Water Resources

CE102: Environmental Studies

Water Resources: A Brief Global Perspective

- **We are facing a growing global water shortage**
  - Linked to the food supply
- **Global hydrologic cycle**
  - Water can be liquid, solid or gas
  - Transfers water from the atmosphere, to land, to oceans, and back to atmosphere
    - Residence time varies from a few days to thousands of years
- **Where is water globally?**
  - 97% in oceans, 2% in ice, 0.001% in atmosphere
  - 99% of all water on earth is unavailable or unusable (salt) to plants and animals
- **Water is the most used resource on earth**
  - Mass of water used 1000x the total production of minerals
  - This is only increasing with greater industrial production and technology

The World's Water Supply

LOCATION	SURFACE AREA (KM²)	WATER VOLUME (KM³)	PERCENTAGE OF TOTAL WATER	ESTIMATED AVERAGE RESIDENCE TIME OF WATER
Oceans	361,000,000	1,230,000,000	97.2	Thousands of years
Atmosphere	510,000,000	12,700	0.001	9 days
Rivers and streams	–	1,200	0.0001	2 weeks
Groundwater (shallow to depth of 0.8 km)	130,000,000	4,000,000	0.31	Hundreds to many thousands of years
Lakes (freshwater)	855,000	123,000	0.01	Tens of years
Ice caps and glaciers	28,200,000	28,600,000	2.15	Tens of thousands of years and longer

Source: U.S. Geological Survey

Hydrology

The science that deals with the depletion and replenishment of water resources, both surface and sub-surface waters including spatial and temporal characteristics of the water in all its aspects such as occurrence, circulation, distribution, physical and chemical properties and impact on environment and living things.
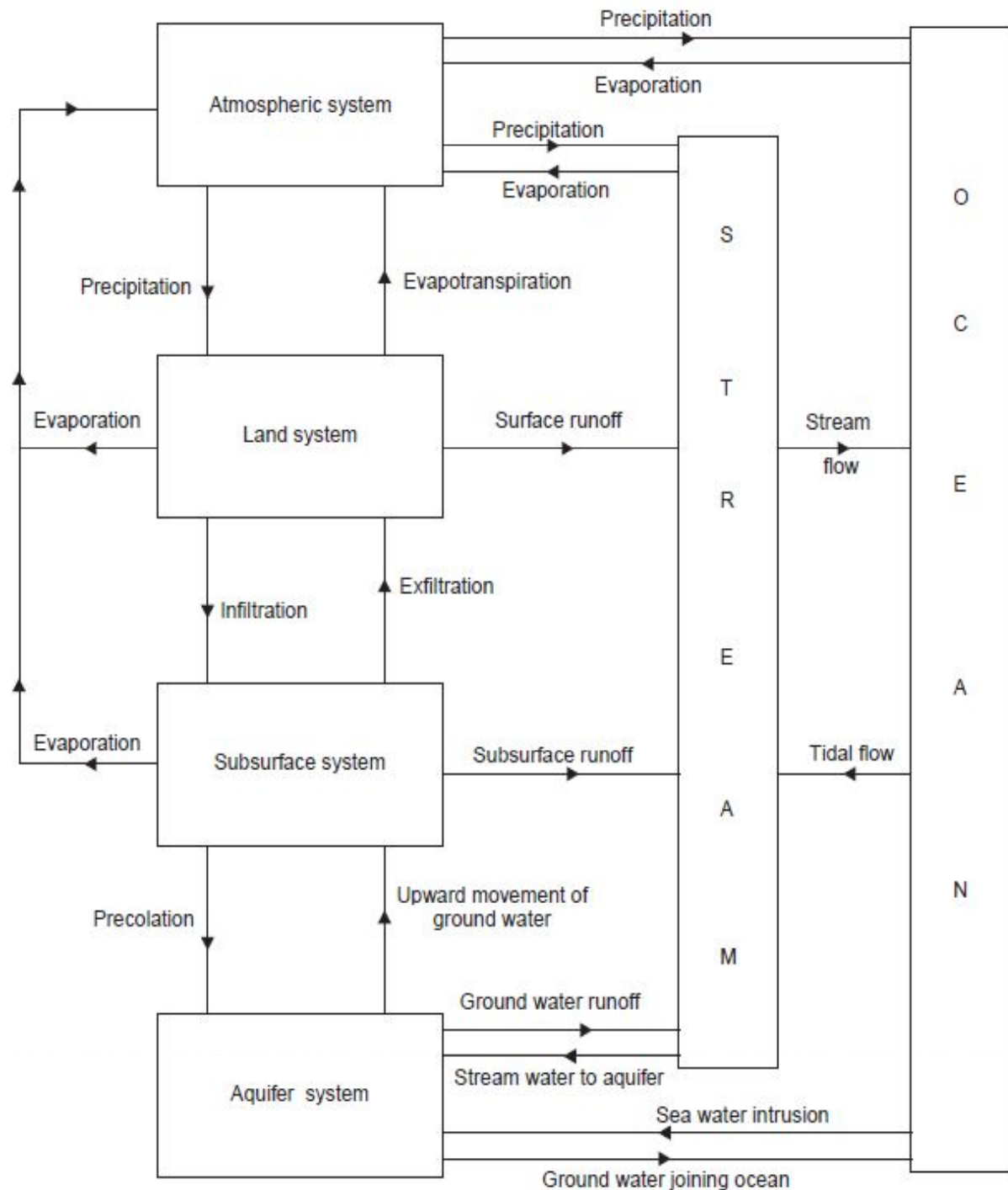
Hydrologic Cycle
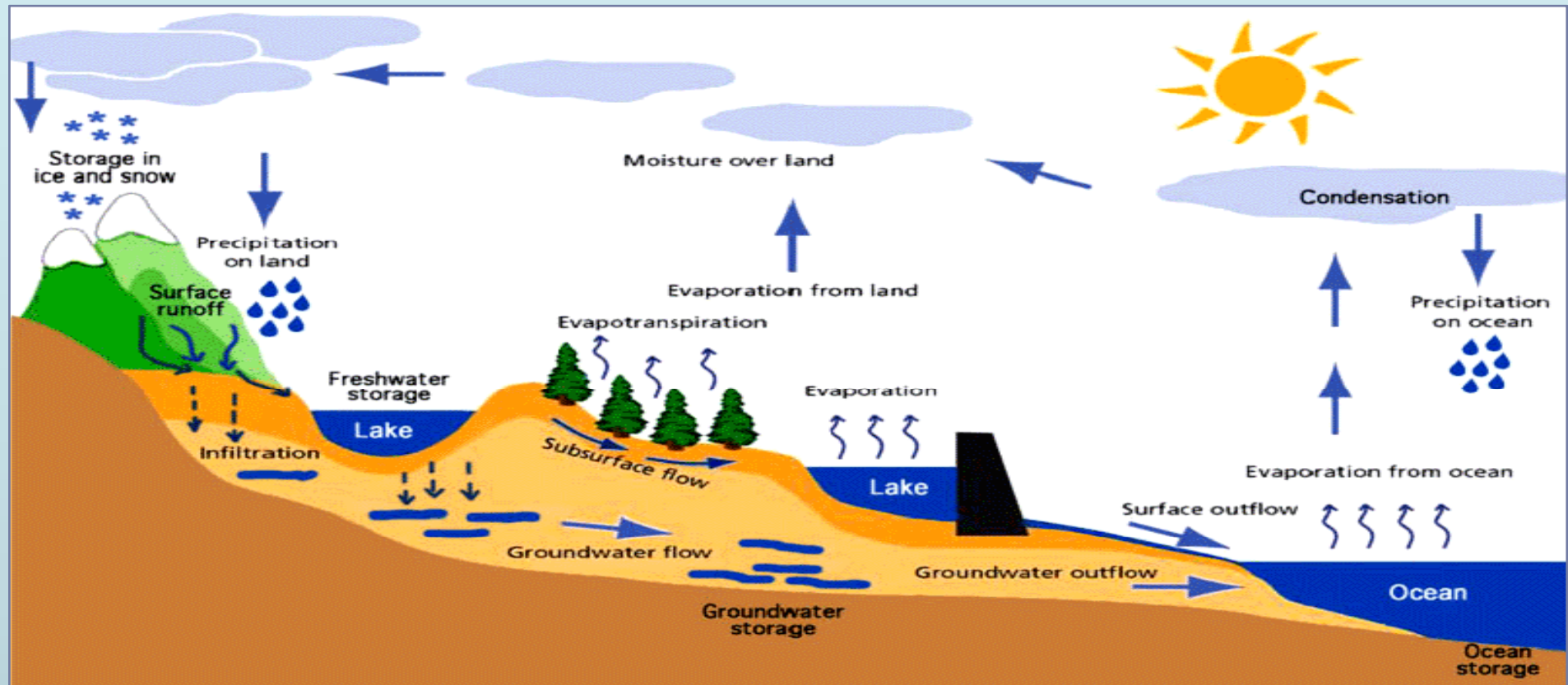
The entire phenomenon of evaporation and precipitation that continues forever and maintain the balance between the loss of water to the atmosphere as vapor from the earth and in gain of water by precipitation such as rain, snow, hail, dew etc. is referred to as **hydrologic cycle.**
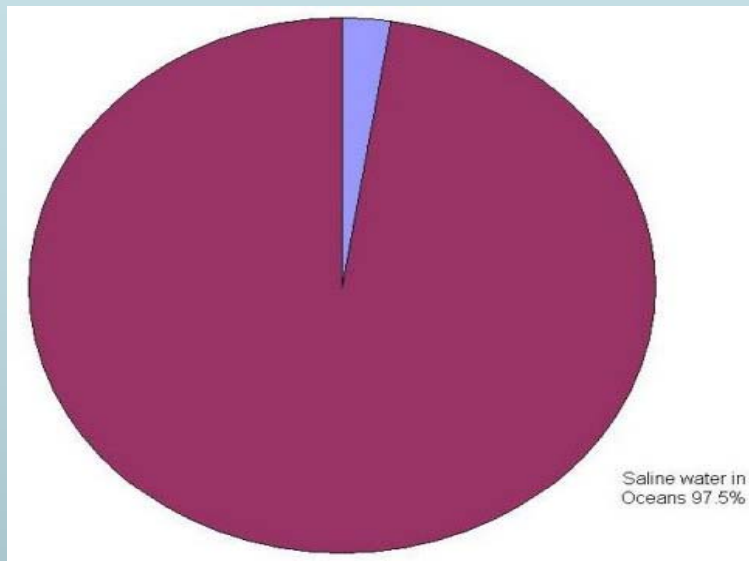
Hydrologic Cycle

