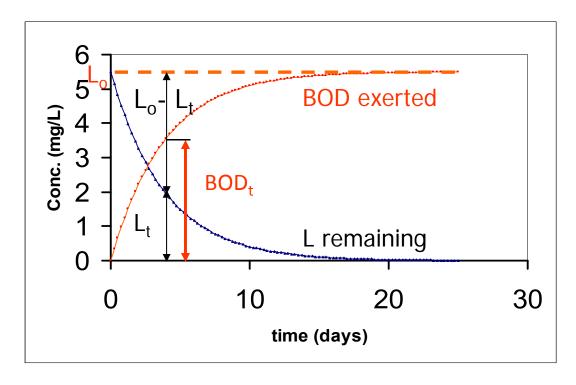
#### If the BOD of the seed is significant, the following equation should be used instead:

$$BOD_t = \frac{\left(DO_{s,i} - DO_{s,t}\right) - \left(DO_{b,i} - DO_{b,t}\right)f}{P}$$

$$DO_{s,i}$$
 = the initial DO of the sample  $f$  = (volume of seed in sample) /  $DO_{b,i}$  = the initial DO of the blank (volume of seed in bl

**Q:** The BOD of a wastewater sample was initially estimated to be 180 mg/L. What volume of the sample should be added to a 300-mL bottle?

Applying the calculated dilution factor, the DO values for the blank and diluted sample after 5 days of incubation were 8.7 and 4.2 mg/L, respectively. What is the BOD<sub>5</sub> of the sample? Assume that the sample and the blank were not seeded.



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

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

$$\frac{dL}{dt} = -kL$$

$$k = \text{first-order reaction constant (day}^{-1})$$

Integration of the equation gives:

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

As 
$$BOD_t = L_0 - L_t$$
,

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

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

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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)
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**Q:** The BOD<sub>5</sub> of a wastewater is 120 mg/L and the BOD rate constant is 0.115 day<sup>-1</sup> at 20°C. What is the ultimate BOD? If the wastewater is incubated at 15°C with a supply of oxygen, how much oxygen will be used by microorganisms in three days?

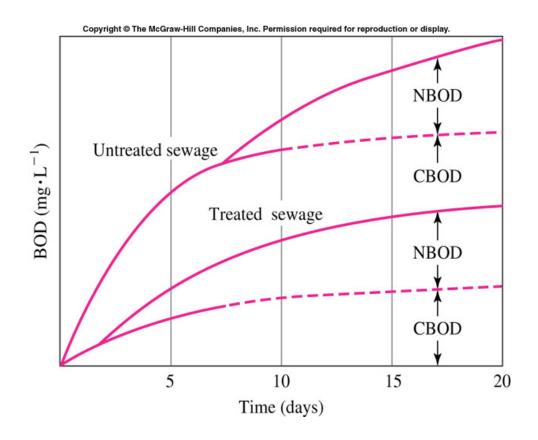
#### Nitrogenous BOD

- So far, our assumption was that the oxygen demand is due to carbon oxidation only
- Organic compounds also contain <u>reduced</u> nitrogen
- The reduced nitrogen is released to form ammonium ion  $(NH_4^+)$
- This may contribute significantly to overall oxygen demand by:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

#### Nitrogenous BOD

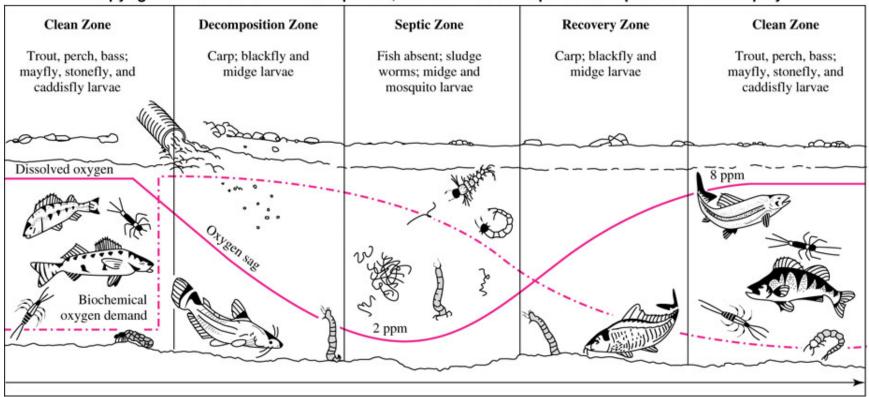
#### The BOD curve when NBOD is significant



