

## Chapter 3

# WATER POLLUTION AND WATER QUALITY MANAGEMENT



King Talal Dam- Jordan

# POLLUTION OF NATURAL WATERS

1. Natural waters:
  - Surface water (lake, river)
  - Groundwater (wells and aquifers)
  - Sea /coast
2. Water pollution sources (point and non-point) and their impacts
3. Parameters to characterize polluted water or wastewater
4. Control of water pollution:
  - Point source prevention by wastewater treatment before discharge
  - Non-point minimization by several management options

# Testing Water for Pollutants

1. Parameters of “water pollution” are also parameters of “wastewater composition”.
2. These parameters are used to quantify and control natural water pollution as well as to characterize wastewater for treatment and other management options (Next).

## Common Parameters with Fresh Water

1. Physical parameters
2. Biological parameters
3. Chemical parameters of: pH, TDS and Radionucleotides.  
(*See also Drinking water quality parameters*).

# Parameters to characterize polluted water

- **Physical Parameters:**

1. Total Suspended Solids: TSS
2. Fat, oil & greases: FOG
3. Turbidity: NTU
4. Color and Odor
5. Temperature

- **Biological Parameters**

1. MPN of microorganisms (virus, bacteria, protozoa,...) /10mL
2. Number of eggs/L (parasites)

- **Chemical Parameters**

1. Dissolved Oxygen: DO
2. Dissolved Organics: BOD, COD
3. Nutrients: TKN, total P
4. Toxic Metals (Pb, Ni, Cr, Hg, ....)
5. Priority Organics: VOCs, PCBs, phenols, etc.
6. pH (acidity, alkalinity)
7. Total Dissolved Solids: TDS
8. Radionucleotides

# Dissolved Oxygen-Demanding Materials

- **Biodegradable Organic Content**

**BOD<sub>5</sub>** is the amount of dissolved oxygen consumed by microorganisms during the biochemical oxidation of organic and inorganic matter to carbon dioxide in 5-day standard test at 20°C.

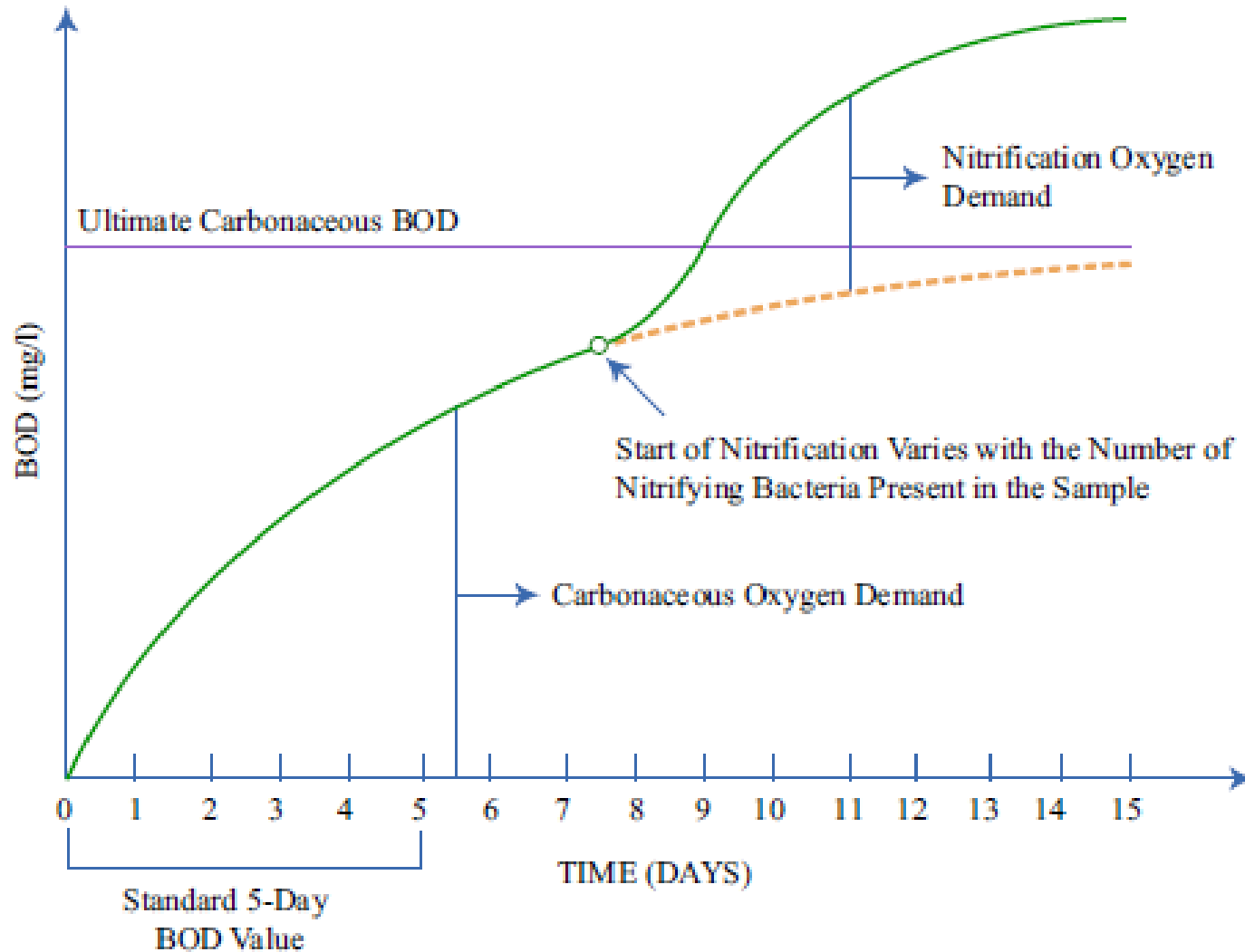
- **Total Oxidizable (Organics & Some Inorganics)**

**COD** is the amount of dissolved oxygen consumed by chemical oxidizing reagents ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) during the reaction with organic and inorganic matter to produce carbon dioxide in a standard test at 20°C.

## Purpose of BOD and COD tests

1. Test the water quality in lakes and rivers.
  2. Determine the amount of oxygen required to oxidize the organic matter in wastewater
  3. Determine the size of treatment system needed (a design factor)
  4. Assess the efficiency of wastewater treatment process by monitoring influent and effluent
  5. Determine compliance with wastewater discharge permits
- ❖ Types: Standard 5-day ( $BOD_5$ ) and Ultimate ( $BOD_u$ ).
    - $BOD_5$  normally represents 2/3 of  $BOD_u$  for domestic wastewater.
  - ❖ BOD is divided into Carbonaceous (CBOD) and Nitrogenous (NBOD).

# Carbonaceous & Nitrogenous BOD



Hypothetical biochemical oxygen demand reaction curve showing the carbonaceous & nitrification reactions.

# BOD Test

- Standardized conditions  
(5 days, 20°C)
- Needs:
  - Incubator
  - Bottles
  - DO meter
  - Dilution water
  - Seed (opt.)
  - Expressed in mg/L
- Procedure:  
(see Text).