This cycle of water amongst earth, oceans, and atmospheric systems is known as Hydrologic cycle where **Sun** and **Coriolis force** play important role in its completion
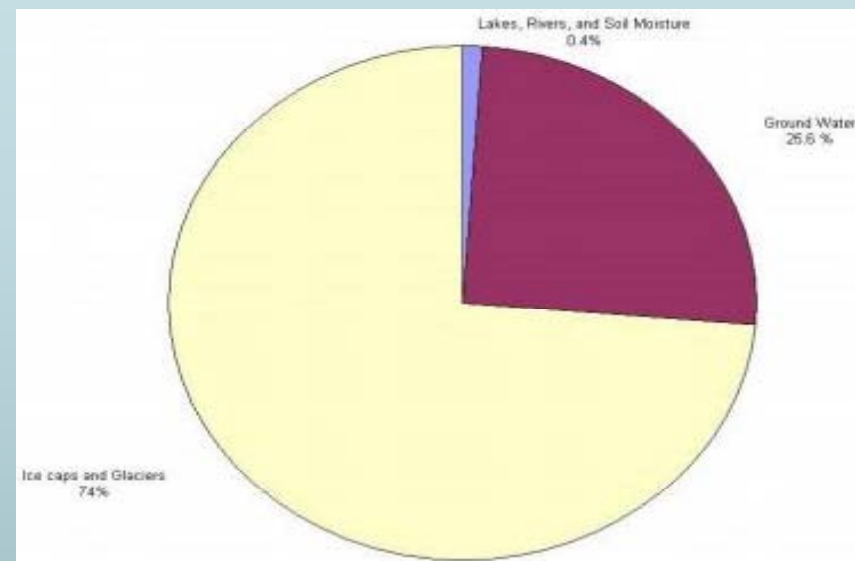
Salient Features of the Hydrologic cycle

❑ Water is conserved: it is neither created nor destroyed.

❑ The earth's total water content in the hydrologic cycle is not equally distributed.

❑ The oceans are the largest reservoirs of water, but since it is saline it is not readily usable for requirements of human survival. The freshwater content is just a fraction of the total water available.

❑ The fresh water distribution is highly uneven, with most of the water locked in frozen polar ice caps.

Saline water in Oceans 97.5%

Lakes, Rivers, and Soil Moisture 0.4%

Ground Water 25.6 %

Ice caps and Glaciers 74%

Total global water content

Global fresh water distribution

Hydrologic cycle and its components

The hydrologic cycle consists of following four key components:

▸ Precipitation

▸ Runoff

▸ Storage

▸ Evapotranspiration

Surface and sub-surface components of hydrologic cycles

Common forms of precipitation

▸ *Drizzle or mist (water droplets of diameters less* than 0.5 mm),

▸ *Rain (water drops of size between 0.5 mm and 6.0 mm),*

▸ *Snow (ice crystals* combining to form flakes with average specific gravity of about 0.1),

▸ *Sleet (rain water drops,* falling through air at or below freezing temperatures, turned to frozen rain drops),

▸ *Hail* (precipitation in the form of ice balls of diameter more than about 8 mm).

▸ Most of the precipitation, generally, is in the form of rains. Therefore, the terms precipitation and rainfall are considered synonymous.

▸ Rainfall, *i.e., liquid precipitation, is considered light when the* rate of rainfall is up to 2.5 mm/hr, moderate when the rate of rainfall is between 2.5 mm/hr and about 7.5 mm/hr, and heavy when the rate of rainfall is higher than about 7.5 mm/hr.

