

# Slide#6 solution

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i) *Ultimate BOD*

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

$$L_0 = \frac{BOD_5}{1 - e^{-5 d \times k}} = \frac{120 \text{ mg/L}}{1 - e^{-5 d \times 0.115 \text{ d}^{-1}}} = \mathbf{274 \text{ mg/L}}$$

ii) *BOD<sub>3</sub> at 15°C*

$$k_{15} = k_{20} \theta^{15-20}, \theta = 1.135 \text{ at } 4-20^\circ\text{C}$$

$$k_{15} = 0.115 \text{ day}^{-1} \times 1.135^{15-20} = 0.0611 \text{ day}^{-1}$$

$$BOD_3 = 274 \text{ mg/L} \times (1 - e^{-0.0611 \text{ day}^{-1} \times 3 \text{ day}}) = \mathbf{45.9 \text{ mg/L}}$$

# Slide#19 solution

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i)  $L_a$  and  $DO_a$

$$L_a = \frac{28.0 \text{ mg/L} \times 1.05 \text{ m}^3/\text{s} + 3.6 \text{ mg/L} \times 7.08 \text{ m}^3/\text{s}}{(1.05 + 7.08) \text{ m}^3/\text{s}} = 6.8 \text{ mg/L}$$

$$DO_a = \frac{1.8 \text{ mg/L} \times 1.05 \text{ m}^3/\text{s} + 7.6 \text{ mg/L} \times 7.08 \text{ m}^3/\text{s}}{(1.05 + 7.08) \text{ m}^3/\text{s}} = 6.9 \text{ mg/L}$$

ii) DO 16 km downstream

$$\text{Initial deficit, } D_a = DO_s - DO_a = 8.5 \text{ mg/L} - 6.9 \text{ mg/L} = 1.6 \text{ mg/L}$$

$$t = \frac{16000 \text{ m}}{0.37 \text{ m/s} \times 86400 \text{ s/day}} = 0.50 \text{ days}$$

$$\begin{aligned} D_t &= \frac{k_d L_a}{k_r - k_d} (e^{-k_d t} - e^{-k_r t}) + D_a (e^{-k_r t}) \\ &= \frac{0.61 \text{ day}^{-1} \times 6.8 \text{ mg/L}}{(0.76 - 0.61) \text{ day}^{-1}} (e^{-0.61 \text{ day}^{-1} \times 0.50 \text{ days}} - e^{-0.76 \text{ day}^{-1} \times 0.50 \text{ days}}) \\ &\quad + 1.6 \text{ mg/L} \times (e^{-0.76 \text{ day}^{-1} \times 0.50 \text{ days}}) \\ &= 2.6 \text{ mg/L} \end{aligned}$$

$$DO_t = DO_s - D_t = 8.5 \text{ mg/L} - 2.6 \text{ mg/L} = \mathbf{5.9 \text{ mg/L}}$$

iii)  $t_c$ ,  $L_c$  &  $DO_c$

$$\begin{aligned} t_c &= \frac{1}{k_r - k_d} \ln \left[ \frac{k_r}{k_d} \left( 1 - D_a \frac{k_r - k_d}{k_d L_a} \right) \right] \\ &= \frac{1}{(0.76 - 0.61) \text{ day}^{-1}} \ln \left[ \frac{0.76 \text{ day}^{-1}}{0.61 \text{ day}^{-1}} \left( 1 - 1.6 \text{ mg/L} \frac{(0.76 - 0.61) \text{ day}^{-1}}{0.61 \text{ day}^{-1} \times 6.8 \text{ mg/L}} \right) \right] \\ &= \mathbf{1.07 \text{ days}} \end{aligned}$$

$$L_c = 1.07 \text{ days} \times 0.37 \text{ m/s} \times 86400 \text{ s/day} = 34200 \text{ m} = \mathbf{34.2 \text{ km}}$$