# BOD Test

$$\text{BOD}_5 \text{ (mg/l)} = (D_0 - D_5) \cdot \text{DF}$$

DF is the dilution factor

DF = volume of diluted sample/  
volume of original water sample

D is dissolved oxygen  
concentration at Time = 0  
and Time = 5 days

## Example:

Determine the  $\text{BOD}_5$  for a 15 mL sample that is diluted with dilution water to a total volume of 300 mL when the initial DO concentration is 8 mg/L and after 5 days, has been reduced to 2 mg/L.

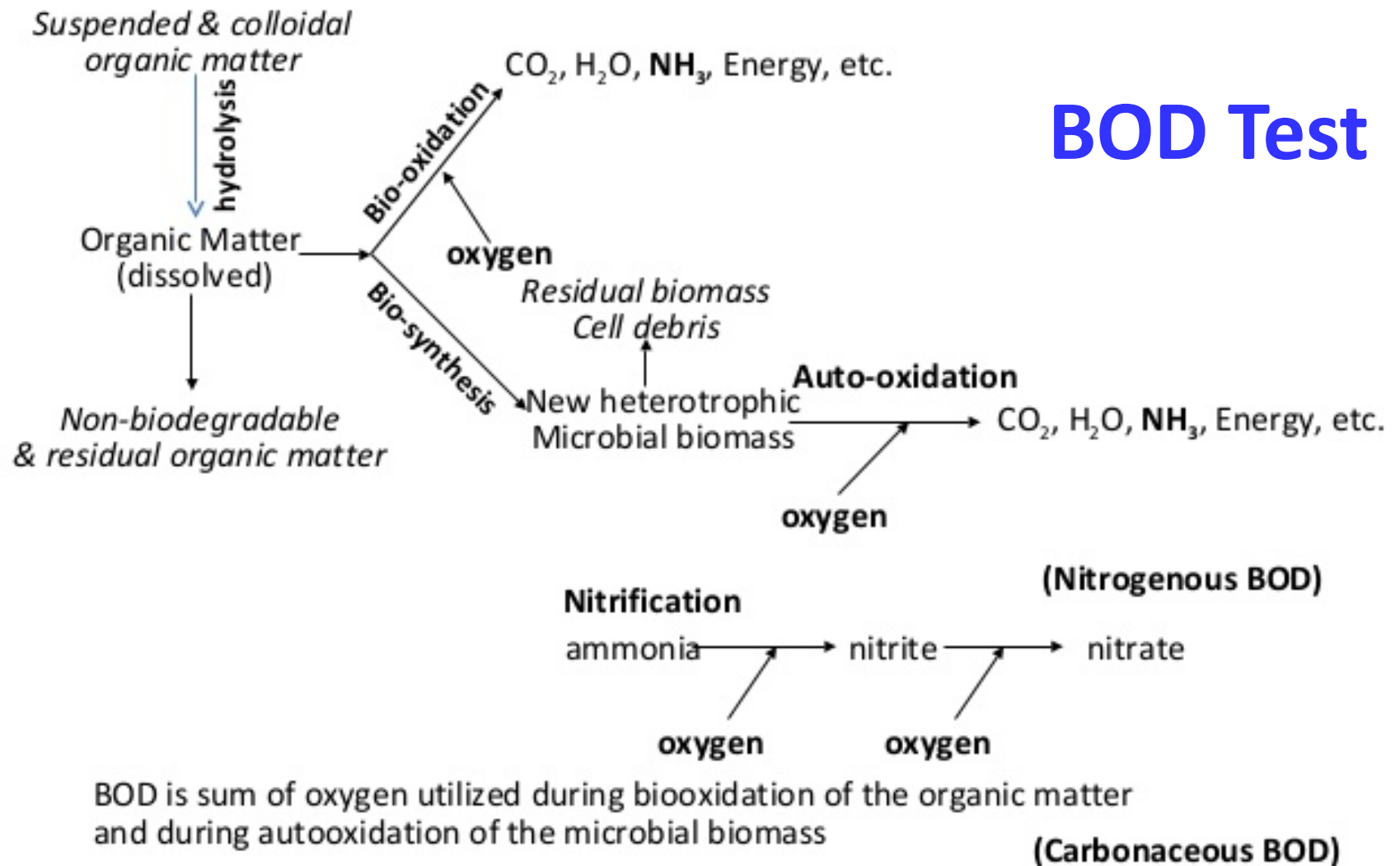
## Solution:

$$D_0 = 8 \quad D_5 = 2$$

$$\text{Dilution factor} = 300/15 = 20$$

$$\text{BOD}_5 \text{ (mg/L)} = (8-2) \cdot 20 = 120 \text{ mg/L}$$

# BOD Test



**Fate of organic matter of the sample in the BOD test**

# BOD Kinetics

- Reaction is aerobic decomposition- when microorganisms use oxygen to consume organic waste dissolved in water.
- The rate at which oxygen is consumed is directly proportional to the concentration of degradable organic matter remaining at any time
- ***BOD is a first order reaction***
  - $L_t$  = Concentration of DO at time “t”
  - $L_o$  = ultimate BOD (Initial or Required DO at  $t=0$ )
  - $L_o - L_t = BOD_t$