▸

Groundwater and Surface water

- Groundwater:
  - Water located below the water table
  - saturated conditions
- Recharge zones
  - Locations where surface waters move into the groundwater
- Discharge zones
  - Locations where water flows or seeps out of groundwater
- Vadose zone
  - Area where water seeps through pore spaces
- Aquifer
  - Underground zone from which groundwater can be obtained
- Cone of Depression
  - Forms in water table elevation when water is pumped from an aquifer

Groundwater and Surface water

- Streams:
  - Effluent stream
    - Flow is maintained during the dry season by seepage into channel from subsurface
    - Perennial stream - flows all year
  - Influent stream
    - Entirely above the water table and flows only in direct response to precipitation
    - Ephemeral stream
- A stream can have reaches that are both of these, or intermittent at varying times of year
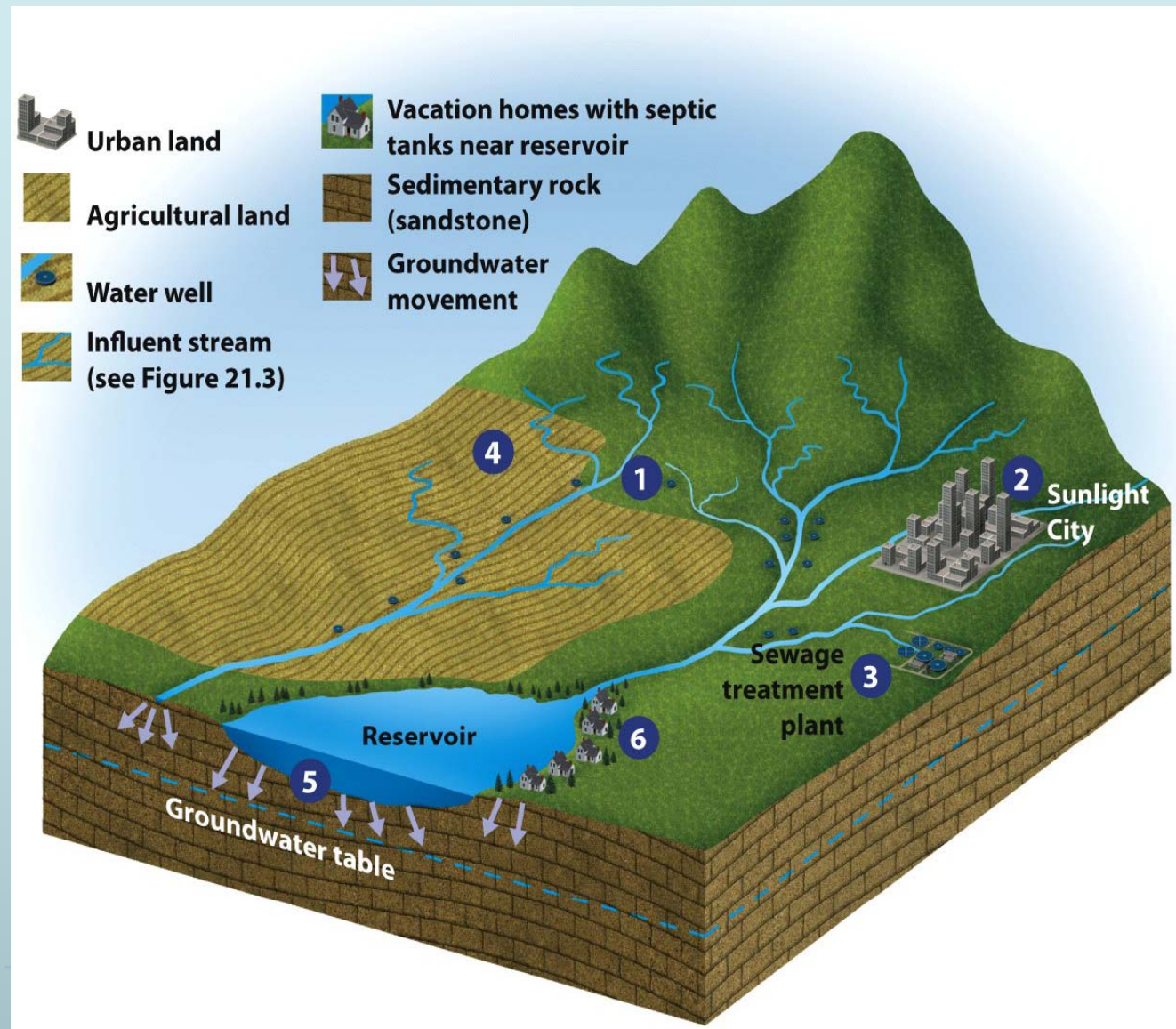
Groundwater and Surface water
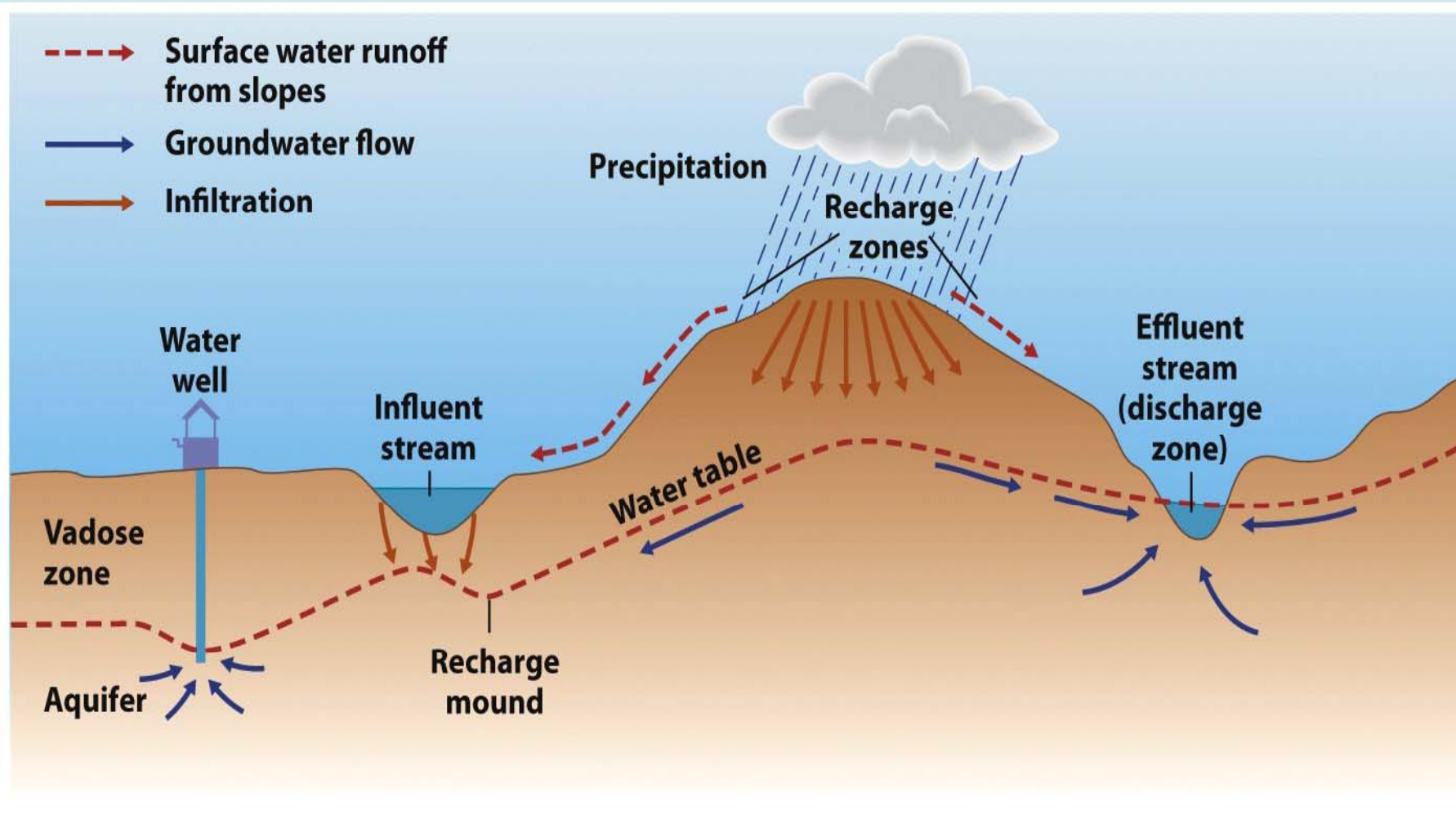
Interactions Between Surface Water and Groundwater