- 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 carbonutilizing bacteria

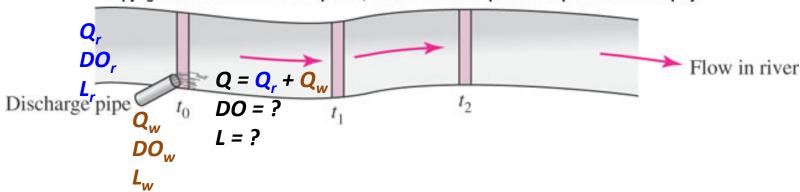
#### DO sag curve

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- Factors causing DO depletion: BOD in water (upstream + waste)
- Factors causing DO increase: reaeration from the atmosphere (+ photosynthesis – neglected)

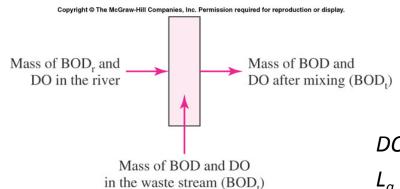
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We will model the DO of a river receiving waste at time  $t_0$ . The river will be modeled as a PFR.

\* The solution for this problem is known as "Streeter-Phelps equation", a well-known equation derived by Streeter and Phelps in 1925.

The DO and ultimate BOD at  $t_0$  are calculated by a mass balance approach:



$$(Q_w + Q_r)DO_a = Q_wDO_w + Q_rDO_r$$
$$(Q_w + Q_r)L_a = Q_wL_w + Q_rL_r$$

 $DO_a$  = DO concentration right after mixing (mg/L)  $L_a$  = ultimate BOD right after mixing (mg/L)



$$DO_a = \frac{Q_w DO_w + Q_r DO_r}{Q_w + Q_r} \qquad L_a = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r}$$

The temperature after mixing is calculated in the same

way:

$$T_a = \frac{Q_w T_w + Q_r T_r}{Q_w + Q_r}$$
  $T_a = \text{temperature after mixing (°C or K)}$ 

## Oxygen deficit

 Oxygen deficit (D): the difference between the saturation DO value and the actual DO concentration

$$D = DO_S - DO$$

Therefore, the oxygen deficit right after mixing is calculated as:

$$D_a = DO_S - \frac{Q_w DO_w + Q_r DO_r}{Q_w + Q_r}$$

 $D_a$  = oxygen deficit right after mixing (mg/L)

- Rate of reaeration
  - Should depend on the stream velocity and depth
  - The reaeration coefficient,  $k_r$  [day<sup>-1</sup>]

$$k_r = \frac{3.9u^{1/2}}{h^{3/2}}$$
  $u$  = average stream velocity (m/s)  $h$  = average stream depth (m)

Rate of reaeration should also depend on oxygen deficit

Rate of reaeration = 
$$\frac{d(DO)}{dt}\Big|_{reaeration} = -\frac{dD}{dt}\Big|_{reaeration} = k_r D$$

– Effect of temperature on  $k_r$ : faster mass transfer at higher temp.

$$k_{r,T}=k_{r,20}\theta^{T-20}$$
  $k_{r,T}=$  reaeration coeff. at temperature  $T$  (day<sup>-1</sup>)  $k_{r,20}=$  reaeration coeff. at 20°C, obtained from  $k_{r,20}=3.9u^{1/2}/h^{3/2}$  (day<sup>-1</sup>)  $\theta=$  temperature coefficient (use 1.024)