# BOD Kinetics

BOD reaction is a **first order reaction**

**Rate of change in reactant concentration  $\propto$  Amount of reactant present at any time**

$$-\frac{dL}{dt} \propto L$$

L= Oxygen equivalent of biodegradable organics present at time t, mg/L

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

$$\frac{dL}{L} = -kdt$$

k =BOD rate constant, day<sup>-1</sup>

Integrating we get,

$$\int \frac{dL}{L} = -k \int dt$$

$$\ln L = -kt + C$$

At time t = 0, L= L<sub>0</sub>

L<sub>0</sub>= Oxygen equivalent of biodegradable organics present at t=0, mg/L

$$\ln \frac{L}{L_0} = -kt$$

$$L = L_0 e^{-kt} \quad \text{or,} \quad L_t = L_0 e^{-kt}$$

L or L<sub>t</sub> is often known as BOD remaining at time t

$$\text{BOD} = y = L_0(1 - e^{-kt})$$

where

$$\text{BOD} = y = L_0 - L$$

# BOD Kinetics

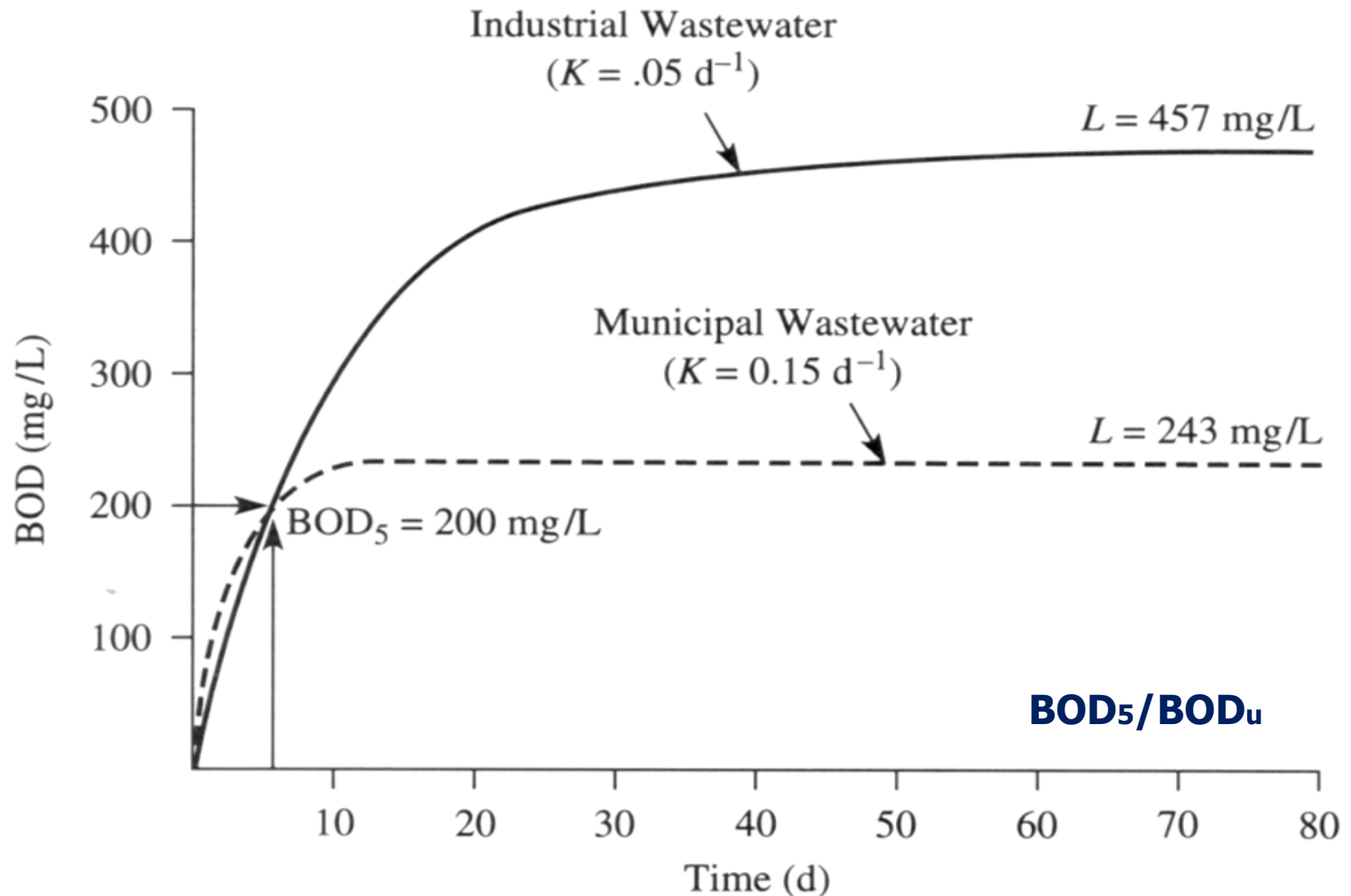
**TABLE 1.4**

**Average BOD rate constants at 20°C**

<b>Substance</b>	<b><math>k_{10}</math>, day<sup>-1</sup></b>
Untreated wastewater	0.15–0.28
High-rate filters and anaerobic contact	0.12–0.22
High-degree biotreatment effluent	0.06–0.10
Rivers with low pollution	0.04–0.08

- Many industrial wastes are difficult to oxidize; they require:
  - a bacterial seed acclimated to the specific waste, or
  - a lag period may occur which yields an erroneous interpretation of the five-day BOD values.

# BOD Data Interpretation



# BOD Data Interpretation

Lab conditions:  $T = 20^{\circ}\text{C}$ ,  $k = 0.11\text{ d}^{-1}$

BOD  
(mg/L)

70

50

20

River Conditions:  $T = 10^{\circ}\text{C}$ ,  $k = 0.03\text{ d}^{-1}$

5

15

Time (d)

30

# BOD Data Interpretation

- Ultimate BOD  
Maximum amount of oxygen consumption possible when waste has been completely degraded
- **Rate Constant,  $k$ :**  
Numerical value of the rate constant  $k$  depends on:
  1. Nature of waste
  2. Ability of organisms in the system to use the waste
  3. Temperature

## Effect of Temperature on $k$ :

- The BOD rate constant is adjusted to the temperature of receiving water using this:  $k_T = k_{20}(\theta)^{T-20}$   
T = temperature of interest ( $^{\circ}\text{C}$ )  
 $k_T$  = BOD rate constant at the temperature of interest ( $\text{d}^{-1}$ )  
 $K_{20}$  = BOD rate constant determined at  $20^{\circ}\text{C}$  ( $\text{d}^{-1}$ )  
 $\theta$  = temperature coefficient (usually 1.05).



# Chemical Oxygen Demand, COD



- The BOD test takes 5 days time and thus not very useful in control of treatment processes.
- The COD test can be used to measure both biodegradable and non biodegradable organic matter. COD test, takes 2 hours Or less in comparison to 5 days for BOD test.
- In COD test, a strong chemical oxidizing agent like **potassium dichromate** is used in acidic medium to oxidize the organic matter present in the waste.
  - Almost all type of organic matter with **a few exceptions** can be oxidized by the action of strong oxidizing agents under acidic conditions.
  - Temperature needed is around 150°C.

# BOD vs. COD

## COD and BOD - Comparatives

**COD**  $\longrightarrow$  Biodegradable + Non-biodegradable

**BOD**  $\longrightarrow$  Biodegradable

$$0 \leq \frac{BOD}{COD} \leq 1$$

For a completely biodegradable wastewater,

$$\frac{BOD_u}{COD} = 0.9 \text{ to } 1$$

For wastewater with  $\frac{BOD_u}{COD} < 0.6$ , it is considered non-biodegradable

Theoretically, for a completely biodegradable wastewater

$$BOD_u = COD$$

## Nitrogen Oxidation

Up to this point we assumed that only C in organic matter is oxidized.

Actually many organic compounds, such as proteins, also contain N that can be oxidized with the consumption of  $O_2$ .

However, mechanisms and rates of N oxidation are distinctly different from those of C oxidation.

*Two processes must be considered separately.*

$O_2$  consumption due to oxidation of C  $\rightarrow$  called carbonaceous BOD (CBOD).  
due to N oxidation  $\rightarrow$  called nitrogenous BOD (NBOD)

Organisms that oxidize C to obtain energy can not oxidize N.

Instead, N is released into water as ammonia ( $NH_3$ )

At normal pH,  $NH_3$  is present as ammonium cation ( $NH_4^+$ )

$NH_3$  from organics + ind. wastes + agricultural runoff (fertilizers) oxidized  $\rightarrow NO_3^-$   
by nitrifying bacteria (*nitrification*)

The overall reaction for ammonia oxidation :



Theoretical NBOD = g of  $O_2$  used / g of N oxidized =  $(4 \times 16) / 14 = 4.57 \text{ g } O_2 / \text{g N}$

# Nutrients

- Nitrogen and phosphorus are considered pollutants when present in high concentration.
- High levels of nutrients cause disturbances in the food web
- Organisms grow rapidly at the expense of others.