- Should be considered part of the same resource
- Nearly all surface water environments have linkages with ground water
  - Ex: withdrawal of groundwater can lower stream flow or lake levels
  - Pollution can spread from one source to the other

Geographic distribution of water resources in India

Table: River Basins and Surface Water Resources in India (CWC, 1994)

Sl. No.	Name (Origin)	Length (km)	Catchment Area (sq. km)	Water Resource Potential (in cubic km)		
				Average Annual	Utilisable Surface Water	Utilised Surface Water (1989)
	MAJOR BASINS					
1.	Indus (Mansarovar)	1114	321289	73.31	46.00	40.00
2.	(*a*) Ganga (Gangotri)	2525	861452	525.02	250.00	—
	(*b*) Brahmaputra (Kailash)	916	236136	597.04	24.00	—
3.	Sabarmati (Aravalli)	371	21674	4.08	1.93	1.80
4.	Mahi (Dhar, MP)	583	34842	11.83	3.10	2.50
5.	Narmada (Amarkantak, MP)	1312	98796	41.27	34.50	8.00
6.	Tapi (Betul, MP)	724	65145	18.39	14.50	—
7.	Brahmani (Ranchi)	799	39033	36.23	18.30	—
8.	Mahanadi (Nazri, MP)	851	141589	66.88	49.99	17.00
9.	Godavari (Nasik)	1465	312812	118.98	76.30	38.00
10.	Krishna (Mahabaleshwar)	1401	258948	67.79	58.00	47.00
11.	Pennar (Kolar)	597	55213	6.86	6.74	5.00
12.	Cauvery (Coorg)	800	81155	21.36	19.00	18.00
	MEDIUM BASINS	—	248505	289.94	87.65	—
	Grand Total		2776589	1878.98	690.01	

Geographic distribution of water resources in India

Table: State-wise Ground Water Resources in India (CWC, 1994)

Sl. No.	State	Utilisable for Irrigation (cubic km)	Net Draft (1989-90) (cubic km)	Stage of Development (%)
1.	Andhra Pradesh	36.86	8.78	23.80
2.	Arunachal Pradesh	1.22	0.00	0.00
3.	Assam	18.42	0.80	4.33
4.	Bihar and Jharkhand	28.43	5.47	19.23
5.	Goa	0.45	0.03	7.71
6.	Gujarat	19.17	7.17	37.40
7.	Haryana	7.25	5.81	80.21
8.	Himachal Pradesh	0.29	0.07	23.55
9.	Jammu & Kashmir	3.74	0.05	1.24
10.	Karnataka	13.76	3.70	26.85
11.	Kerala	6.59	1.01	15.28
12.	M.P. and Chattishgarh	50.76	7.33	14.44
13.	Maharashtra	32.10	7.74	24.11
14.	Manipur	2.68	0.00	0.00
15.	Meghalaya	1.04	0.00	0.00
16.	Mizoram	NA	NA	NA
17.	Nagaland	0.62	0.00	0.00
18.	Orissa	19.79	1.41	7.13
19.	Punjab	16.05	15.76	99.21
20.	Rajasthan	10.80	5.82	53.89
21.	Sikkim	NA	NA	NA
22.	Tamil Nadu	22.43	13.56	60.44
23.	Tripura	2.14	0.10	4.54
24.	U.P. and Uttaranchal	71.25	26.76	37.49
25.	West Bengal	18.74	4.10	21.90
26.	Union Territories	0.53	0.40	74.25
	Grand Total	385.10	115.81	30.07

Geographic distribution of water resources in India

Table: Annual Requirements of Fresh Water for Various Purposes including Irrigation in India
(CWC, 1994)
(*Unit:* cubic km i.e. 0.1 Mha.m)

	Annual Water Requirement for	1985 Surface water	1985 Ground water	2025 Surface water	2025 Ground water
1.	Irrigation	320	150	510	260
2.	Other uses	40	30	190	90
*(i)	Domestic and Livestock	16.70		46.00	
*(ii)	Industries	10.00		120.00	
*(iii)	Thermal Power	2.70		4.00	
*(iv)	Miscellaneous	40.60		110.00	
	Subtotal	360	180	700	350
	Total	540		1050	

*Approximate

Water Use

- Off-stream use
  - Refers to water removed from its source for use
  - May be returned to source after use
  - Consumptive use- water is not returned to its source
    - Plant or animals water use (evaporates in the tissue, or is used to make new organs)
    - Industrial use
- In-stream use
  - Water left in its source for use
  - Navigation, hydroelectric power, fish and wildlife habitats, and recreation
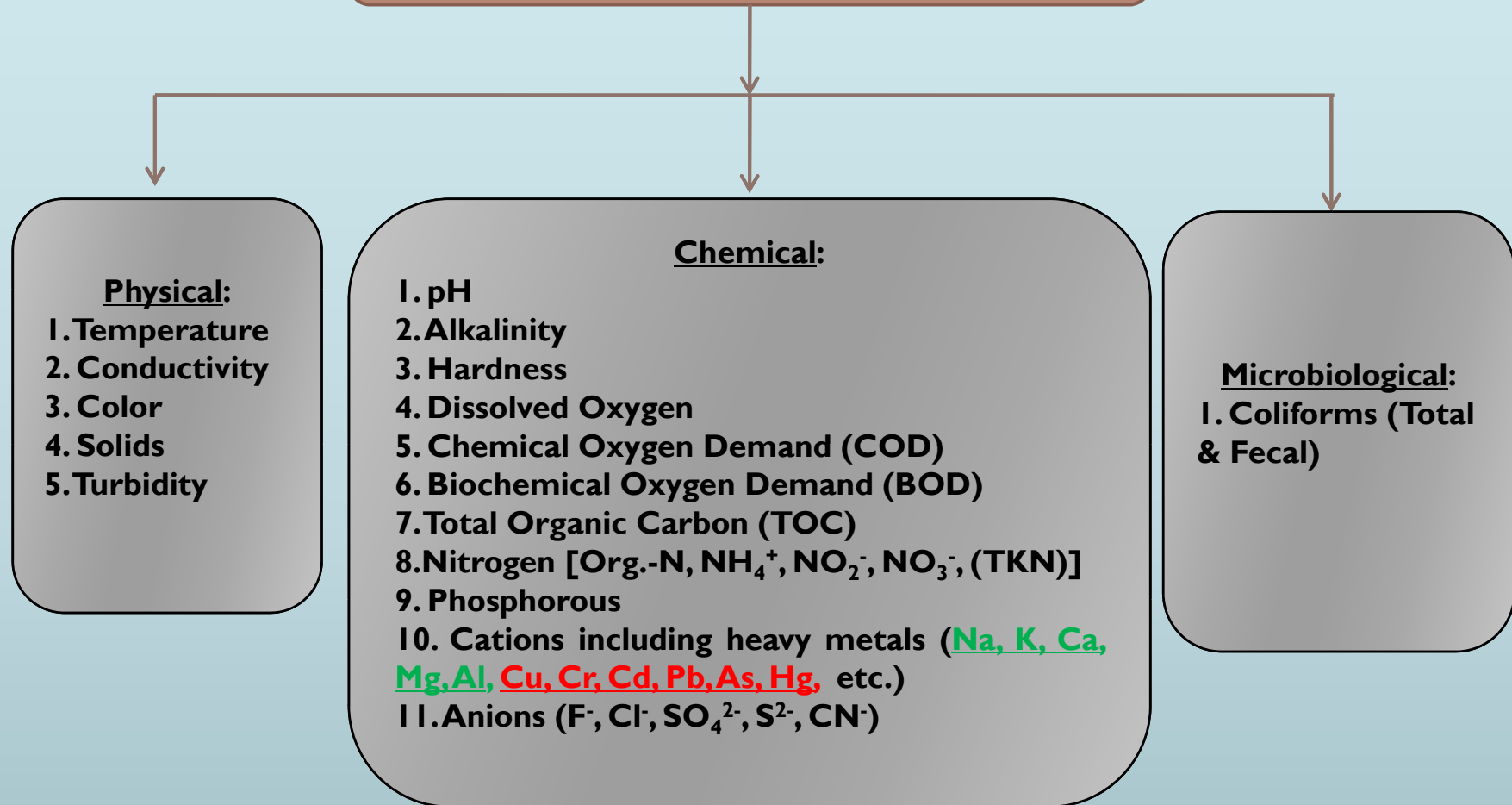
Water Conservation