$$\begin{aligned} D_c &= \frac{k_d L_a}{k_r - k_d} (e^{-k_d t_c} - e^{-k_r t_c}) + D_a (e^{-k_r t_c}) \\ &= \frac{0.61 \text{ day}^{-1} \times 6.8 \text{ mg/L}}{(0.76 - 0.61) \text{ day}^{-1}} (e^{-0.61 \text{ day}^{-1} \times 1.07 \text{ days}} - e^{-0.76 \text{ day}^{-1} \times 1.07 \text{ days}}) \\ &\quad + 1.6 \text{ mg/L} \times (e^{-0.76 \text{ day}^{-1} \times 1.07 \text{ days}}) \\ &= 2.8 \text{ mg/L} \end{aligned}$$

$$DO_c = DO_s - D_c = 8.5 \text{ mg/L} - 2.8 \text{ mg/L} = \mathbf{5.7 \text{ mg/L}}$$

# Slide#24 solution

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$$R = 1 + \left(\frac{\rho_b}{\eta}\right) K_{oc} \cdot f_{oc} = 1 + \frac{1.5 \frac{g}{cm^3}}{0.4} \cdot 27.0 \text{ cm}^3/g \cdot 0.02 = 3.03$$

$$v'_{cont} = \frac{v'_{water}}{R} = \frac{4.7 \times 10^{-6} \text{ m/s}}{3.03} = 1.55 \times 10^{-6} \text{ m/s}$$

$$t = \frac{10 \text{ m}}{1.55 \times 10^{-6} \text{ m/s} \times 86400 \text{ s/d}} = 75 \text{ days}$$

# Water quality II

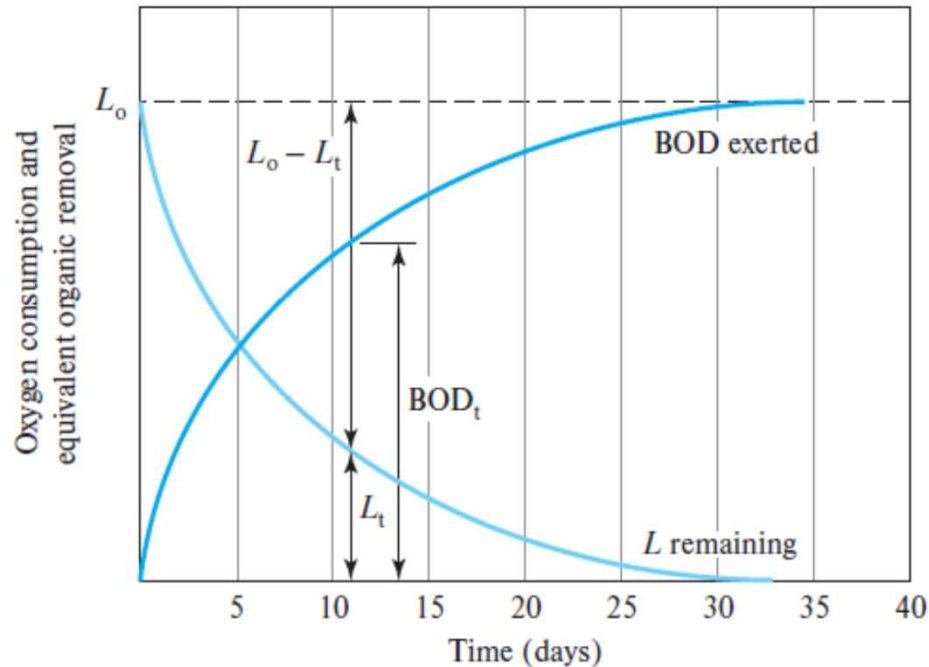
# Today's lecture

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- Modeling the BOD
- Nitrogenous BOD
- Dissolved oxygen (DO) dynamics in rivers
- Groundwater quality

# 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 (cont'd)

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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  $BOD_t = L_0 - L_t$ ,

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



# BOD rate constant

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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 effect

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

$k_T$  = BOD rate constant at temperature  $T$  °C ( $\text{day}^{-1}$ )

$k_{20}$  = BOD rate constant at 20 °C ( $\text{day}^{-1}$ )