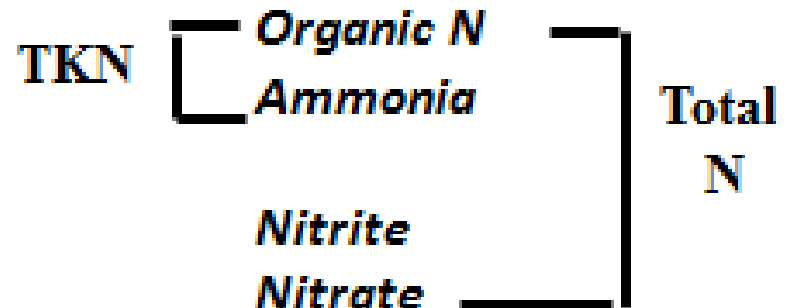
- **Major sources of nutrients**

**(N, P):**

1. Phosphorus-based detergent
2. Fertilizer and agricultural runoff
3. Food-processing wastes
4. Animal and human waste.

- $\text{TKN} = 40\% \text{ Organic} + 60\% \text{ Free NH}_3$
- Typical concentrations:  
Ammonia-N = 10-50 mg/L  
Organic N = 10-35 mg/L
- No nitrites or nitrates in untreated wastewater

- **Forms of nitrogen:**



**TKN:** Total Kjeldahl Nitrogen

## Nutrients: Forms of phosphorus in wastewater

- **Phosphorus**

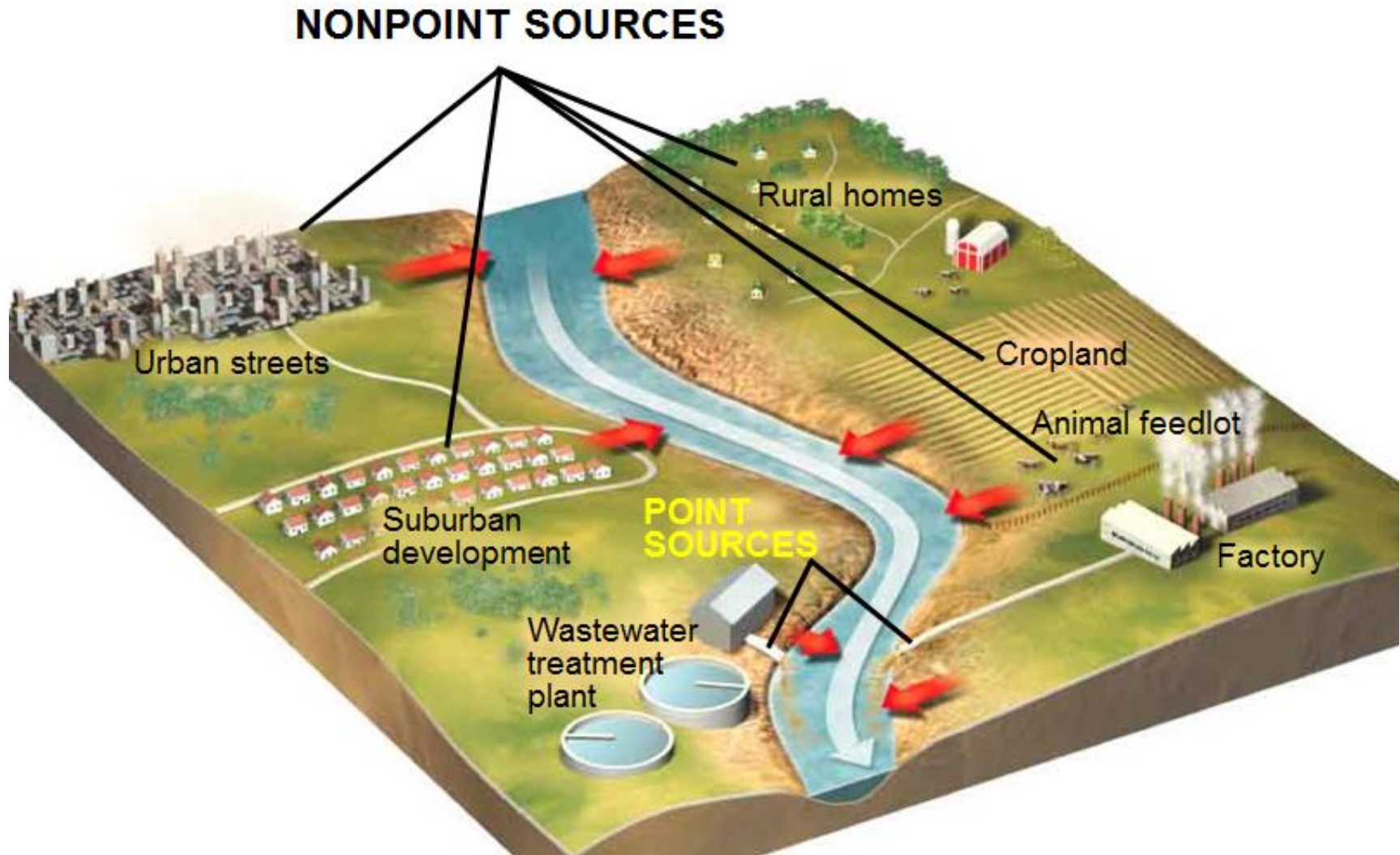
- Raw wastewater contains 4 – 16 mg/L as P
- Effluent may restrict to less than 1 mg/L as P

Forms are:

1. Orthophosphate:  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}_3\text{PO}_4$
2. Polyphosphate (polymerized; important *in* biological phosphorous removal)
3. Organic phosphorous (low in raw wastewater)

Measurement: Titration (direct or after acid digestion)

# Point and Nonpoint Sources





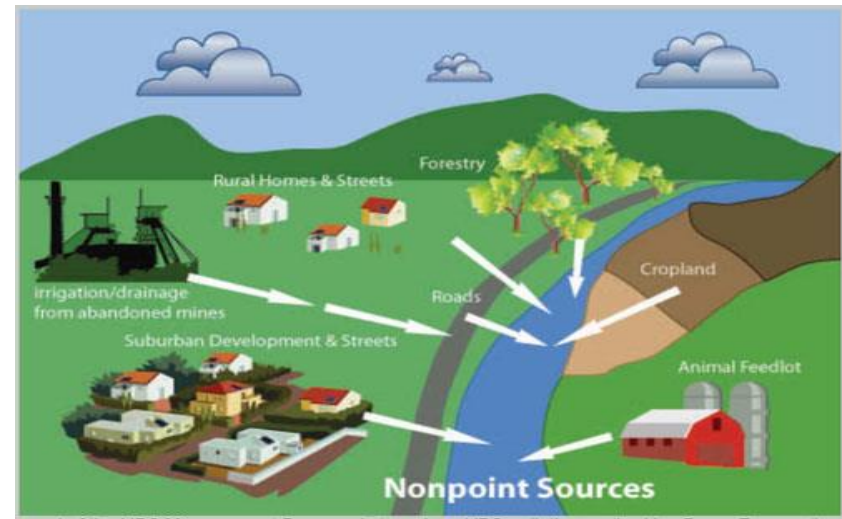
# Point Sources of Water Pollutants

1. Located at specific places.
2. Easy to identify, monitor and regulate
3. Include **domestic** sewage and **industrial** wastewater.
4. Collected by a network of pipes or channels and conveyed to a single point of discharge in the receiving natural water (river, lake, sea).
5. Can be controlled by waste minimization and proper wastewater **treatment**.



