

## Water Quality Management

### 1. Introduction

In order to know “how much waste can be tolerated by a water body”,

We have to know

- (1) the type of pollutants discharged,
- (2) the manner in which they affect water quality, and
- (3) how water quality is affected by natural factors (e.g., mineral heritage, geometry, and the climate)

Impurities in Environmental Media (eg., Water or Air)

- Directly hazardous to human health (allergic reactions, short-term illnesses, chronic illnesses, acute toxicity, birth defects, cancer, and death)
- Aesthetic (including the taste, odor, color and clarity)
- Impact on the environment (e.g., carbon dioxide)
- Beneficial (e.g., Dissolved oxygen)

### 2. Water Pollutants and Their Sources

#### 2.1 Point Sources vs. Nonpoint Sources

Point sources (e.g., domestic sewage, industrial sewage, etc.: 점오염원)

Non-point sources (e.g., agricultural runoff, urban runoff, etc.: 비점오염원)

#### 2.2 Oxygen Demanding Material

- Oxygen demanding material: anything that can be oxidized in the receiving water resulting in the consumption of dissolved molecular oxygen
- biodegradable organic matter, and certain inorganic compounds (e.g.,  $\text{NH}_4^+$  +  $2\text{O}_2 \rightarrow \text{NO}_3^-$  (nitrate) +  $\text{H}_2\text{O}$  +  $2\text{H}^+$ )



- DO (dissolved oxygen, 용존산소): critical to aquatic lives, e.g., trout > 7.5 mg/L, and carp (잉어) > 3 mg/L, mudfish (미꾸라지) > ?

### 2.3 Nutrients (영양물질)

- Primary nutrients: N(질소) and P(인)
- When nutrient levels become excessive, the food web is disturbed. i.e., “Eutrophication” (부영양화)
- Major sources of nutrients: phosphorus-based detergents, fertilizers, food-processing wastes, animal and human excrement, etc.

### 2.4 Pathogenic Organisms

- Pathogen microorganisms: bacteria, viruses, protozoa (Cryptosporidium, Giardia, etc.) excreted by diseased persons and animals
- Escherichia coli (E. coli) is an indicator organism. Although many coliforms are harmless, the presence of these indicates the potential for water contamination by sewage, feces, and more pathogenic organisms. Many strains of E. coli are normal and are prevalent inhabitants of the intestinal tract of warm-blooded animals.

### 2.5 Suspended Solids (부유물질)

- Settleable solids (침전성 물질) > 10  $\mu\text{m}$
- Suspended solids > 1  $\mu\text{m}$
- $10^{-3} \mu\text{m} < \text{Colloidal solids} < 1.2 \mu\text{m}$
- Dissolved solid (용존 물질)

- (1) decrease visibility
- (2) decrease transmission (suspended particles may be host to microorganisms.)
- (3) transport and delivery of toxic materials (heavy metals and toxic organics are found in particulate form.)
- (4) acute respiratory health effects (for airborne particulates)



- Total solids (TS, 105°C), Suspended solids (SS, 0.45μm), Total dissolved solids (TDS), Total volatile solids (TVS, 550°C), Volatile suspended solids (VSS)
- PM<sub>x</sub>: particulate matter (입자상물질) smaller than x micrometers in aerodynamic diameter (e.g, PM<sub>10</sub>, PM<sub>2.5</sub>)

Table Most prevalent dissolved ions in natural waters, along with typical molar concentrations

Ion	Seawater (M)	River water (M)
Na <sup>+</sup>	0.47	0.23 x 10 <sup>-3</sup>
Mg <sup>2+</sup>	0.053	0.15 x 10 <sup>-3</sup>
Ca <sup>2+</sup>	0.010	0.33 x 10 <sup>-3</sup>
K <sup>+</sup>	0.010	0.03 x 10 <sup>-3</sup>
Cl <sup>-</sup>	0.55	0.16 x 10 <sup>-3</sup>
SO <sub>4</sub> <sup>2-</sup>	0.028	0.07 x 10 <sup>-3</sup>
HCO <sub>3</sub> <sup>-</sup>	0.0024	0.86 x 10 <sup>-3</sup>

- Ion concentrations are typically 100-1000 times higher in seawater than in freshwater. Bicarbonate is an exception. Why? Due to electroneutrality

## 2.6 Toxic Metals

- Cadmium

Sources: metal plating, rechargeable batteries, smelting (제련), refining, mine drainage, industrial wastewater, corrosion of galvanized pipe in the water distribution system, etc.

Cadmium's chemical similarity to zinc interferes with enzymes proper function.

High blood pressure, kidney damage, lung tumors by inhalation, Probable human



carcinogens.

- Chromium

Sources: trace constituent of ordinary soils, coal burning, stainless steel

Cr(III) is an essential trace nutrient in human; Cr(VI) causes a suite of adverse health effects. However, environmental standards do not distinguish among the oxidation states due to the possibility of conversion of Cr(III) to Cr(VI).

Liver and kidney damage, internal hemorrhage (출혈), respiratory disorders, cancer.

- Lead

Sources: pigments in paint, glazes of dishes, pipe in water distribution systems, gasoline additive

Anemia (빈혈), kidney damage, high blood pressure, central nervous system effects, Probable human carcinogen.

- Mercury

Sources: combustion of coal, manufacture of electrical components, production of chlorine and hydroxide, fungicide, additives to paints, amalgam of silver dental fillings

Central nervous system dysfunction (역기능), paralysis (마비), blindness, birth defects, 미나마타 병.

## 2.7 Radionuclides

- Atomic weapons

- Nuclear power plant (mining, refining, transport, storage, use, and disposal)

- Medical purposes

- The greatest source of population exposure to ionizing radiation is not industrial, military, or medical uses, but rather the radionuclides that are naturally present in the environment, for example,  $^{222}\text{Rn}$ .

- Radon is created constantly in all soil and earth base materials by the radioactive



decay of radium. Most exposure to radon occurs indoors and the dominant source of indoor radon is the soil within a few meters of the building structure. Building materials and groundwater are also potential sources of indoor radon.

- Since radon is chemically inert, it does not pose a significant direct health threat. However, radon decay produces a series of three short-lived radio-isotopes whose inhalation does pose a direct health hazard, increasing the risk of lung cancer. When inhaled, they may deposit onto respiratory tissues and undergo further radioactive decay to  $^{210}\text{Pb}$ .

## 2.8 Toxic Organic Compounds

- Formaldehyde (HCHO)

Sources: A widely used industrial chemical, components in resins for bonding and laminating, preservative in cosmetics, manufacturing lacquers, dyes, and plastics, also can be formed in photochemical smog by degradation of other organics, byproduct of incomplete combustion and wood and tobacco smoke, and auto exhaust.

Irritating to mucous membranes (점막) at low concentrations, nasal cancer in laboratory mice and rats, inconclusive evidence for human cancer.

- Chlorofluorocarbons (CFCs)

A family of chemicals that contain one or two carbon atoms attached to mix of chlorine, fluorine, and hydrogen atoms, e.g.,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CHClF}_2$ , Working fluid in refrigeration units which replace ammonia and sulfur dioxide of which leakage cause hazardous conditions,

Sources: Refrigeration units (refrigerators, air conditions), aerosol propellants, foaming agents

CFCs are very little toxic. CFCs are very stable in the environment and persist long enough in the atmosphere to be transported through the troposphere into the stratosphere. There, intense UV radiation decomposes them and the liberated chlorine atoms act in a catalytic cycle, destroying ozone. Stratospheric ozone absorbing UV radiation from the sun.