$\theta$  = temperature coefficient

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

# Modeling BOD

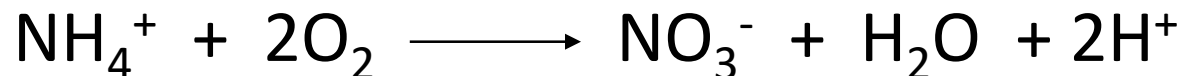
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**Q:** The  $BOD_5$  of a wastewater is 120 mg/L and the BOD rate constant is  $0.115 \text{ day}^{-1}$  at  $20^\circ\text{C}$ . What is the ultimate BOD? If the wastewater is incubated at  $15^\circ\text{C}$  with a supply of oxygen, how much oxygen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

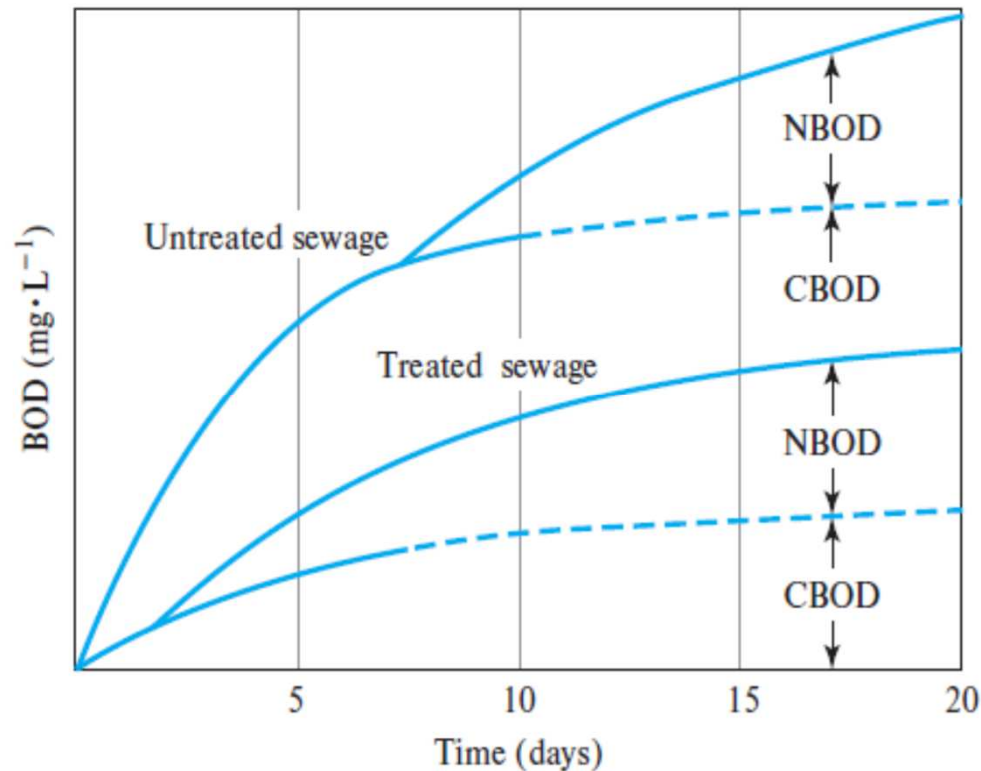
# Nitrogenous BOD

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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:

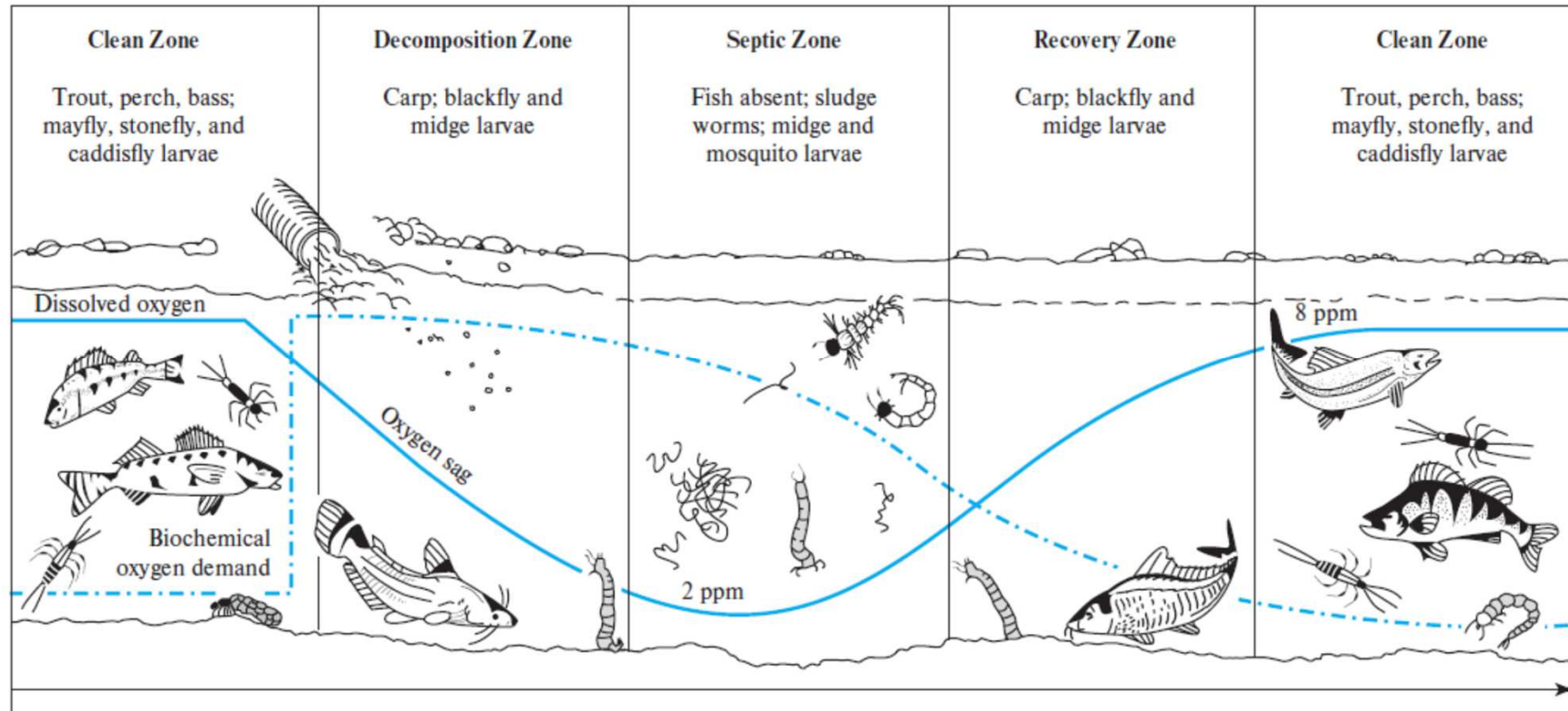


# BOD curve when NBOD is significant



- 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

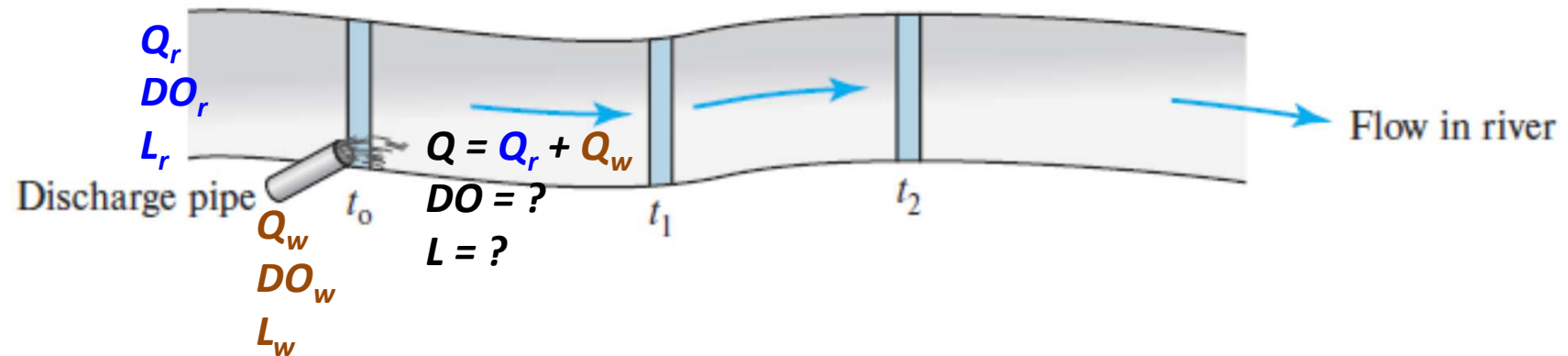
# Water quality in rivers: DO sag curve



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

# Modeling the DO along a river

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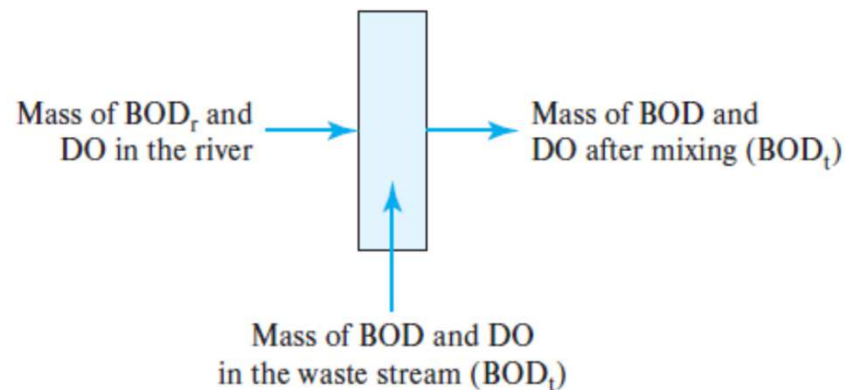
We will model the DO of a river receiving waste at time  $t_0$ . The river will be modeled as a PFR.

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

# DO modeling: initial conditions

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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<sub>a</sub> = DO concentration right after mixing (mg/L)*

*L<sub>a</sub> = ultimate BOD right after mixing (mg/L)*



$$DO_a = \frac{Q_wDO_w + Q_rDO_r}{Q_w + Q_r}$$

$$L_a = \frac{Q_wL_w + Q_rL_r}{Q_w + Q_r}$$

# DO modeling: initial conditions (cont'd)

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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<sub>a</sub> = temperature after mixing ( °C or K)*

*T<sub>w</sub> = temperature of the waste stream ( °C or K)*

*T<sub>r</sub> = temperature of the river before mixing ( °C or K)*



# Oxygen deficit

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- 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, $k_r$

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

$$k_r = \frac{3.9u^{1/2}}{h^{3/2}} \quad \begin{array}{l} u = \text{average stream velocity (m/s)} \\ h = \text{average stream depth (m)} \end{array}$$

- Rate of reaeration should also depend on oxygen deficit

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

- 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 coefficient at temperature  $T$  (day<sup>-1</sup>)  
 $k_{r,20}$  = reaeration coefficient 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, $k_d$

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- 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

$$\begin{aligned} \text{Rate of deoxygenation} &= - \left. \frac{d(DO)}{dt} \right|_{\text{deoxygenation}} = \left. \frac{dD}{dt} \right|_{\text{deoxygenation}} \\ &= k_d L \end{aligned}$$