# Nonpoint Sources of Water Pollutants

1. Broad, diffuse areas that increase during rainstorms and snowmelt times
2. Difficult to identify and control & Expensive to cleanup
3. Major sources are agricultural activities, sediment eroded from the lands, fertilizers and pesticides, bacteria from livestock and food processing wastes. May come from Industrial factories and mining activities as well as other sources.



1. Can be reduced by changing land use practices.
2. Use vegetation to reduce soil erosion.
3. Use planting buffer zones around crop fields & animal feedlots to reduce runoff.
4. Reduce use of fertilizers & pesticides in farming.
5. Keep feedlots away from slopes, surface water and flood zones.



# Lake Eutrophication

- Process of slow increase in nutrient levels and biological productivity that converts a lake with clear water (**Oligotrophic**) to a shallow lake or dry land that is rich in organisms and organic material (**Eutrophic**).
- Increase in biological productivity and ecosystem succession caused by human activities that speeds up the process of lake aging and drying.
- **Nutrient enrichment of lakes** mostly from runoff of plant nutrients (nitrates and phosphates):
  1. During hot dry weather can lead to algae blooms.
  1. Cause turbidity, color and bad odor.
  2. Dissolved oxygen drops DO & Fish kills.
  3. Decrease of photosynthesis.



# Eutrophication

## Oligotrophic

Cold, Deep,  
Low Nutrients



## Mesotrophic

Increasing in  
Nutrient Load



## Eutrophic

Shallow, Warm,  
High Nutrient Load



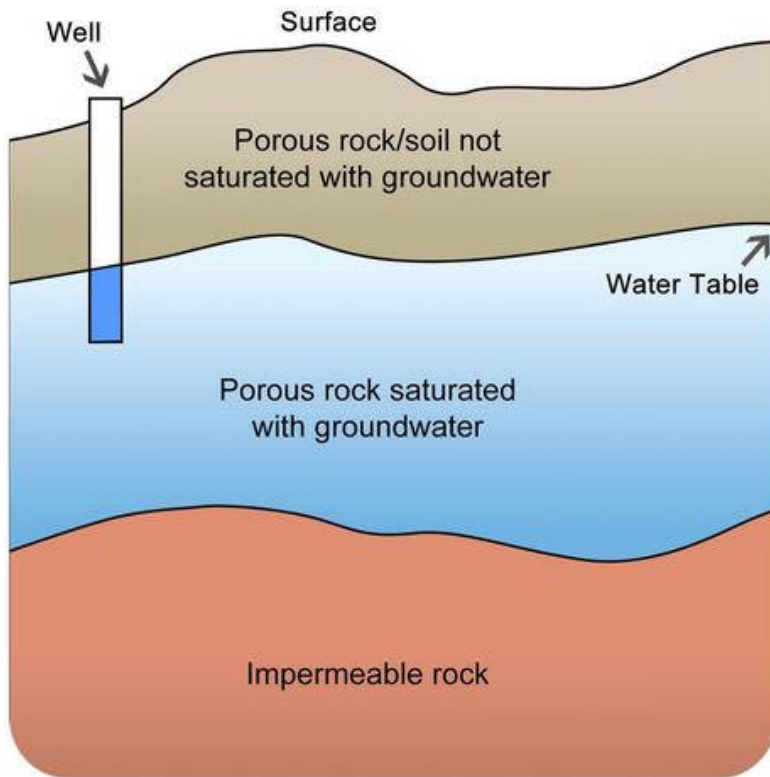
## Control of Eutrophication

- 1) Advanced wastewater treatment (remove N,P) before discharge to lakes.
- 2) Control household detergents (P).
- 3) Soil conservation/control soil erosion that leads to suspended solids.
- 4) Remove excess weed growth.

# Ground Water

**Definition:** the water that lies beneath the ground surface, filling the spaces between rocks. They originate from rain and snow.

Groundwater and Water Table



- **Type of Groundwater reservoirs:**
  1. aquifer: a body of saturated rock or sediment through which water can move easily
  2. water table: top level of aquifer.
  3. spring: a place where water flows **naturally** from rock onto the land surface.
  4. well: a deep hole, generally cylindrical, that is dug or **drill** into the ground to extract water from aquifer.
  5. recharge: the addition of new water to the saturated zone.

# Groundwater Pollution

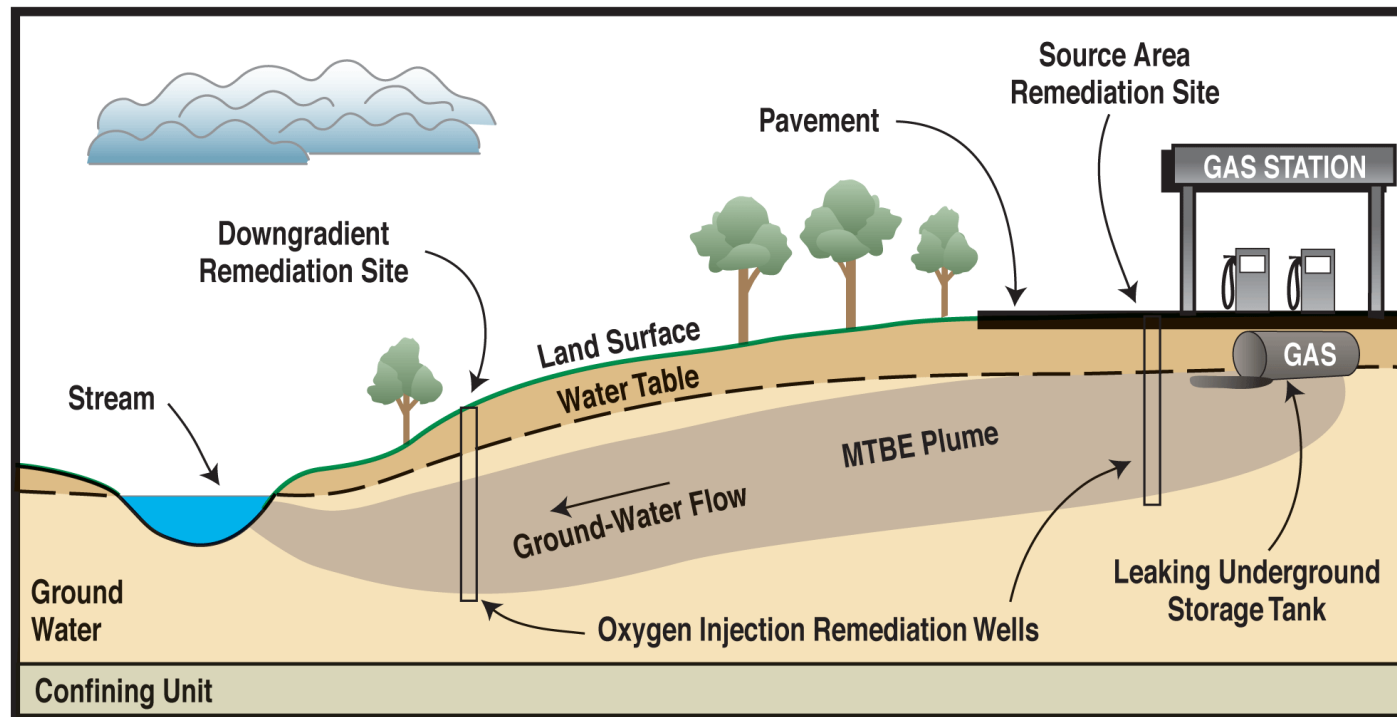
- **Type of sources:** both Point Source (contaminants have an identifiable source) and Nonpoint Source Pollution (contaminant source cannot be found). Land-use activities commonly responsible for groundwater pollution in the urban areas. Many causes and sources are possible.
- **Type of pollutants:**
  1. Agrochemicals (pesticides, herbicides, fertilizers) that find their way into ground water when rain or irrigation water leaches the poisons downward into the soil.
  2. Storm runoff: where rain leach pollutants from city dumps (uncontrolled solid and liquid waste) into groundwater supplies.
  3. Heavy metals together with household chemicals and poisons can be concentrated in groundwater beneath solid waste landfills or dumps.