- Benzene (C<sub>6</sub>H<sub>6</sub>)

Sources: Octane-boosting component in gasoline, Solvent, by-product of the incomplete combustion of hydrocarbon fuels, tobacco smoke,  
Human carcinogen, leukemia (백혈병), Hodgkin's disease.

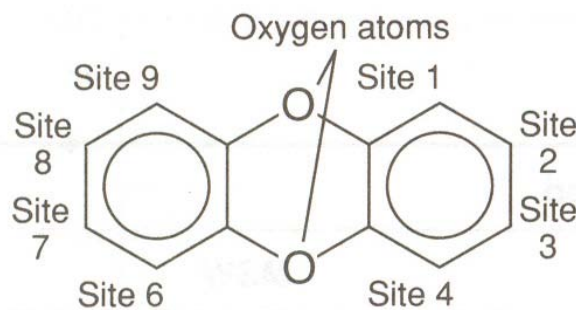
- Chlorinated solvents (Halogenated organics)

Organic molecules that contain one or more halogen atoms (e.g., dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), trichloroethylene (TCE, C<sub>2</sub>HCl<sub>3</sub>), trichloroethane (TCA, C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>), tetrachloroethylene (PCE, perchloroethylene, C<sub>2</sub>Cl<sub>4</sub>)

Sources: industrial applications, dry-cleaning, hazardous waste disposal sites  
Known or suspected human carcinogens

- Dioxins (e.g, 2,3,7,8-TCDD)

A group of compounds that have a double aromatic ring structure coupled by two oxygen atoms (e.g., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin)



Sources: not produced intentionally, by-products in the manufacturing of some pesticides and during the combustions of plastics and chlorinated solvents, bleaching paper pulp with chlorine, relatively persistent in environment.

One of the most highly toxic organic compounds, although the levels at which health effects occur are controversial,

- Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs (polycyclic aromatic hydrocarbons) or PNA (polynuclear aromatic compounds), is the presence of multiple benzene rings fused together.



Sources: do not have significant industrial uses, formed by the incomplete combustion of hydrocarbon fuels (soot from diesel engines, smoke from wood fires, barbeques, or cigarettes), coal tar, wood and other biomass as a cooking fuel (especially for Benzo(a)pyrene ( $C_{20}H_{12}$ )).

Benzo(a)pyrene ( $C_{20}H_{12}$ ) is one of the first chemicals shown to be carcinogenic.

## 2.9 Compounds Causing Odor, Taste, or Color

Impurities	Taste
Metals	Fe, Mn, Cu, and Zn
Chlorine	from drinking water disinfection
Chlorinated organics	from disinfection or groundwater contamination (e.g., THMs)
Total dissolved solids (TDS)	< 1200 mg/L acceptable, < 650 mg/L preferred
	<b>Odor</b>
Hydrogen sulfide ( $H_2S$ )	anaerobic degradation of sulfur compounds
Geosmin	from blue-green algae
Phenolic odor	chlorine reacting with phenols in water
	<b>Color</b>
Fe and Mn	Red or brownish
Humic and Fulvic acids	reddish brown
Tannins	dissolved plant materials, brownish

## 2.10 Other Pollutants

- Endocrine-Disrupting Chemicals (EDCs, 내분비계 장애물질)

TABLE 8-1 Endocrine-Disrupting Chemicals

Group 1 Chlorinated Organics	Group 2 Industrial Chemicals	Group 3 Polymers with Molecular Weights ≤ 1000	Group 4 Substances Controlled under the Toxic Substances Control Act	Group 5 Pesticides
2,4,5-Trichlorophenol (S)	Hydrazine (P)	Fluoropolyol	PAHs (K)	Malathion (S)
PCB (K)	Bisphenol A (P)	Methoxypolysiloxane (P)	Triazines (K)	1,2-Dibromo-3-chloropropane
2,3,7,8-TCDD (K)	Transplatin (S)	Polyethylene oxide (S)	Lead (K)	Pyrethroids (S)
Pentachlorophenol (K)	Benzoflumethiazide	Poly(isobutylene)	Mercury (K)	Dicamba (S)
	Propanthelinebromide (S)	Polyurethane (S)	Endosulfans	Aldicarb (P)
	p-Nitrotoluene		Kepone (S)	Aldicarb nitrofen (S)
	Obidoxime chloride (S)			

P = probable EDC; S = suspected EDC; K = known EDC; PCB = polychlorinated biphenyl; TCDD = tetrachlorodibenzo-p-dioxin; PAH = polycyclic aromatic hydrocarbons.

Source: O. A. Sadik, and D. M. Witt. Monitoring endocrine-disrupting chemicals. Environ. Sci. Technol. 33: 368A-374A, 1999.

- Arsenic: Bangladesh, India, Taiwan, etc.
- Heat: Cooling water can change the ecosystem of the receiving water body (e.g., increased production of clams and oysters, decreased salmon and trouts, decreased DO, etc.)

### 3. Water Quality Management in Rivers

This is not to say that “the oxygen-demanding wastes and nutrients” are always the most significant pollutants in rivers; rather, no other pollutant category has as much overall effect on rivers.

#### 3.1 Effect of Oxygen-Demanding Wastes on Rivers

- The introduction of oxygen-demanding material into a river causes depletion of the dissolved oxygen (DO) in the water;
- This poses a threat to fish and other forms of aquatic life;
- However, since oxygen is continuously being replenished from the atmosphere, we have to know the competing processes.

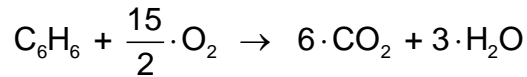
#### 3.2 BOD (Biochemical Oxygen Demand, 생화학적산소요구량)





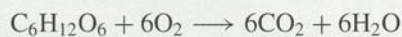
ThOD (Theoretical Oxygen Demand) = The amount of oxygen required to oxidize a organic substance to CO<sub>2</sub> and H<sub>2</sub>O

e.g., 1 mg/L of benzene (C<sub>6</sub>H<sub>6</sub>, M.W. 78g/mol) needs 7.5mol \* 32g-O<sub>2</sub>/mol \* 1/78g-benzene \* 1mg-benzene/L = 3.08 mg/L of ThOD.



**EXAMPLE 8-1** Compute the ThOD of 108.75 mg · L<sup>-1</sup> of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>).

**Solution** We begin by writing a balanced equation for the reaction.



Next, compute the gram molecular weights of the reactants using the table on the inside front cover of the book.

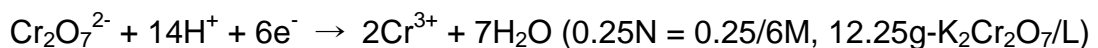
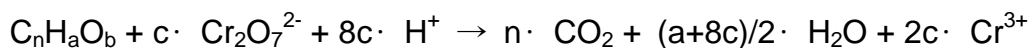
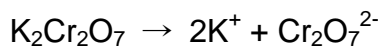
Glucose	Oxygen
6C = 72	(6)(2)O = 192 g · mol <sup>-1</sup>
12H = 12	
6O = 96	
180 g · mol <sup>-1</sup>	

Thus, it takes 192 g of oxygen to oxidize 180 g of glucose to CO<sub>2</sub> and H<sub>2</sub>O.