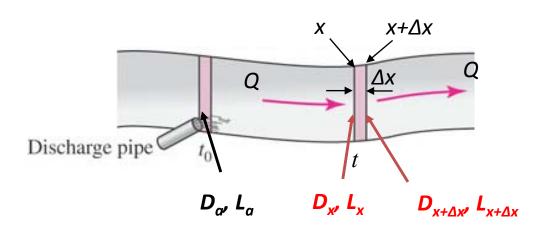
- Rate of deoxygenation
  - Rate of oxygen consumption by microorganisms
  - Assume that the first-order deoxygenation rate constant is equal to the BOD rate constant, k
  - The assumption is valid for deep, slow-moving streams
  - The rate of deoxygenation

Rate of deoxygenation = 
$$-\frac{d(DO)}{dt}\Big|_{deoxygenation} = \frac{dD}{dt}\Big|_{deoxygenation}$$
  
=  $k_dL$ 

 $k_d$  = first-order deoxygenation rate constant [T<sup>-1</sup>]

– Effect of temperature on  $k_d$ : use the equation for k!

$$k_T = k_{20} \theta^{T-20}$$
  $\theta = 1.135 \text{ for } 4\text{-}20^{\circ}\text{C} \text{ and}$  1.056 for 20-30°C



Steady-state D (= $DO_s$ -DO) balance for a thin plate at time t:

$$0 = QD_x - QD_{x+\Delta x} + k_dL_x \cdot \Delta V - k_rD_x \cdot \Delta V \qquad \Delta V = \text{volume of the CV} = A \cdot \Delta x$$
 (A = cross-sectional area)

With rearrangements and  $\Delta x \rightarrow 0$ , we obtain:

$$\frac{dD}{dt} = k_d L - k_r D$$

Governing equation: 
$$\frac{dD}{dt} = k_d L - k_r D$$

+ Initial conditions:

at t=0, 
$$D=D_a$$
 and  $L=L_a$ 

#### **Solution:**

$$D_{t} = \frac{k_{d}L_{a}}{k_{r} - k_{d}} \left( e^{-k_{d}t} - e^{-k_{r}t} \right) + D_{a} \left( e^{-k_{r}t} \right)$$

 $D_t$  = oxygen deficit in a river after flowing downstream from the mixing point for time *t* 

(Note 
$$DO_t = DO_s - D_t$$
)

## **Critical point**

 Critical point: the point where the DO is the lowest on the DO sag curve

$$t_c = \frac{1}{k_r - k_d} ln \left[ \frac{k_r}{k_d} \left( 1 - D_a \frac{k_r - k_d}{k_d L_a} \right) \right]$$

 $t_c$  = the time to the critical point [T]

• The critical deficit,  $D_c$ 

$$D_{c} = \frac{k_{d}L_{a}}{k_{r} - k_{d}} \left( e^{-k_{d}t_{c}} - e^{-k_{r}t_{c}} \right) + D_{a} \left( e^{-k_{r}t_{c}} \right)$$

**Q:** A city disposes of 1.05 m³/s of treated sewage having ultimate BOD of 28.0 mg/L and DO of 1.8 mg/L into a river. At the upstream from the outfall, the river flowrate is 7.08 m³/s, and the ultimate BOD and DO of the river are 3.6 and 7.6 mg/L, respectively. At the river temperature, the saturation value of DO is 8.5 mg/L, the deoxygenation coefficient,  $k_d$ , 0.61 day<sup>-1</sup>, and the reaeration coefficient,  $k_r$  0.76 day<sup>-1</sup>. The velocity of the river downstream from the outfall is 0.37 m/s.

- 1) Calculate the ultimate BOD and DO just downstream from the outfall. Assume complete mixing.
- 2) Calculate the DO 16 km downstream from the outfall.
- 3) Calculate the critical time, distance, and the minimum DO.

# Reading assignment

Textbook Ch 9 p. 392-418