# Groundwater Pollution Control

1. Keep toxic chemicals out.
2. Ban hazardous waste disposal in landfills and injection wells
3. Store harmful liquids in above-ground tanks with leak detection and collection systems
4. Install monitoring wells near landfills & underground fuel tanks
5. Cleanup: Pump to surface, clean, and return to aquifer (expensive).

## Groundwater Pollution by Fuel Leak

(MTBE):  
*Methyl tert-butyl ether*





# WATER QUALITY MANAGEMENT

1. WATER QUALITY MANAGEMENT The science that predicts how much waste is too much for a body of water
2. Assimilated waste: the amount of waste that can be tolerated by a body of water. It is determined by knowing the type of pollutants discharged and their effect on water quality.

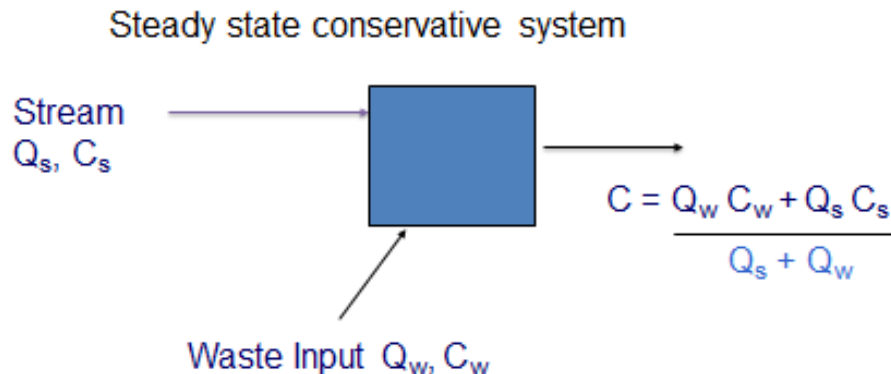


# Water quality management in rivers

- Main goal is to control the discharge of pollutants so that water quality is not degraded above the natural background level
- Controlling waste involves:
  - 1) Measuring pollutants levels (x,z, t)
  - 2) Predicting their effect on the water quality
  - 3) Determining background water quality that would be present without human intervention
  - 4) Evaluate the levels acceptable for intended uses of the water

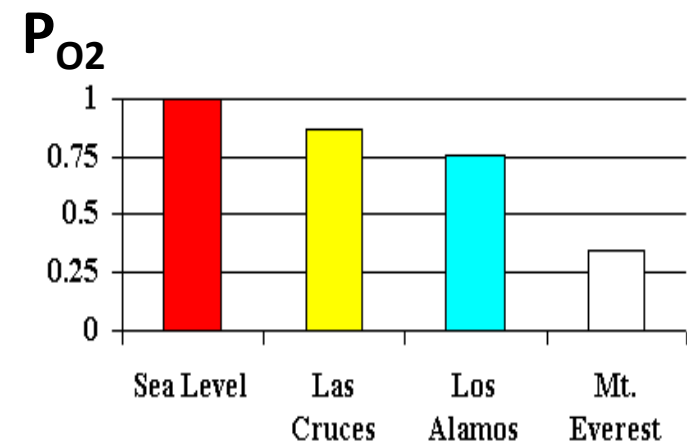
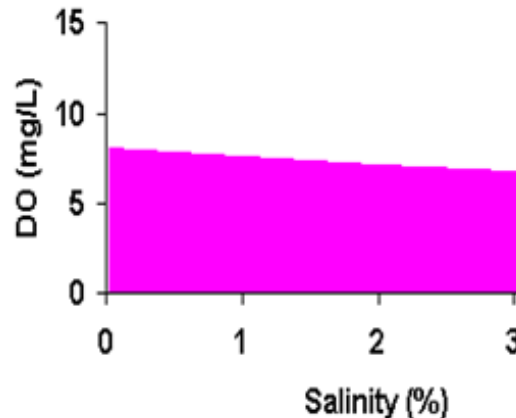
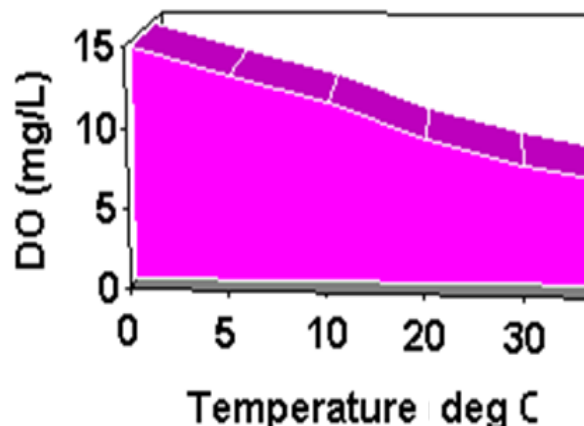
## Simple Mass Balance

Input rate - Output rate - decay rate = Accumulation rate



# Dissolved Oxygen in Natural Water

- Aquatic aerobic organisms need oxygen to survive.
- Max amount in clean water is ~9 mg/L (**Henry's Law**)
- Aqueous DO concentration varies with temperature, salinity, elevation ( $P_{O_2}$  decreases as elevation increases), turbulence.