The ThOD of 108.75 mg · L<sup>-1</sup> of glucose is

$$(108.75 \text{ mg} \cdot \text{L}^{-1} \text{ of glucose}) \left( \frac{192 \text{ g} \cdot \text{mol}^{-1} \text{ O}_2}{180 \text{ g} \cdot \text{mol}^{-1} \text{ glucose}} \right) = 116 \text{ mg} \cdot \text{L}^{-1} \text{ O}_2$$

COD (Chemical Oxygen Demand) = using a strong chemical oxidizing agent using 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (chromic acid, MW = 294) solution (1mL = 2mg of O<sub>2</sub>) as a chemical oxidant



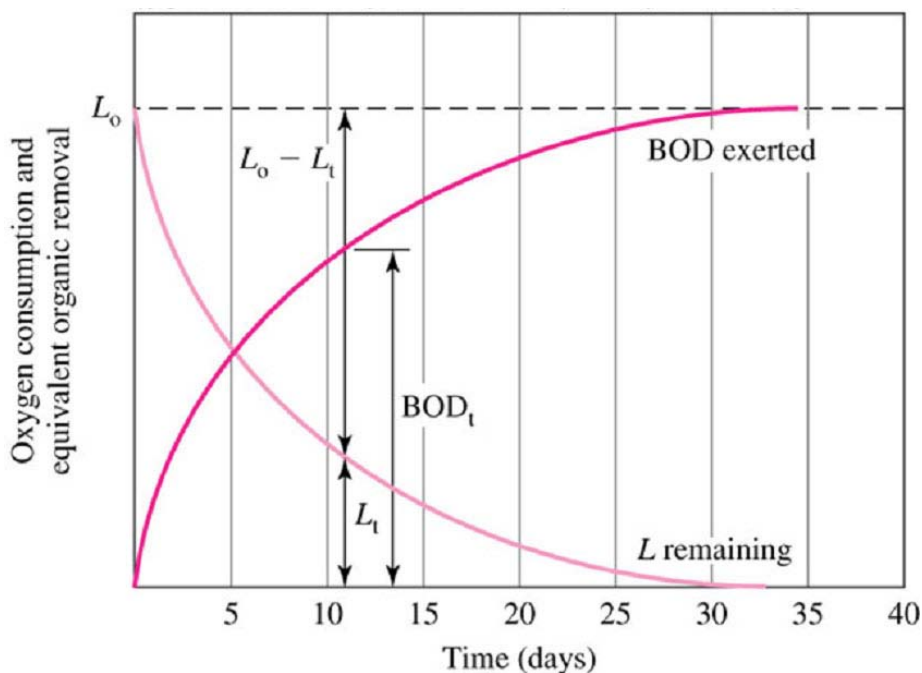
Since 8g-O<sub>2</sub>/water-L = 1N O<sub>2</sub> and the oxidation power of 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution is equal to that of 0.25N of O<sub>2</sub> in water, 1mL of 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution is equivalent to 2mg of O<sub>2</sub> in water



BOD (Biochemical Oxygen Demand) = based on the biochemical reaction by microorganisms

BOD < ThOD, COD because (1) not all of carbon can be degraded by microorganisms (e.g., non-biodegradable organic compounds); and (2) some of carbon converted to new bacterial cells

Typical oxygen consumption in a closed container



$$\frac{dL_t}{dt} = -k \cdot L_t \quad (1^{\text{st}}\text{-order reaction})$$

$$L_t = L_0 \cdot e^{-k \cdot t}$$

where  $L_t$  = oxygen equivalent of the organic remaining at time,  $t$ , mg/L;

$L_0$  = oxygen equivalent of the organic at time,  $t=0$ ; and

$k$  = reaction rate constant (or BOD rate constant, 0.35-0.70 for raw wastewater, 0.12-0.23 for polluted river water), 1/day.

$$BOD_t = L_0 - L_t = L_0 \cdot (1 - e^{-k \cdot t}) = L_0 \cdot (1 - 10^{-K \cdot t})$$



where  $BOD_t$  = ultimate BOD; and

$K$  = reaction rate constant in base 10,  $k = 2.303(K)$ .

$BOD_t$  = direct proportion to the concentration of degradable organic matter;

$k$  (or  $K$ ) = (1) nature of the waste

Sample	$k(20^\circ\text{C})$ ( $\text{day}^{-1}$ )
Raw sewage	0.35–0.70
Well-treated sewage	0.12–0.23
Polluted river water	0.12–0.23

(2) the ability of the microorganisms (microorganisms have to be acclimated to the waste before incubation, especially for the industrial wastes); and

(3) the temperature

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

where  $T$  = temperature of interest,  $^\circ\text{C}$ ;

$k_T$  = BOD rate constant at the temperature of interest, 1/day;

$k_{20}$  = BOD rate constant determined at  $20^\circ\text{C}$ , 1/day; and

$\theta$  = temperature coefficient (1.135 between  $4$ - $20^\circ\text{C}$ , 1.056 between  $20$ - $30^\circ\text{C}$ ).

### 3.4 Laboratory Measurement of BOD

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

where  $DO_{b,t}$  = DO in blank after  $t$  days of incubation, mg/L;

$DO_{s,t}$  = DO in sample after  $t$  days of incubation, mg/L; and

$P$  = dilution factor

Seeding(식중)한 경우?

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



where  $DO_{s,i}$  = initial DO of the sample, mg/L;

$DO_{b,i}$  = initial DO of the blank (seed) control, mg/L; and

$f$  = (% seed in diluted sample) / (% seed in seed control)

If,  $f = 1$  and  $DO_{s,i} = DO_{b,i}$

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

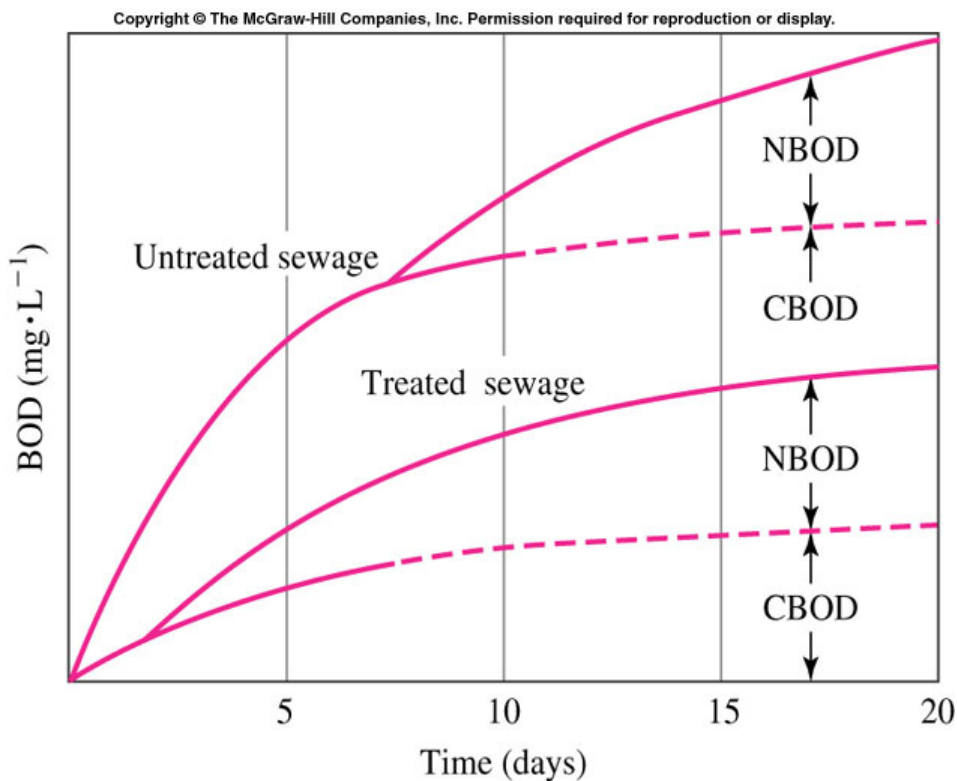
(Homework) Example 8-4, and 5, p.279

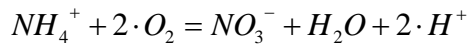
### Additional Notes on BOD

- $BOD_5$  has been chosen as the standard value because there was no river in England of which travel time to the sea is greater than 5 days.
- However,  $BOD_t$  is actually a better indicator of total waste strength.