- Careful use and protection of water resources
    - Involves both quantity and quality of water
    - Important component of sustainable water use
- Three components
    - Agricultural Use
    - Domestic Use
    - Industrial Use
- Advanced planning of Water Management may include
    - Reuse of wastewater
    - Develop surface water and use groundwater in dry years
    - In wet years pump excess surface water underground to recharge groundwater

Water Quality

Water Quality Parameters

Physical:
1. Temperature
2. Conductivity
3. Color
4. Solids
5. Turbidity

Chemical:
1. pH
2. Alkalinity
3. Hardness
4. Dissolved Oxygen
5. Chemical Oxygen Demand (COD)
6. Biochemical Oxygen Demand (BOD)
7. Total Organic Carbon (TOC)
8. Nitrogen [Org.-N, NH_4^+, NO_2^-, NO_3^-, (TKN)]
9. Phosphorous
10. Cations including heavy metals (Na, K, Ca, Mg, Al, Cu, Cr, Cd, Pb, As, Hg, etc.)
11. Anions (F^-, Cl^-, SO_4^{2-}, S^{2-}, CN^-)

Microbiological:
1. Coliforms (Total & Fecal)

Conductivity

❑ Conductivity is a measure of electricity carrying capacity of water

❑ Conductivity of a water sample gives us a measure of the concentration of dissolved (inorganic) ions in that samples

❑ Water with high conductivity generally has high dissolved solids concentrations

❑ Waters with high dissolved solids often have unpleasant tastes, and hence are not suitable for drinking purposes

❑ Unit of measurement for conductivity is Siemens (S) or mho/cm (mho: reciprocal of ohm) [1 S = 1 mho/cm]

Solids

▸ Solids are defined as the matter that remains as *residue upon evaporation* and drying at 103°C to 105°C overnight.

▸ Total Solids in a sample consist of *total dissolved solids* and *total suspended solids*.

▸ Total dissolved solids are materials in liquid that will pass through a filter paper with 2.0 μm or smaller pore size and remains as *residue upon evaporation* and drying at 180°C overnight.

▸ Fixed solids corresponds to the matter that remains as *residue upon muffling (ignition)* at 550°C for 1h or 600°C for 15 mins.

▸ While Volatile solids corresponds to the matter loss upon muffling or high temperature oxidation and volatilization.

Solids
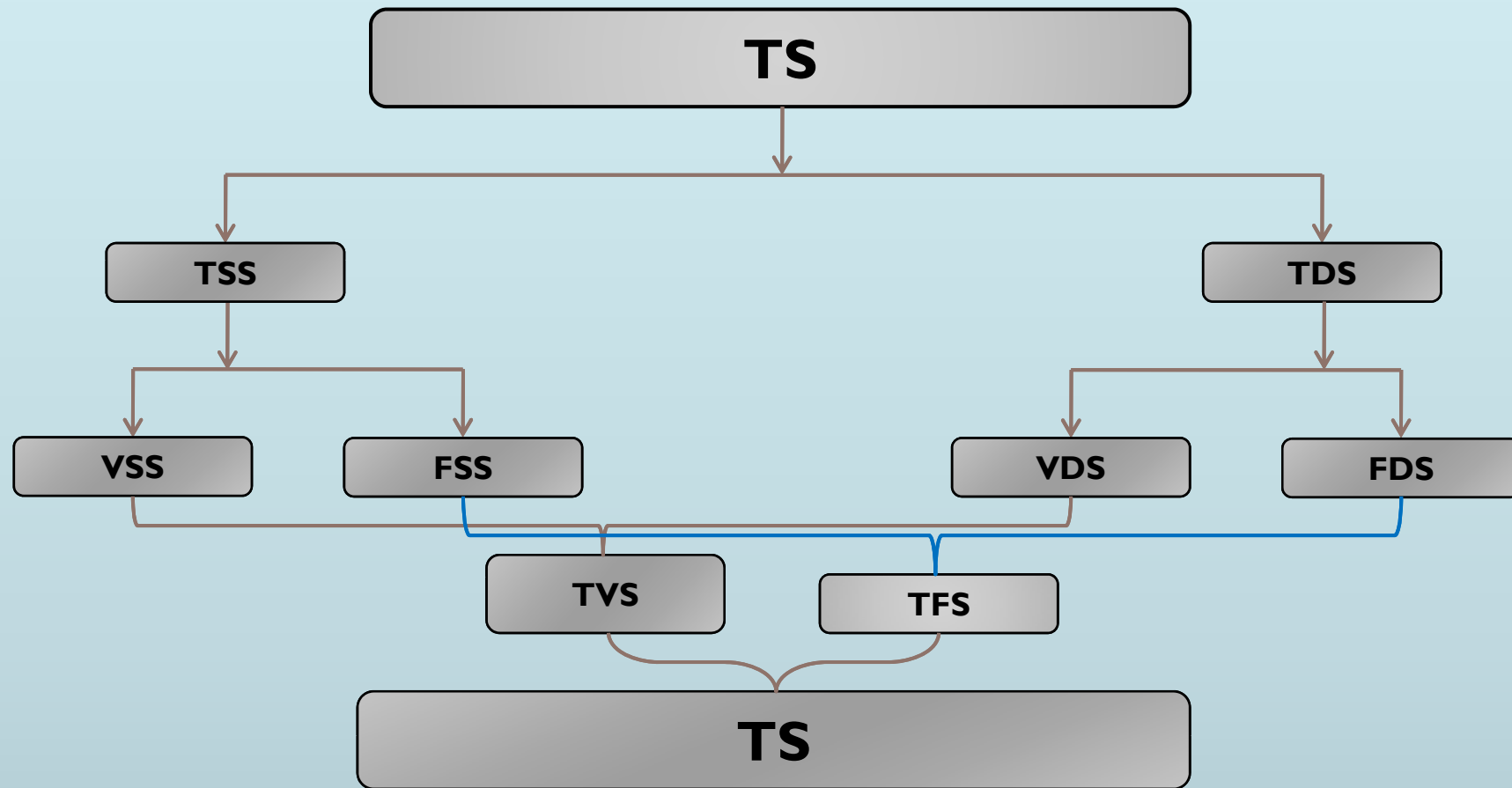
TS: Total Solids; **TSS**: Total Suspended Solids; **TDS**: Total Dissolved Solids; **TVS**: Total Volatile Solids; **TFS**: Total Fixed Solids; **VSS**: Volatile Suspended Solids; **FSS**: Fixed Suspended Solids; **VDS**: Volatile Dissolved Solids; **FDS**: Fixed Dissolved Solids; <u>All expressed in mg/L</u>