# Parameters Affecting Natural Water DO

## 1) Effect of temperature

- Hot (process cooling) water from an industrial plant → Causes DO saturation level to decrease

## 2) Effect of salinity

- Salt from roads and irrigated fields runs off into water bodies → Causes DO saturation level to decrease

## 3) Effect of elevation

- $\text{PO}_2$  decreases as elevation increases
- DO: At 1500 m elevation: ~ 7 mg/L; at sea level ~ 9 mg/L

## 4) Effect of turbulence

- A turbulent stream (violent mixing) will replenish DO quickly
- A slow, sluggish stream (or lake) will replenish DO slowly

# Dissolved Oxygen

1. If the discharge of oxygen- demanding wastes is within the self-purification capacity, the DO is high
2. If the amount of waste increases, it can result in detrimental changes in plant and animal life
3. Objective of **water quality management** is to assess the capability of a stream to absorb waste

## Temperature effect

1. Oxygen use speeds up as the temperature increases and slows down as the temperature decreases.
2. Oxygen use is caused by the metabolism of microorganisms.
3. BOD rate constants depend on Temperature of receiving water throughout the year.
4. Comparing data from various locations at different T values to determine the effect.

# Temperature effect on Solubility of O<sub>2</sub> in water

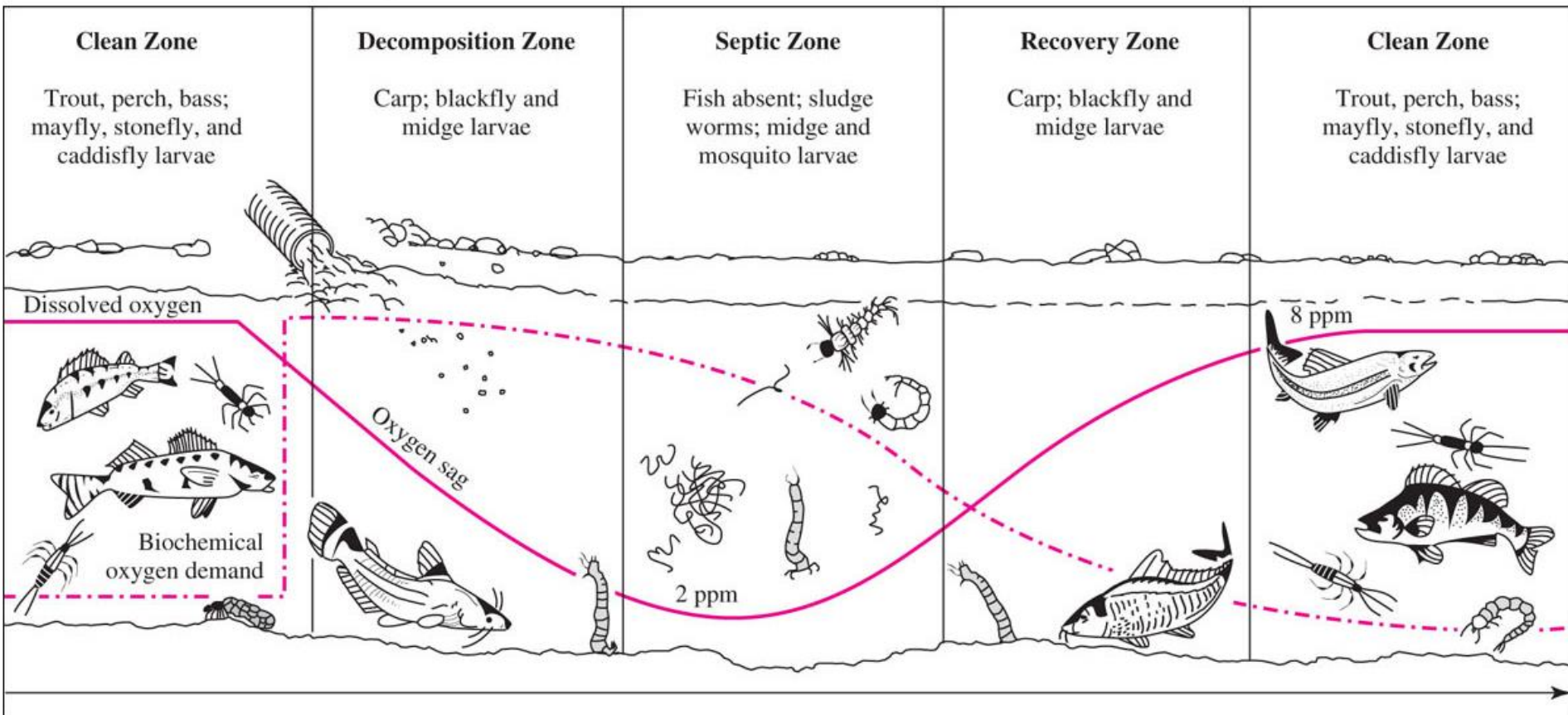
Values of saturated dissolved oxygen, DO<sub>s</sub>, as function of ambient temperature

Temperature (°C)	Oxygen (mg/L)	Temperature (°C)	Oxygen (mg/L)
0	14.6	13	10.6
1	14.2	14	10.4
2	13.8	15	10.2
3	13.5	16	10.0
4	13.1	17	9.7
5	12.8	18	9.5
6	12.5	19	9.4
7	12.2	20	9.2
8	11.9	21	9.0
9	11.6	22	8.8
10	11.3	23	8.7
11	11.1	24	8.5
12	10.8	25	8.4

# Do Sag Curve

- DO concentration **dips** as oxygen-demanding materials are oxidized and then **rises** as oxygen is replenished from atmosphere and photosynthesis
- **Major sources of oxygen:**
  - 1) Reaeration from the atmosphere
  - 2) Photosynthesis of aquatic plants
- **Factors of oxygen depletion:**
  - 1) BOD of waste discharge
  - 2) DO in waste discharge is less than that in the river
  - 3) Nonpoint source pollution
  - 4) Respiration of organisms and aquatic plants

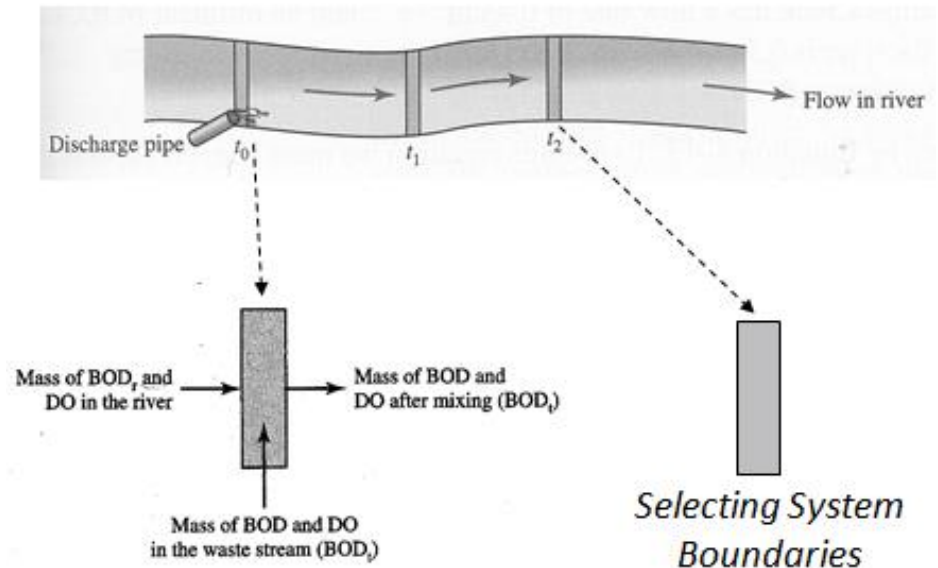
# DO & BOD in stream receiving waste



# Steps in Developing the DO Sag Curve

- 1) Determine the initial conditions (at mixing point)
- 2) Determine the re-aeration rate from stream geometry & *field measurement*.
- 3) Determine the de-oxygenation rate from BOD test and stream geometry
- 4) Calculate the DO deficit as a function of time
- 5) Calculate the time and deficit at the *critical point*