### 3.5 Nitrogen Oxidation

- Carbonaceous BOD (CBOD) vs. Nitrogenous BOD (NBOD)





$$\frac{4 \times 16}{14} = 4.57 \text{ g } O_2 / \text{g } N$$

- The actual NBOD is a little less than the theoretical value because of new cells of microorganisms; however, the difference is negligible.

- EXAMPLE 8-6** (a) Compute the theoretical NBOD of a wastewater containing  $30 \text{ mg} \cdot \text{L}^{-1}$  of ammonia as nitrogen.  
 (b) If the wastewater analysis was reported as  $30 \text{ mg} \cdot \text{L}^{-1}$  of ammonia ( $\text{NH}_3$ ), what would the theoretical NBOD be?

**Solution** In the first part of the problem, the amount of ammonia was reported as  $\text{NH}_3\text{-N}$ . Therefore, we can use the theoretical relationship developed from Equation 8-11.

$$\text{Theoretical NBOD} = (30 \text{ mg } \text{NH}_3\text{-N} \cdot \text{L}^{-1})(4.57 \text{ mg } O_2 \cdot \text{mg}^{-1} \text{ N}) = 137 \text{ mg } O_2 \cdot \text{L}^{-1}$$

To answer part (b), we must convert milligrams per liter of ammonia to milligrams per liter as  $\text{NH}_3\text{-N}$  by multiplying by the ratio of gram molecular weights of N to  $\text{NH}_3$ .

$$(30 \text{ mg } \text{NH}_3 \cdot \text{L}^{-1}) \left( \frac{14 \text{ g } \text{N} \cdot \text{mol}^{-1}}{17 \text{ g } \text{NH}_3 \cdot \text{mol}^{-1}} \right) = 24.7 \text{ mg } \text{N} \cdot \text{L}^{-1}$$

Now we may use the relationship developed from Equation 8-11.

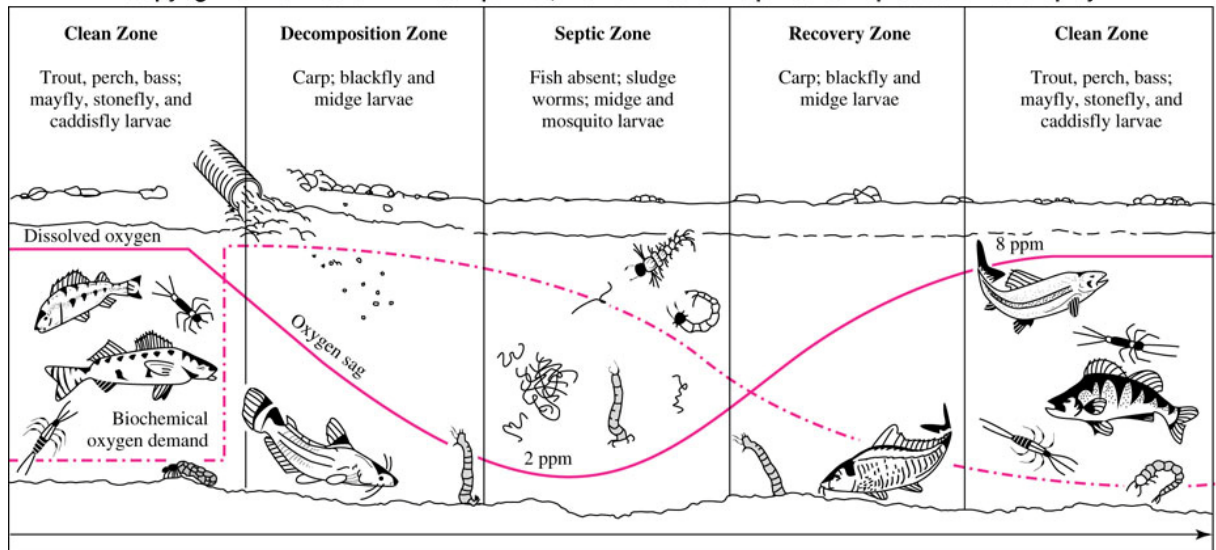
$$\text{Theoretical NBOD} = (24.7 \text{ mg } \text{N} \cdot \text{L}^{-1}) \left( \frac{4.57 \text{ mg } O_2}{\text{mg } \text{N}} \right) = 113 \text{ mg } O_2 \cdot \text{L}^{-1}$$

### 3.6 DO Sag Curve

- DO is an indicator of the general health of the river.
- "self-purification"
- DO level and aquatic animals

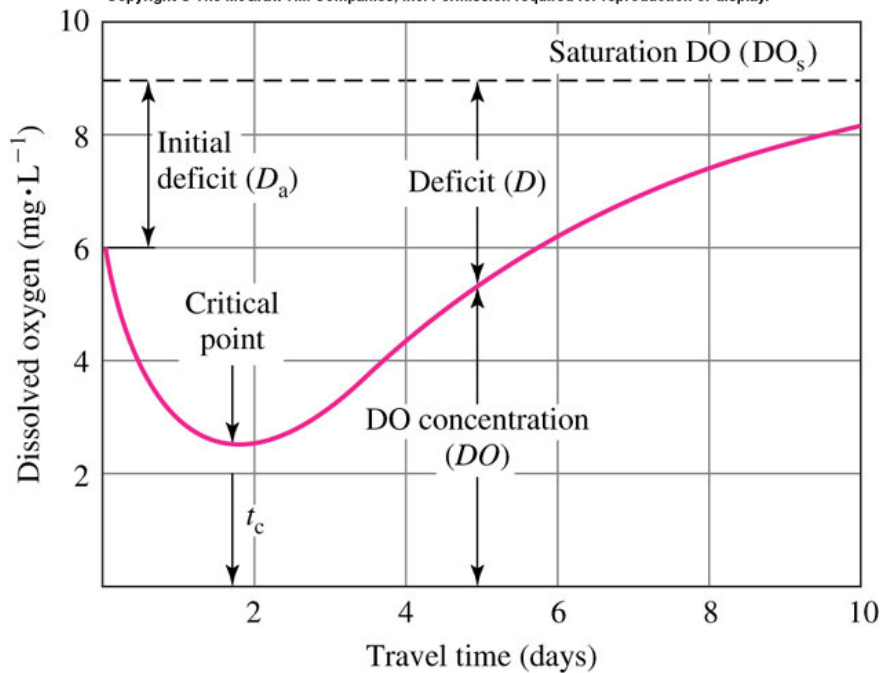


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- Typical DO sag curve

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Oxygen sources : atmosphere, photosynthesis of aquatic plants

DO depletions : initial BOD, carbonaceous and nitrogenous BOD of the waste discharged, non-point source pollution, respiration of living organisms in water and sediments, etc.