Color

❑ Color is generally determined by the visual comparison method.

❑ The color in natural waters is due to the presence of natural organic matter, i.e., dissolved extracts of rotting leaves, trees, branches, animals, etc., picked up by water flowing over the ground as runoff.

❑ Color in domestic wastewaters is due to the presence of human wastes

❑ Color in industrial wastewaters may be due to specific chemicals, i.e. dyes etc.

❑ Unit of measurement for color is mg Pt-Co/L

Turbidity

❑ Scattering of light by suspended (particulate) or colloidal matter in water, gives water a turbid appearance

❑ Turbid waters have an aesthetically unappealing quality, and hence are unsuitable for drinking purpose

❑ Additionally, turbid water may also contain a high concentration of microorganisms

❑ Unit of measurement for turbidity is NTU (Nephelometric Turbidity Unit)

pH

- pH is defined as: $pH = -\log[H^+]$ when H^+ ion concentration is expressed in moles/L

- It is a measure of acidity i.e. hydrogen ion, i.e., $[H^+]$ concentration in water

- Neutral pH, i.e., pH of pure water is 7

- High pH (>7) means that the water is alkaline

- Low pH (<7) means that the water is acidic

- Also in all aqueous solutions, $[H^+].[OH^-] = K_w = 10^{-14}$ (at 25°C).

| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |

Acid   **Neutral**   **Alkaline**
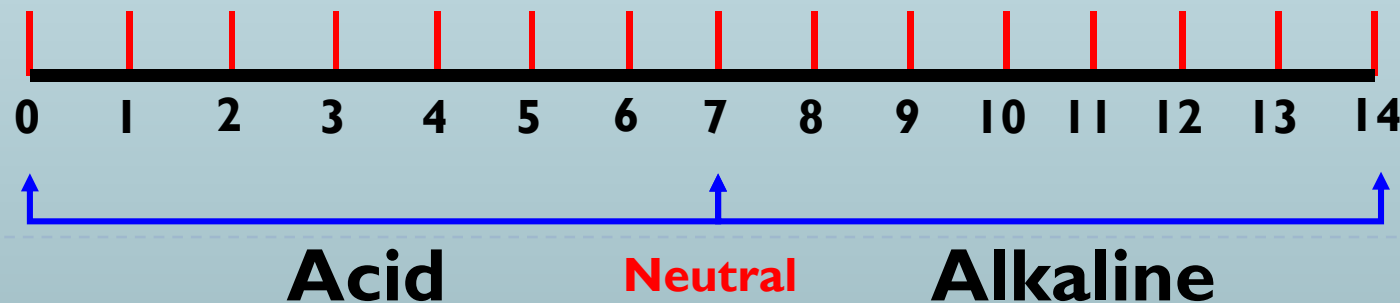
Alkalinity

- Alkalinity is the measure of the acid neutralizing capacity (ANC) of water sample expressed as mg/L of equivalent of $CaCO_3$

- Alkalinity in water is caused by the presence of the following ions: CO_3^{2-}, HCO_3^-, hydroxyl, etc.

- Total alkalinity of water is the sum of CO_3^{2-}, HCO_3^- and OH^- concentration in water

- Unit of measurement for Alkalinity is mg/L as $CaCO_3$

- Alkalinity (mg/L as $CaCO_3$)

$$= M^- \text{ (in mg/L)} \times EW \text{ of } CaCO_3$$

$$\text{i.e. } 50 / EW \text{ of } M^-$$

- **pH <4.5: All aqueous carbonate species is present as H_2CO_3*(i.e. either CO_2 (aq) or carbonic acid)**
- **4.5<pH<8.3: H_2CO_3* and HCO_3^- will dominate**
- **8.3<pH<12.3: HCO_3^- and CO_3^{2-} will dominate**
- **pH>12.3: All aqueous carbonate species is present as CO_3^{2-}**

Hardness

- Hardness of water, on economical aspect is considered as the soap consuming capacity or the ability to resist foam or lather formation upon soap application.

- Hardness of water is generally caused due to the presence of multivalent cations, mainly Ca^{++} and Mg^{++} in water

- Hard waters have many disadvantages, primarily scale formation (i.e., $CaCO_3$ deposition) and enhanced capacity to precipitate soap

- Total hardness of water is the sum of Ca++ and Mg++ concentration in water

- Unit of measurement for Hardness is mg/L as $CaCO_3$

- Hardness (mg/L as $CaCO_3$)

$$= M^{2+} \text{ (in mg/L)} \times EW \text{ of } CaCO_3$$

$$\text{i.e. } 50 / EW \text{ of } M^{2+}$$

Alkalinity and Hardness

Alkalinity

Total titratable bases

bicarbonate

HCO_3^-

carbonate

CO_3^{2-}

Hardness

Total divalent salts

calcium

Ca^{2+}

magnesium

Mg^{2+}

Calcium bicarbonate
$Ca(HCO_3)_2$

Calcium carbonate
$CaCO_3$

Magnesium bicarbonate
$Mg(HCO_3)_2$

Magnesium carbonate
$MgCO_3$

Calculation of Carbonate- & Non-carbonate Hardness

H = Total Hardness (Calcium + Magnesium) in mg/L as $CaCO_3$
T = Total Alkalinity (Carbonate + Bicarbonate) in mg/L as $CaCO_3$

Case I   If   **H > T:**
                                Non-carbonate Hardness = H - T
                                Carbonate Hardness = T

Case II   If   **H $\leq$ T:**
                                Carbonate Hardness = H
                                Non-carbonate Hardness = 0

Non-carbonate Hardness is formerly called as *permanent hardness* because it cannot be removed or precipitated by boiling and the anions participating are sulfate, chloride and nitrate.
Carbonate hardness is formerly called as *temporary hardness* because it can be precipitated by prolonged boiling

Dissolved Oxygen (DO)