## ***Streeter-Phelps model***



# Initial Mixing

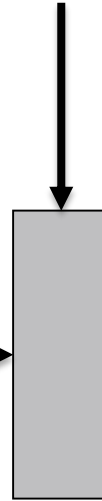
$Q_w$  = waste flow ( $\text{m}^3/\text{s}$ )  
 $\text{DO}_w$  = DO in waste ( $\text{mg/L}$ )  
 $L_w$  = BOD in waste ( $\text{mg/L}$ )

$Q_r$  = river flow ( $\text{m}^3/\text{s}$ )  
 $\text{DO}_r$  = DO in river ( $\text{mg/L}$ )  
 $L_r$  = BOD in river ( $\text{mg/L}$ )

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

$$D = DO_s - DO$$

$$D_a = DO_s - \frac{Q_w DO_w + Q_r DO_r}{Q_{mix}}$$



$Q_{mix}$  = combined flow ( $\text{m}^3/\text{s}$ )  
 $\text{DO}$  = mixed DO ( $\text{mg/L}$ )  
 $L_a$  = mixed BOD ( $\text{mg/L}$ )

## Mass Balance for the Model:

- 1) Not a Steady-state situation
- 2) rate  $\text{O}_2$  accum = rate  $\text{O}_2$  in – rate  $\text{O}_2$  out + produced – consumed
- 3) rate  $\text{O}_2$  accum = rate  $\text{O}_2$  in – rate  $\text{O}_2$  consumed

Kinetics: Both re-oxygenation and deoxygenation are 1<sup>st</sup> order

# Streeter-Phelps Model

The last differential equation can be integrated to:

$$D = \frac{k_1 L_o}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + D_o e^{-k_2 t}$$

It can be observed that the minimum value,  $D_c$  is achieved when  $dD/dt = 0$ :

$$\frac{dD}{dt} = k_1 L_o e^{-k_1 t} - k_2 D = 0$$

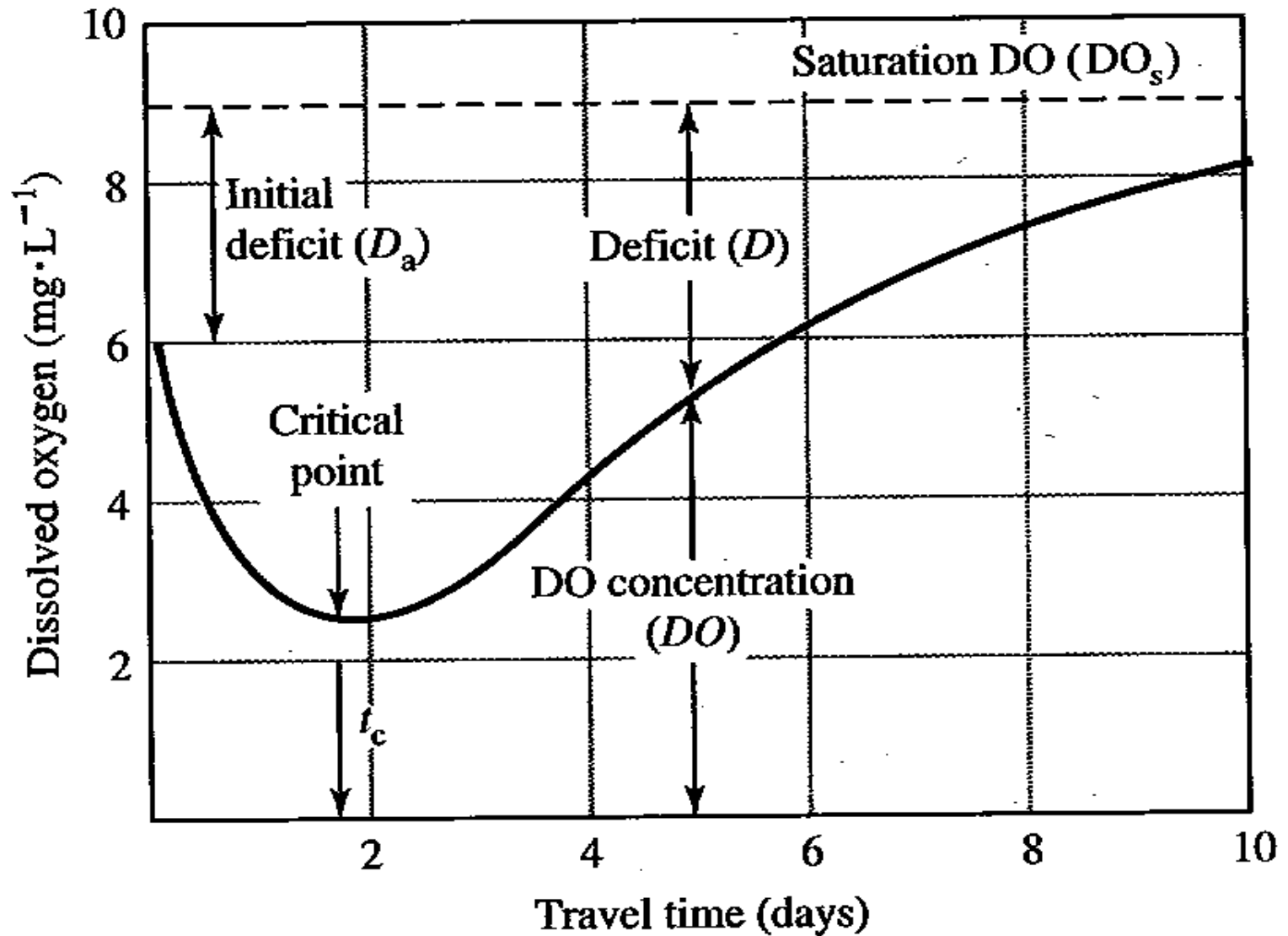
$$D_c = \frac{k_1}{k_2} L_o e^{-k_1 t}, \text{ since } D \text{ is then } D_c$$

Substituting this last equation in the first, when  $D = D_c$  and solving for  $t = t_c$ :

$$t_c = \frac{1}{k_2 - k_1} \ln \left\{ \frac{k_2}{k_1} \left[ 1 - \frac{D_o (k_2 - k_1)}{k_1 L_o} \right] \right\}$$



# Dissolved Oxygen Sag Curve



# REFERENCES

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