Mass Balance approach

$$DO = \frac{Q_w \cdot DO_w + Q_r \cdot DO_r}{Q_w + Q_r}$$

where DO = DO concentration in the river after mixing, g/m<sup>3</sup>;

Q<sub>w</sub> = volumetric flow rate of wastewater, m<sup>3</sup>/sec;

Q<sub>r</sub> = volumetric flow rate of wastewater, m<sup>3</sup>/sec;

DO<sub>w</sub> = DO concentration in the wastewater, g/m<sup>3</sup>; and

DO<sub>r</sub> = DO concentration in the river, g/m<sup>3</sup>.

$$L_a = \frac{Q_w \cdot L_w + Q_r \cdot L_r}{Q_w + Q_r}$$

where L<sub>a</sub> = ultimate BOD after mixing;

L<sub>w</sub> = ultimate BOD of the wastewater, mg/L; and

L<sub>r</sub> = ultimate BOD of the river, mg/L.

$$T_f = \frac{Q_w \cdot T_w + Q_r \cdot T_r}{Q_w + Q_r}$$

where T<sub>f</sub> = temperature after mixing;

T<sub>w</sub> = temperature of the wastewater; and

T<sub>r</sub> = temperature of the river.



**EXAMPLE 8-7** The town of Viracocha discharges  $17,360 \text{ m}^3 \cdot \text{day}^{-1}$  of treated wastewater into the Pachacamac Creek. The treated wastewater has a  $\text{BOD}_5$  of  $12 \text{ mg} \cdot \text{L}^{-1}$  and a BOD decay constant,  $k$ , of  $0.12 \text{ day}^{-1}$  at  $20^\circ\text{C}$ . Pachacamac Creek has a flow rate of  $0.43 \text{ m}^3 \cdot \text{s}^{-1}$  and an ultimate BOD,  $L_0$ , of  $5.0 \text{ mg} \cdot \text{L}^{-1}$ . The DO of the river is  $6.5 \text{ mg} \cdot \text{L}^{-1}$  and the DO of the wastewater is  $1.0 \text{ mg} \cdot \text{L}^{-1}$ . Compute the DO and initial ultimate BOD,  $L_0$ , after mixing.

**Solution** The DO after mixing is given by Equation 8-17. To use this equation we must convert the wastewater flow to compatible units, that is, to cubic meters per second.

$$Q_w = \frac{(17,360 \text{ m}^3 \cdot \text{day}^{-1})}{(86,400 \text{ s} \cdot \text{day}^{-1})} = 0.20 \text{ m}^3 \cdot \text{s}^{-1}$$

The DO after mixing is then

$$\text{DO} = \frac{(0.20 \text{ m}^3 \cdot \text{s}^{-1})(1.0 \text{ mg} \cdot \text{L}^{-1}) + (0.43 \text{ m}^3 \cdot \text{s}^{-1})(6.5 \text{ mg} \cdot \text{L}^{-1})}{0.20 \text{ m}^3 \cdot \text{s}^{-1} + 0.43 \text{ m}^3 \cdot \text{s}^{-1}} = 4.75 \text{ mg} \cdot \text{L}^{-1}$$

Before we can determine the initial ultimate BOD after mixing, we must first determine the ultimate BOD of the wastewater. Solving Equation 8-6 for the ultimate BOD,  $L_0$ :

$$L_0 = \frac{\text{BOD}_5}{(1 - e^{-kt})} = \frac{12 \text{ mg} \cdot \text{L}^{-1}}{(1 - e^{-(0.12 \text{ day}^{-1})(5 \text{ days})})} = \frac{12 \text{ mg} \cdot \text{L}^{-1}}{(1 - 0.55)} = 26.6 \text{ mg} \cdot \text{L}^{-1}$$

Note that we used the subscript of 5 days in  $\text{BOD}_5$  to determine the value of  $t$  in the equation. Now setting  $L_w = L_0$ , we can determine the initial ultimate BOD after mixing,  $L_a$ , using Equation 8-18.

$$L_a = \frac{(0.20 \text{ m}^3 \cdot \text{s}^{-1})(26.6 \text{ mg} \cdot \text{L}^{-1}) + (0.43 \text{ m}^3 \cdot \text{s}^{-1})(5.0 \text{ mg} \cdot \text{L}^{-1})}{0.20 \text{ m}^3 \cdot \text{s}^{-1} + 0.43 \text{ m}^3 \cdot \text{s}^{-1}} = 11.86, \text{ or } 12 \text{ mg} \cdot \text{L}^{-1}$$

### Oxygen Deficit

$$D = \text{DO}_s - \text{DO}$$

where  $D$  = oxygen deficit, mg/L;

$\text{DO}_s$  = saturation concentration of DO, mg/L (see Table A.2, p.682, example,  $14.62 \text{ mg/L}$  at  $0^\circ\text{C}$  and  $9.17 \text{ mg/L}$  at  $20^\circ\text{C}$ , and  $7.63 \text{ mg/L}$  at  $30^\circ\text{C}$ ); and

$\text{DO}$  = actual concentration of DO, mg/L.

### Initial Deficit

- In order to complete the DO sag curve, the initial deficit ( $D_a$ ) should be estimated.





$$D_a = DO_s - DO = DO_s - \frac{Q_w \cdot DO_w + Q_r \cdot DO_r}{Q_w + Q_r}$$

- Since wastewater commonly has a higher temperature than river water, it is important to identify the temperature after mixing for determining  $DO_s$ .

### DO Sag Equation

For the constituent of oxygen,

$$\frac{\partial C}{\partial t} = D_x \cdot \frac{\partial^2 C}{\partial x^2} - v_x \cdot \frac{\partial C}{\partial x} + \sum(\text{reactions})$$

If the dispersion is ignored (i.e., Streeter-Phelps model) under steady-state conditions ( $dC/dt = 0$ ), the equation is reduced to an ordinary differential equation.

$$v_x \cdot \frac{dC}{dx} = v_x \frac{d(DO)}{dx} = \sum(\text{reactions})$$

- Assumptions for Streeter-Phelps model
  - (1) The river is completely and uniformly mixed
  - (2) No dispersion (as shown in F. 8-11, p. 286) – It is not true!!!
  - (3) Two reactions: reaeration and deoxygenation

$$\text{Rate of reaeration} = k_r \cdot (DO_s - DO) = k_r \cdot D$$

where  $k_r$  = reaeration coefficient [1/T].

Reaeration rate is very much dependent on (1) the physical characteristics of the river, and (2) temperature.

$$k_r = \frac{3.9 \cdot u^{0.5}}{h^{1.5}}$$

where  $k_r$  = reaeration coefficient at 20°C, 1/day.

$$k_r = k_{r,20} \cdot \theta^{(T-20)}$$

Correction for different temperature is required ( $\theta=1.024$ ).