- Dissolved Oxygen (DO) concentration in natural waters is of great importance as it is critical for the sustainability of aquatic ecosystems
- DO derives from atmosphere or oxygen-producing biological processes (e.g., photosynthesis)
- The normal DO level of a healthy surface water body ranges from 8-10 mg/L, while the value for groundwater may be as low as 1-2 mg/L
- Reduction of DO values to less than 4 mg/L results in difficulties and even death for aquatic animals
- Low DO values may indicate organic pollution and/or presence of reduced species in the water bodies, resulting in DO depletion of the water
- Following Henry's Law, the rate of oxygen transfer in water is given by:

$$\frac{dC}{dt} = K_L a(C_S - C)$$

where, C_s = Saturated oxygen concentration, mg/L

C = Oxygen concentration at any time 't', mg/L

$K_L a$ = Oxygen transfer rate coefficient, h^{-1}

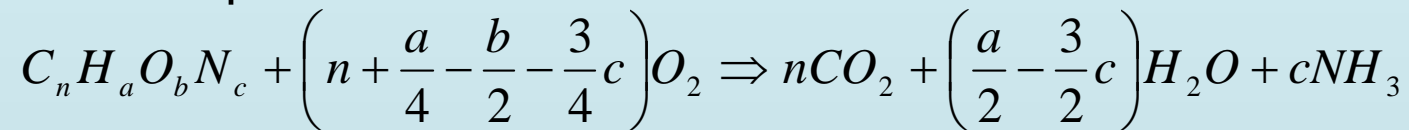$C_s - C$ = Dissolved oxygen deficit, mg/L

Oxygen Demand

▸ It is a measure of the amount of organic and inorganic matter present in water

▸ Relates to oxygen consumption in a river or lake as a result of a pollution discharge

▸ Measured in several ways:

  ▸ Theoretical Oxygen Demand (ThOD)

  ▸ Chemical Oxygen Demand (COD)

  ▸ Biochemical Oxygen Demand (BOD)
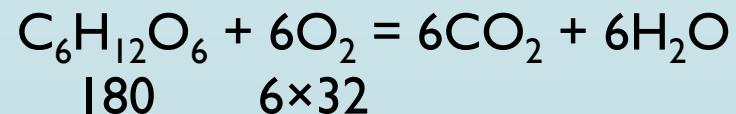
Theoretical Oxygen Demand (ThOD)

Generalized balanced equation:

$$C_n H_a O_b N_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c \right) O_2 \Rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c \right) H_2O + cNH_3$$

Example for Glucose:

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$
$$180 \qquad 6\times32$$

Oxygen Demand (OD)

$$= \frac{6 \times M_{O_2}}{M_{C_6H_{12}O_6}} = \frac{6 \times 32}{180} mg\ O_2\ /\ mg\ of\ Glu\cos e = 1.07 mg\ O_2\ /\ mg\ of\ Glu\cos e$$

If glucose concentration in water is 360 mg/L, ThOD is:
$$1.07 \times 360 \text{ mg/L} = \underline{385.2 \text{ mg/L}}$$

Practice for: Sucrose (**$C_{12}H_{22}O_{11}$**), Glycine ($C_2H_5NO_2$), Acetic acid (CH_3COOH), etc.
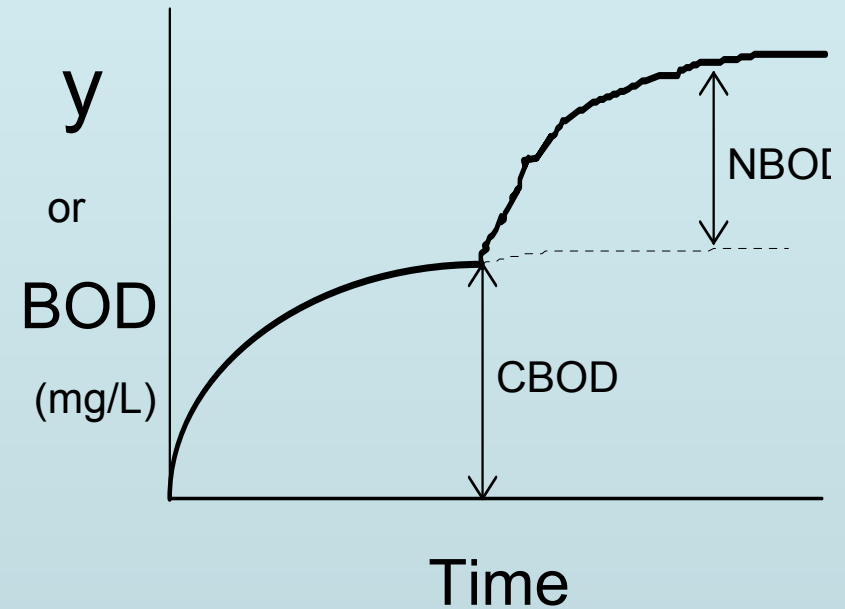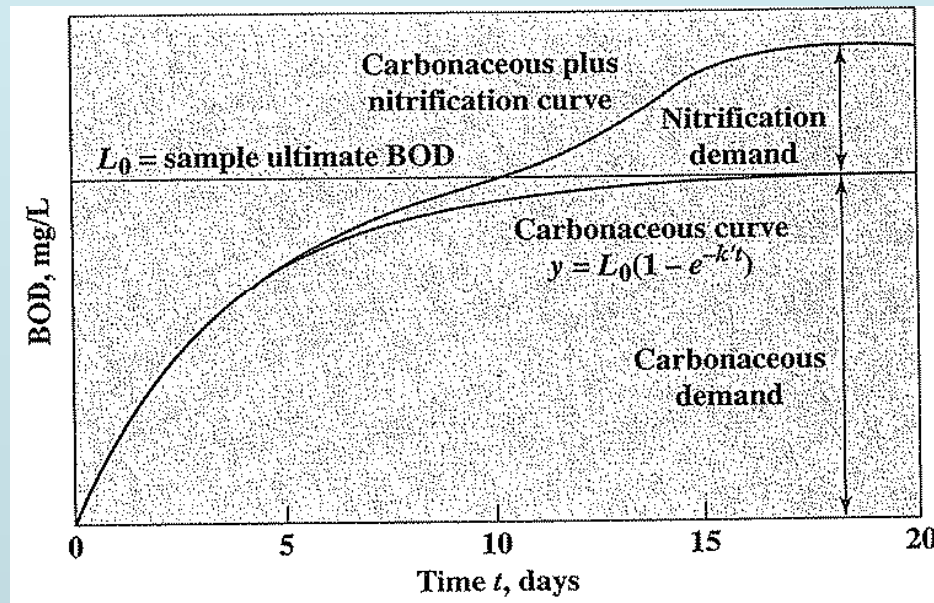
Chemical Oxygen Demand

- COD value represents the amount of oxygen that will be required to completely oxidize all organic matter in the sample to CO_2

- Measure of oxygen equivalent of the organic matter present in the water sample that is susceptible to oxidation by a strong chemical oxidant (acid + heat)

- Known (but excess) amount of Potassium dichromate ($K_2Cr_2O_7$), a strong oxidizing agent is added to the sample under acidic conditions to find the amount of organic compound in water sample

- Acidic condition is ensured by the addition of concentrated sulphuric acid (H_2SO_4) in the presence of Ag_2SO_4 as catalyst

- The mixture is heated (digested) at 150 ± 2^0C for 2 h

- COD is expressed in mg/L

Biochemical Oxygen Demand

▸ BOD is the amount of dissolved oxygen utilized by microbes for the biochemical oxidation of organic (carbonaceous BOD) and inorganic (nitrogenous BOD) matter

▸ BOD determination involves the measurement of the dissolved oxygen (DO) used by microorganisms in the biochemical oxidation of organic matter