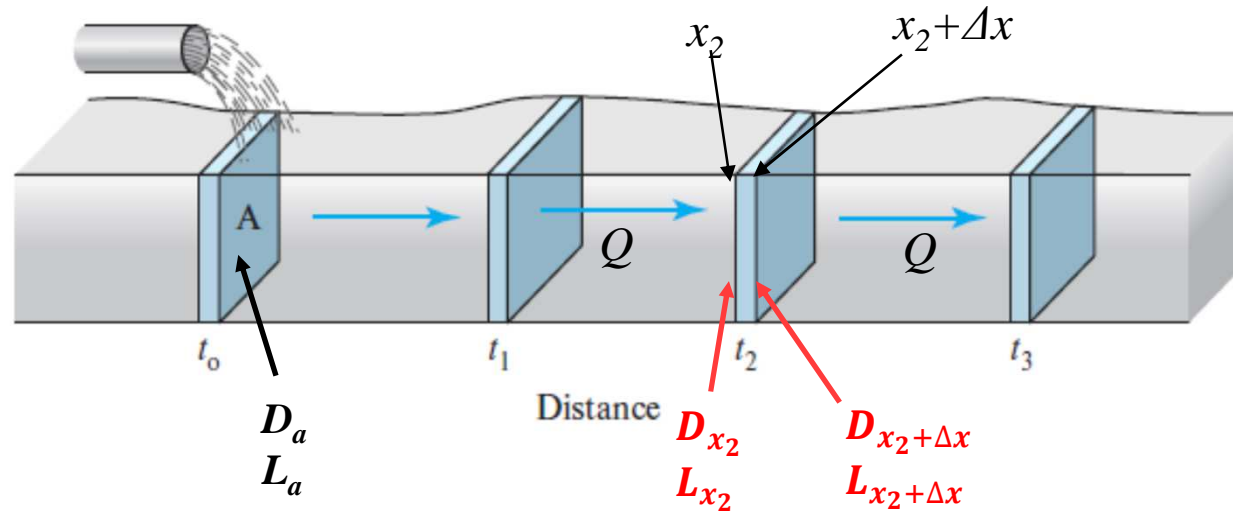
$k_d$  = first-order deoxygenation rate constant [ $T^{-1}$ ]

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

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

$\theta = 1.135$  for 4-20 °C & 1.056 for 20-30 °C

# DO modeling: applying mass balance approach



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

$$0 = QD_x - QD_{x+\Delta x} + k_d L_x \cdot \Delta V - k_r D_x \cdot \Delta V$$

$\Delta V = \text{volume of the CV} = A \cdot \Delta x$   
 ( $A = \text{cross-sectional area}$ )

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

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

# DO modeling: governing eq. & solution

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

+ Initial conditions:

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

**Solution:**

$$D_t = \frac{k_d L_a}{k_r - k_d} (e^{-k_d t} - e^{-k_r t}) + D_a (e^{-k_r t})$$

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

(Note  $DO_t = DO_s - D_t$ )

# Critical point

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- 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,  $D_c$

$$D_c = \frac{k_d L_a}{k_r - k_d} (e^{-k_d t_c} - e^{-k_r t_c}) + D_a (e^{-k_r t_c})$$

# Modeling DO along a river

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**Q:** A city disposes of  $1.05 \text{ m}^3/\text{s}$  of treated sewage having ultimate BOD of  $28.0 \text{ mg/L}$  and DO of  $1.8 \text{ mg/L}$  into a river. At the upstream from the outfall, the river flowrate is  $7.08 \text{ m}^3/\text{s}$ , and the ultimate BOD and DO of the river are  $3.6$  and  $7.6 \text{ mg/L}$ , respectively. At the river temperature, the saturation value of DO is  $8.5 \text{ mg/L}$ , the deoxygenation coefficient,  $k_d$ ,  $0.61 \text{ day}^{-1}$ , and the reaeration coefficient,  $k_r$ ,  $0.76 \text{ day}^{-1}$ . The velocity of the river downstream from the outfall is  $0.37 \text{ m/s}$ .

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

# Groundwater quality

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- Contamination of groundwater (aquifer) can result from:
  - Discharge from improperly operated or located septic systems
  - Leaking underground storage tanks (USTs)
  - Improper disposal of hazardous and other chemical wastes
  - Spills from pipelines or transportation accidents
  - Recharge of groundwater with contaminated surface water
  - Leaking dumps and landfills
  - Leaking retention ponds or lagoons