**EXAMPLE 8-9** A stream containing no biochemical oxygen demand (this is a hypothetical situation and rarely occurs) has a DO of  $5.00 \text{ mg} \cdot \text{L}^{-1}$  and a flow rate,  $Q$ , of  $8.70 \text{ m}^3 \cdot \text{s}^{-1}$ . The temperature of the stream is  $18^\circ\text{C}$ . The average velocity in the stream is  $0.174 \text{ m} \cdot \text{s}^{-1}$ . The average depth,  $H$ , of the stream is 5 m. Determine the reaeration coefficient,  $k_r$ , and the rate of reaeration.

**Solution** To solve this problem we must first determine the reaeration coefficient at  $20^\circ\text{C}$ , using Equation 8-26.

$$k_r = \frac{3.9u^{1/2}}{h^{3/2}} = \frac{3.9(0.174 \text{ m} \cdot \text{s}^{-1})^{1/2}}{(5.00 \text{ m})^{1.5}}$$

$$= \frac{3.9(0.417)}{11.18} = 0.146 \text{ day}^{-1}$$

We must also take into account the fact that the stream is not at  $20^\circ\text{C}$  but at  $18^\circ\text{C}$ . Thus we must use the equation

$$k_r = k_{r,20}\theta^{(T-20)} = (0.146)(1.024)^{(18-20)} = 0.139 \text{ day}^{-1}$$

The oxygen deficit is calculated by taking the difference between the saturation value ( $9.54 \text{ mg} \cdot \text{L}^{-1}$ —from Appendix A-2) and the dissolved oxygen concentration:

$$D = 9.54 - 5.0 = 4.54 \text{ mg} \cdot \text{L}^{-1}$$

Thus, according to Equation 8-25, the rate of reaeration equals

$$(0.139 \text{ day}^{-1})(4.54 \text{ mg} \cdot \text{L}^{-1}) = 0.632 \text{ mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$$

Most models,  $k_d = k$

$$\text{Rate of deoxygenation} = k_d \cdot L_t = k_d \cdot L_0 \cdot \exp(-k \cdot t) = k_d \cdot L_0 \cdot \exp(-k_d \cdot t)$$

where  $L_t$  = oxygen equivalent of the organic remaining at given time  $t$  [ $\text{M}/\text{L}^3$ ];

$L_0$  = oxygen equivalent of the organic at time,  $t = 0$  [ $\text{M}/\text{L}^3$ ] (initial measured BOD);

$k_d$  = deoxygenation rate [ $1/\text{T}$ ]; and;

$k$  = BOD rate constant [ $1/\text{T}$ ].

For deep and slow-moving river,  $k_d = k$

For turbulent, shallow, and rapidly-moving stream,

Bosko's method

$$k_d = k \cdot \eta \frac{u}{h}$$

where  $k_d$  = deoxygenation rate constant at  $20^\circ\text{C}$ , 1/day;

$k$  = BOD rate constant at  $20^\circ\text{C}$ , 1/day;



$u$  = average speed of stream flow, m/sec;

$h$  = average depth of stream, m; and

$\eta$  = bed-activity coefficient (0.1 for stagnant deep water - 0.6 for rapidly flowing water).

Correction for different temperature is required (not using the method for  $k_r$ )

**EXAMPLE 8-10** Determine the deoxygenation rate constant for the reach of Pachacamac Creek (Examples 8-7 and 8-8) below the wastewater outfall (discharge pipe). The average speed,  $u$ , of the stream flow in the creek is  $0.03 \text{ m} \cdot \text{s}^{-1}$ . The depth,  $h$ , is 5.0 m and the bed-activity coefficient,  $\eta$ , is 0.35. What is the rate of deoxygenation, in units of  $\text{mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$ ?

**Solution** From Example 8-7, the value of the BOD decay constant,  $k$ , is  $0.12 \text{ day}^{-1}$ . Using Equation 8-26, the deoxygenation rate constant,  $k_d$ , at  $20^\circ\text{C}$  is

$$k_d = 0.12 \text{ day}^{-1} + \frac{0.03 \text{ m} \cdot \text{s}^{-1}}{5.0 \text{ m}}(0.35) = 0.1221, \text{ or } 0.12 \text{ day}^{-1}$$

Note that the units are not consistent. As we have noted before, empirical expressions, such as that in Equations 8-26 and 8-30, may have implicit conversion factors. Thus, you must be careful to use the same units as those used by the author of the equation.

We also note that the deoxygenation rate constant of  $0.1221 \text{ day}^{-1}$  is at  $20^\circ\text{C}$ . In Example 8-8, we noted that the stream temperature was  $10^\circ\text{C}$ . Thus, we must correct the estimated  $k_d$  value using Equation 8-7.

$$\begin{aligned} k_d \text{ at } 10^\circ\text{C} &= (0.1221 \text{ day}^{-1})(1.135)^{10-20} = (0.1221)(0.2819) \\ &= 0.03442, \text{ or } 0.034 \text{ day}^{-1} \end{aligned}$$

From Example 8-7, we know that the ultimate BOD immediately after mixing,  $L_t$ , is  $12 \text{ mg} \cdot \text{L}^{-1}$ . Then using Equation 8-28, we obtain

$$\begin{aligned} \text{Rate of deoxygenation} &= k_d L_t \\ &= 0.034 \text{ day}^{-1} \times 12 \text{ mg} \cdot \text{L}^{-1} \\ &= 0.408 \text{ mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1} \end{aligned}$$

$$v_x \cdot \frac{d(\text{DO})}{dx} = k_r \cdot D - k_d \cdot L$$

Using the oxygen deficit,  $D$  ( $= \text{DO}_s - \text{DO}$ )

$$v_x \cdot \frac{dD}{dx} = k_d \cdot L - k_r \cdot D$$

Since Time =  $x/v_x$

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



Then,

I.C. at  $t = 0$ ,  $D = D_a$  and  $L = L_a$

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

also, we can get the critical point ( $t_c$ ), the lowest point on the DO sag curve, by differentiating the previous eq.

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

### Nitrogenous BOD

The DO sag curve incorporated with nitrogenous BOD is as follows;

$$D = \frac{k_d \cdot L_a}{k_r - k_d} \cdot (e^{-k_d \cdot t} - e^{-k_r \cdot t}) + D_a \cdot e^{-k_r \cdot t} + \frac{k_n \cdot L_n}{k_r - k_n} \cdot (e^{-k_n \cdot t} - e^{-k_r \cdot t})$$

where  $k_n$  = nitrogenous deoxygenation coefficient, 1/day; and

$L_n$  = ultimate nitrogenous BOD after mixing, mg/L.

Can we get the critical point ( $t_c$ ), the lowest point on the DO sag curve, by differentiating the previous eq.? (No. then, only by a trial and error solution)

### Other Factors

Oxygen sources : photosynthesis of aquatic plants

DO depletions : non-point source pollution, respiration of living organisms in water and sediments, etc.

### Management Strategy

- DO standard is set to protect the most sensitive species in the particular river.
- $L_a$  and  $D_a$  control methods (Increasing the efficiency of existing treatment process, Adding additional treatment steps, Adding oxygen to the discharged wastewater, etc.)
- The worst condition is when river flows slow and temperature is high.



### 3.7 Effect of Nutrients on Water Quality in Rivers

#### Nitrogen

- In high concentration,  $\text{NH}_3\text{-N}$  is toxic to fish;
- $\text{NH}_3$  (and  $\text{NO}_3^-$ ) serve as nutrients for algae; and
- Conversion of  $\text{NH}_3$  to  $\text{NO}_3^-$  consumes large quantities of DO.

#### Phosphorus

- a vital nutrient for the growth of algae; and
- cycle in the water body (especially in the lake).

#### Management Strategy

- Strategy associated with excessive nutrients is based on source control.
- $\text{CO}_2$  for plants cannot be controlled.
- Natural weathering of rock minerals has been little controlled (acid rain accelerates the weathering!)
- Nitrogen and phosphorus removal in wastewater before discharge is the most practical control.

## 4. Water Quality Management in Lakes

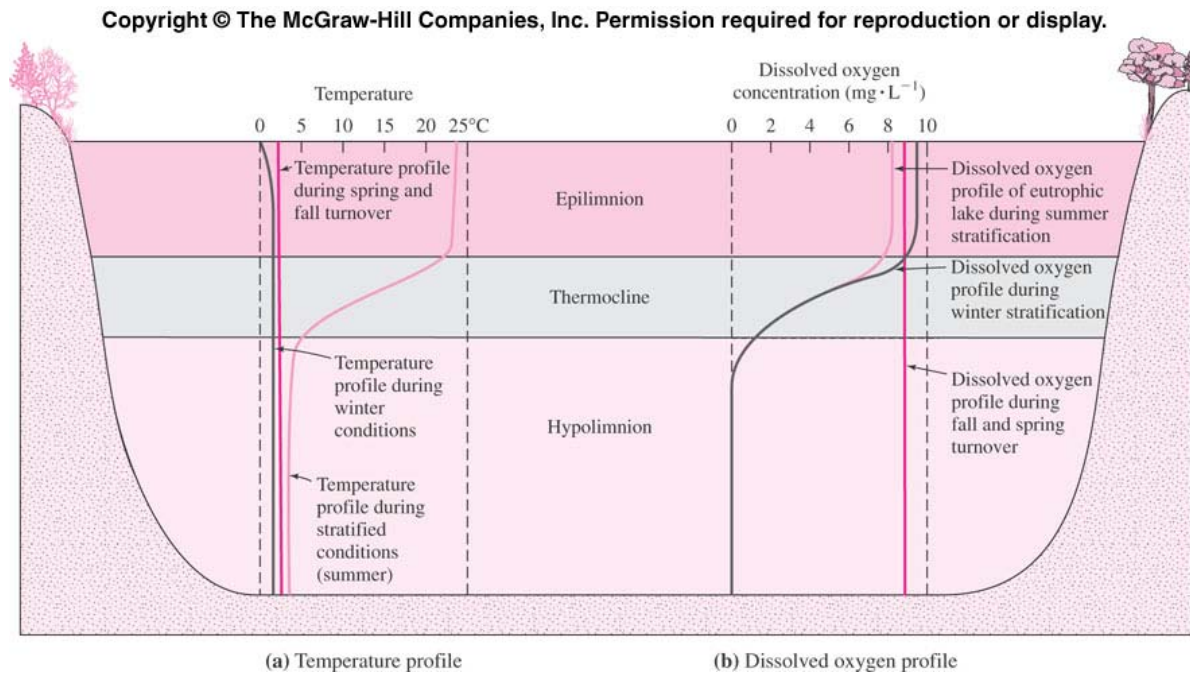
- Pathogens in the bathing beach;
- Toxic chemicals from industrial discharges;
- Phosphorus is the dominant pollutants in the lake system.
- “Limnology”

### 4.1 Stratification(성층현상) and Turnover

- Epilimnion (표수층) : an upper layer of well-mixed, warm water
- Hypolimnion (심수층): a poorly mixed and cool water



- Thermocline (수온약층) : the boundary with sharp temperature change



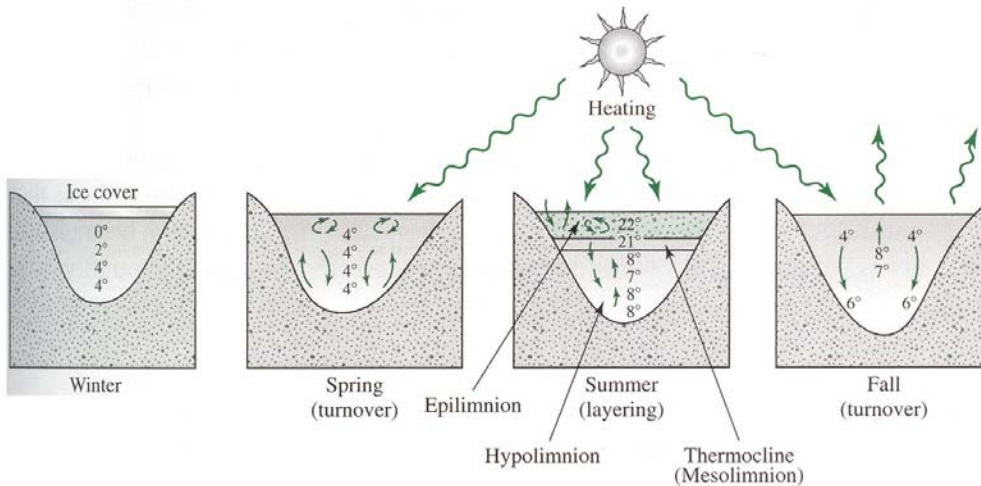
- The depth of the epilimnion is related to the size of the lake (e.g., 1 meter to 20 meters).
- Once formed, lake stratification is very stable. As the summer progresses, the stability increases because the temperature difference between epilimnion and hypolimnion increases (the epilimnion continues to warm, while the hypolimnion remains at a constant temperature).

## Turnover



**FIGURE 4-19**

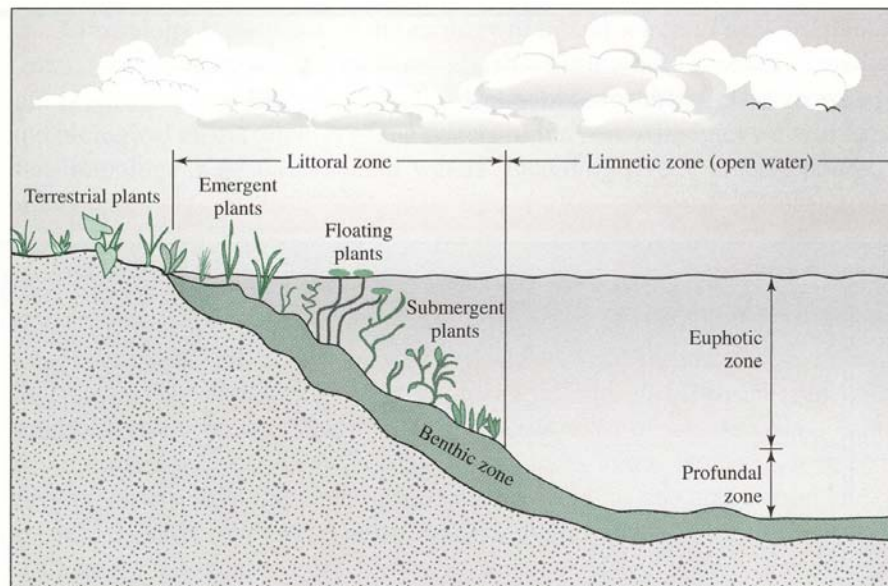
Overturn in stratified lakes. (Source: *The Great Lakes: An Environmental Atlas and Resource Book Geology*, 3rd ed. Jointly produced by Government of Canada, Toronto, Ont., and the U.S. Environmental National Program Office, Chicago, 1995. Also available at <http://www.epa.gov/glnpo/atlas/glat-ch2.html#1>)



## 4.2 Biological Zones

**FIGURE 4-20**

Biological zones in a temperate lake (Source: *From Water on the Web* <http://wow.nrri.umn.edu/wow/under/primer/page10.html>)



- Euphotic zone : sunlight can penetrate. Turbidity, color, suspended solids.
- Light compensation level : 1% of unattenuated sunlight
- Profundal zone :
- Littoral zone : near the shore in which rooted water plants can grow, cannot



extend deeper than the euphotic zone.