<http://www.septicrepairny.com>



<http://www.apexenvirotech.com>



# Non-aqueous phase liquid (NAPL) in aquifer

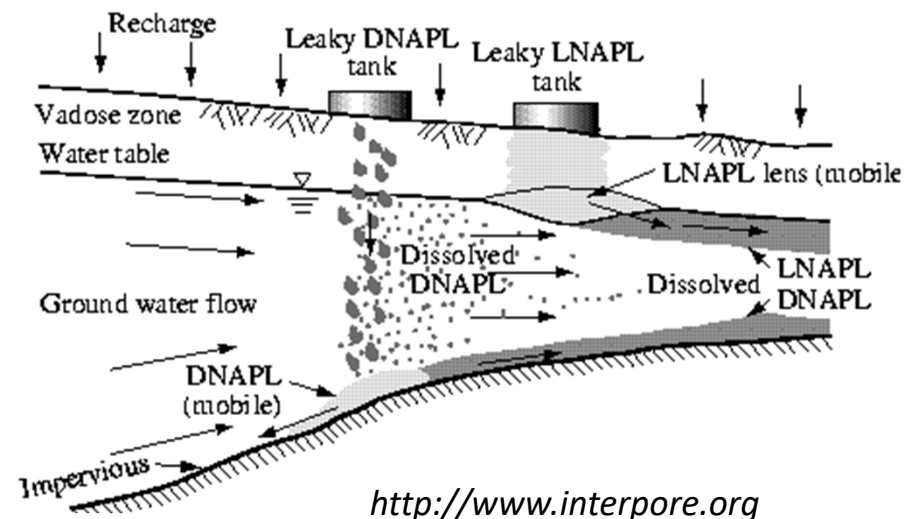
- Many chemicals are only sparingly soluble in water
- They may migrate in aquifer as a separate non-aqueous phase

- **Light NAPL (LNAPL)**

- lighter than water, float on the water table
- example: gasoline (includes BTEX)

- **Dense NAPL (DNAPL)**

- Denser than water, sink in the aquifer until reaching an impermeable layer
- Example: TCE, PCE



# Transport of dissolved contaminants

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- **Advection**: transport of dissolved contaminants by average movement of groundwater (seepage velocity)
- **Dispersion**: spreading of contaminants by i) deviation of groundwater velocity from average and ii) molecular diffusion
- Many contaminants move slower than the groundwater seepage velocity because of: **sorption** (adsorption + absorption)
- Retardation coefficient: the extent to which chemicals are retarded in water

$$R = \frac{v'_{water}}{v'_{cont}}$$

*R = retardation coefficient*

*v'\_{water} = seepage velocity of groundwater*

*v'\_{cont} = linear velocity of contaminant*

# Retardation coefficient

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For neutral hydrophobic organic contaminants, the retardation coefficient,  $R$ , can be obtained by

$$R = 1 + \left( \frac{\rho_b}{\eta} \right) K_d$$

$\rho_b$  = bulk density of soil (g/cm<sup>3</sup>)  
 $\eta$  = porosity of soil  
 $K_d$  = sorption coefficient of the contaminant between soil and water (cm<sup>3</sup>/g)  
= (conc. in soil at equilibrium) / (conc. in water at equilibrium)

As hydrophobic organic contaminants mainly sorb to organic matter in soil, the  $K_d$  can be written as

$$K_d = K_{oc} \cdot f_{oc}$$

$K_{oc}$  = sorption coefficient to the organic carbon fraction of soil (g/cm<sup>3</sup>)  
= (conc. in organic carbon at equilibrium) / (conc. in water at equilibrium)  
 $f_{oc}$  = fraction of organic carbon in soil

Thus,

$$R = 1 + \left( \frac{\rho_b}{\eta} \right) K_{oc} \cdot f_{oc}$$

# Transport of contaminants in groundwater

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**Q:** A plume of benzene is migrating in groundwater flowing at a seepage velocity of  $4.7 \times 10^{-6}$  m/s. Using the following properties of the aquifer material and benzene, calculate the time for the center of the benzene plume to move 10 m in the direction of groundwater flow.

***Aquifer material properties***

*Bulk density: 1.5 g/cm<sup>3</sup>*

*Porosity: 0.4*

*Fraction of organic carbon: 0.02*

***Benzene property***

*Sorption coefficient to the organic carbon fraction: 27.0 cm<sup>3</sup>/g*

# Suggested readings

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[ENG] pp. 410 – 435, 452 – 456

[KOR] pp. 397 – 425, 444 – 449