- Benthic zone : Sediments (worms, insects, or bacteria depending on DO)
- Biological zone vs. Stratification : Only rarely, bottom of the euphotic zone coincides with the thermocline.

### 4.3 Lake Productivity

- Oligotrophic lakes(빈영양호):  
at low level of productivity  
Euphotic zone can extend into the hypolimnion, which is aerobic.  
Cold-water game fish.
- Mesotrophic lakes:
- Eutrophic lakes(부영양호):  
At high level of productivity  
Euphotic zone may not penetrate into the epilimnion.  
Warm-water game fish
- Senescent lakes

### 4.4 Eutrophication (부영양화)

- Evolution of lakes : oligotrophic, mesotrophic, eutrophic, senescent, marshes, and eventually filling.
- The time for this process depends on (1) the original size of the lake and (2) the rate at which sediments and nutrients are introduced.

### 4.5 Algal Growth Requirements

#### Carbon

- inexhaustible source, the atmosphere

#### Nitrogen

- Nitrification vs. Denitrification
- The blue-green algae which can fix nitrogen from the atmosphere, (1) has a





competitive advantage over green algae, (2) causes odor and taste problems, and (3) produces toxins to kill fish.

### Phosphorus

- Phosphorus is taken up by the algae in the inorganic form ( $\text{PO}_4^{3-}$ ) and incorporated into organic compounds.
- inorganic form returned from decomposition of algae, undecomposed organic matter, precipitates of iron, aluminum, and calcium, bound to clay particles

### Trace elements

- Lack of any one nutrient will limit the total algal population. (Liebig's law of the minimum).

## **4.6 The Limiting Nutrients**

- Phosphorus is deemed the "limiting nutrient".
- Chlorophyll a, is found in all algae, so is used to distinguish the amount of algae in the water from other organic solids such as bacteria.

## **4.7 Algae Control of Phosphorus in Lakes**

### Precipitation with chemicals and Dredging (준설)

#### Municipal and Industrial Wastewaters

- Advanced wastewater treatment process (N, P)
- Banning phosphate detergents

#### Septic Tank Seepage from Remoted Houses

- Increase the adsorption capacity of the soil;
- A sewer to collect the wastewater and transport it to a treatment facility.

#### Agricultural Runoff

- flushed or with soil particles



- To fertilize more often with smaller amounts;
- To stop soil erosion

#### 4.8 Acidification of Lakes

- Due to the air pollution (NO<sub>x</sub>, SO<sub>x</sub>, etc.)
- To the extent that the carbonate buffer capacity of the lake does not exceed, the pH of the lake will not be changed.
- Effects: (1) failure to reproduce, (2) gill damage resulting in respiratory problems, (3) failure of eggs to hatch, (4) interference with Ca uptake (with molluscs)

### 5. Water Quality Management in Estuaries

- Estuaries are complex and specialized ecosystems. Abundant life-giving nutrients, cradle of many birds and fishes resulting in diverse species
- Much of the sediments and pollutants are filtered, buffer the forces of the ocean, absorbing floodwaters.
- “red and brown tides” resulting in low DO
- Pathogens
- Toxic chemicals
- Nonnative or exotic species (e.g., in the ballast water, on the hulls of ships, etc.)

### 6. Water Quality Management in Oceans

런던협약- 폐기물 및 기타 물질의 투기에 의한 해양오염 방지에 관한 협약 London Convention (Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972)

해양투기란 선박, 항공기 등을 이용하여 폐기물을 다량으로 해양에 버리는 것을 말한다. The vessel used for marine disposal-- uses ships and aircraft devices to dump large amounts of waste into the ocean

해양에 투기되어 온 물질로는 (1) 강 하구 또는 호수의 바닥에서 나온 준설토, (2) 산업폐



기물, (3) 하수도의 오물 또는 슬러지, (4) 핵폐기물 또는 방사능 폐기물 등이 있다. Substances that have been dumped in the ocean are: dredges from the bottom of estuaries and lakes, (2) industrial wastes, (3) sewage rubbish or sludge, (4) contain nuclear or radioactive wastes, etc.

런던협약에 명시된 규제 대상물질에는 사실상 모든 폐기물이 포함되어 있다. 단, 전면 금지하는 경우와 사전에 특별 허가증을 요하는 경우, 일반 허가증을 요하는 경우로 나눈다. The regulations stated at the London Convention virtually contain all waste materials. However, in the case that everything is prohibited and there is a special circumstance that requires a license, there are several ways to handle the situation

1. 전면 금지물 (Black list): 유기 할로젠, 수은, 카드뮴, 지속성 플라스틱류, 원유, 석유 생산물 및 고준위 방사성 물질 등 Prohibited substances (Black list): Organic halogen, mercury, cadmium, persistent plastics, crude oil, petroleum products, high level radioactive substances, etc.
2. 특별허가증을 요하는 물질 (Gray list): 납, 구리, 아연, 유기 실리콘, 시안, 불소, 살충제, 니켈 및 중저준위 방사능 물질 Substances that require special permission (Gray list): Lead, copper, zinc, organic silicon, cyanide, fluoride, pesticides, nickel, low and middle level radioactive materials
3. 일반 허가 물질 (White list): 1 과 2 이외의 모든 폐기물 Allowed general substances (White list): Waste not included in the previous 2 lists

우리나라는 1993년 9월에 이 협약에 가입하였고, 그 결과 2005년부터 하수슬러지의 해양폐기가 전면 중지되었다. 하지만, 음폐수를 포함한 유기성 폐수의 해양 투기는 계속되었으며, 2012년 전면 중단 예정이다. Korea registered for this convention in September of 1993. Since 2005, marine disposal of sewage sludge has been stopped/suspended on the front. However, still some organic wastewater are being dumped in the ocean and it will be completely stopped in 2012.

## 7. Groundwater Quality

- Retardation:
- Retardation factor

$$R = \frac{v_{\text{water}}}{v_{\text{cont}}}$$

where  $R$  = retardation factor

$v_{\text{water}}$  = the linear velocity of the groundwater

$v_{\text{cont}}$  = the linear velocity of the contaminant

$$R = 1 + \frac{\rho_b \cdot K_p}{n_t} = 1 + \frac{(1-n_t) \cdot \rho_s \cdot K_p}{n_t}$$

where  $\rho_b$  = bulk density of the soil

$\rho_s$  = bulk density of the soil solid

$K_p$  = partition coefficient of the contaminant between soil and groundwater

$n_t$  = total porosity of the soil

for hydrophobic contaminants,

$$K_p = f_{\text{oc}} \cdot K_{\text{oc}}$$

where  $f_{\text{oc}}$  = fraction of organic carbon in the soil

$K_{\text{oc}}$  = partition coefficient of the contaminant between soil organic carbon and groundwater