▸ Biochemical oxidation is a slow process and theoretically takes an infinite time for completion

▸ Within a 20-day period, the oxidation is about 95-99 percent complete, and in the 5-day period used for the BOD test, oxidation is 60-70 percent complete

▸ The five-day biochemical oxygen demand (BOD_5) at 20°C is the most widely used parameter for quantifying biodegradable organic pollution, applied to both wastewater and surface waters

▸ Five-day BOD at 20°C is equivalent to three-day BOD at 27°C

▸ BOD is expressed in mg/L

Biochemical Oxygen Demand

Carbonaceous plus nitrification curve

Nitrification demand

L_0 = sample ultimate BOD

Carbonaceous curve $y = L_0(1 - e^{-k't})$

Carbonaceous demand

BOD, mg/L

Time t, days

y or BOD (mg/L)

NBOD

CBOD

Time

| CARBONACEOUS OXYGEN DEMAND (CBOD) | + | NITROGENEOUS OXYGEN DEMAND (NBOD) | = | BOD |

CBOD:

$$C_{Org.} + O_2 \longrightarrow CO_2 + H_2O$$

NBOD:

$$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-$$

Nitrogenous BOD (NBOD)

$$NH_3 + 1.5O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + H_2O + H^+$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{\text{Nitrobacter}} NO_3^-$$

Complete Reaction:

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H_2O + H^+$$
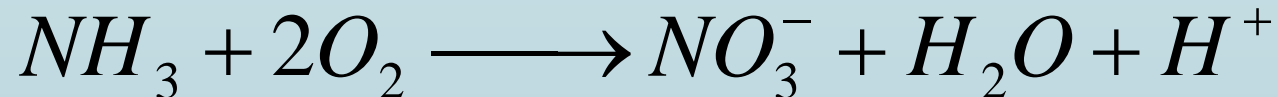
Oxygen Demand:

        2 moles oxygen/mole of ammonia

        i.e., 3.76 mg oxygen/mg ammonia

        i.e., 4.57 mg oxygen/mg NH_4^+-N

Calculation of BOD$_5$

Case I: When unseeded dilution water is used

$$BOD = \frac{DO_i - DO_f}{P} \quad \textbf{OR} \quad BOD = \left(DO_i - DO_f\right) \times D$$

where:

DO$_i$ = initial dissolved O$_2$ concentration

DO$_f$ = final or 5-day dissolved O$_2$ concentration

P = volumetric fraction

D = dilution factor = 1/P

Example: 5 ml wastewater is added to a 300 ml BOD bottle and then incubated for 5 days at 20^{0}C.

$$DO_i = 8 \text{ mg/L} \qquad DO_f = 2 \text{ mg/L}$$

$$P = \frac{5}{300} = 0.0167 \quad D = 300/5 = 60$$

$$BOD_5 = \frac{8 - 2}{0.0167} = 360 \text{ mg/L}$$

Calculation of BOD$_5$

Case II: When seeded dilution water is used

$$BOD_5 \ (mg/L) = \frac{(D_i - D_f) - f(B_i - B_f)}{P}$$

where:

D_i = initial DO concentration of sample, mg/L

D_f = final or 5-day DO concentration, mg/L

B_i & B_f = initial and final or 5-day DO concentrations of the seed or blank

P = volumetric fraction

f = fraction of seed in the incubated sample = $1 - P$

Example: 5 ml wastewater is added to a 300 ml BOD bottle, filled them with seeded dilution water and then incubated for 5 days at 20^{0}C.

Sample: D_i = 8 mg/L D_f = 1.7 mg/L

Blank or Seed: B_i = 8.2 mg/L B_f = 8.0 mg/L

$P = \dfrac{5}{300}$ = 0.0167 $1 - P$ = 0.9833

$$BOD_5 = \frac{(8 - 2) - 0.9833 \times (8.2 - 8.0)}{0.0167} = 347.50 \ \text{mg/L}$$

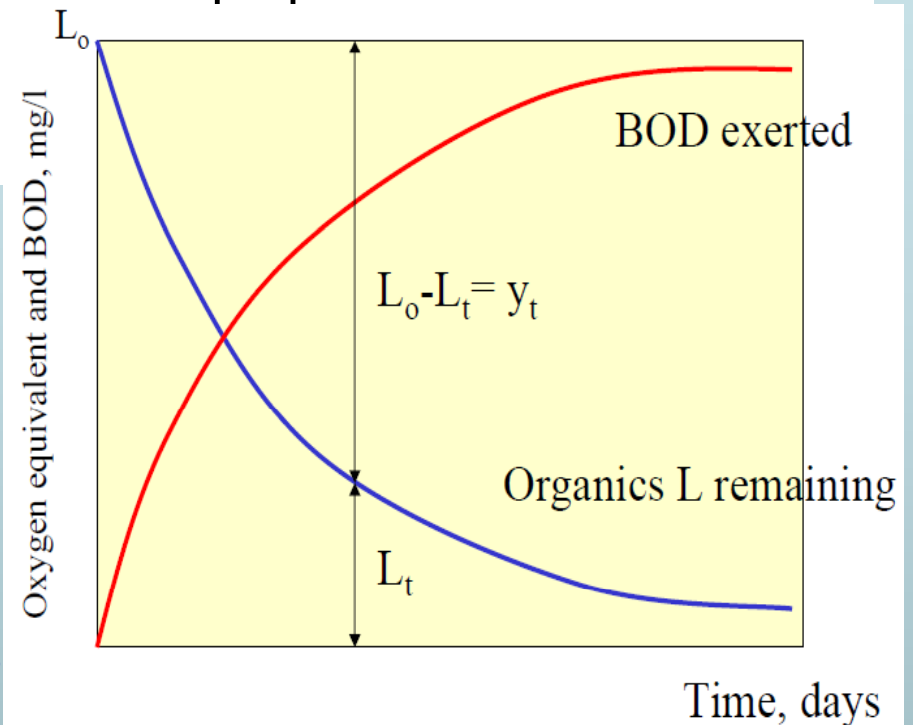*Think:* **Why seeding is required?**

BOD Kinetics

- BOD_5 only represents the oxygen consumed in 5 days and is about 60-70% of total BOD or ultimate BOD

- Total BOD or ultimate BOD or BOD at any time period can be determined knowing the BOD kinetics

- *Assumption:* Organic matter utilization by the microorganisms is first-order reaction i.e. rate at which organics utilized is proportional to the amount available

- Mathematically, this can be expressed as:

$$\frac{dL_t}{dt} = -kL_t \quad \textit{(Note the −ve sign)}$$

where:

L_t = oxygen equivalent of the organic matter at time 't', mg/L

k = BOD reaction constant, d^{-1}

[Figure: Graph with x-axis "Time, days" and y-axis "Oxygen equivalent and BOD, mg/l". Red curve labeled "BOD exerted" rising toward L_o. Blue curve labeled "Organics L remaining" decreasing. Labels: L_o, $L_o - L_t = y_t$, L_t.]

BOD Kinetics

$$\frac{dL_t}{L_t} = -k \; dt$$

• The equation can be rearranged and integrated as follows:

$$\int_{L_0}^{L_t} \frac{dL_t}{L_t} = -k \int_0^t dt$$

L_0 = total oxygen equivalent of the organic matter at time 0 i.e. initially, mg/L

$$\ln\left(\frac{L_t}{L_0}\right) = -kt$$
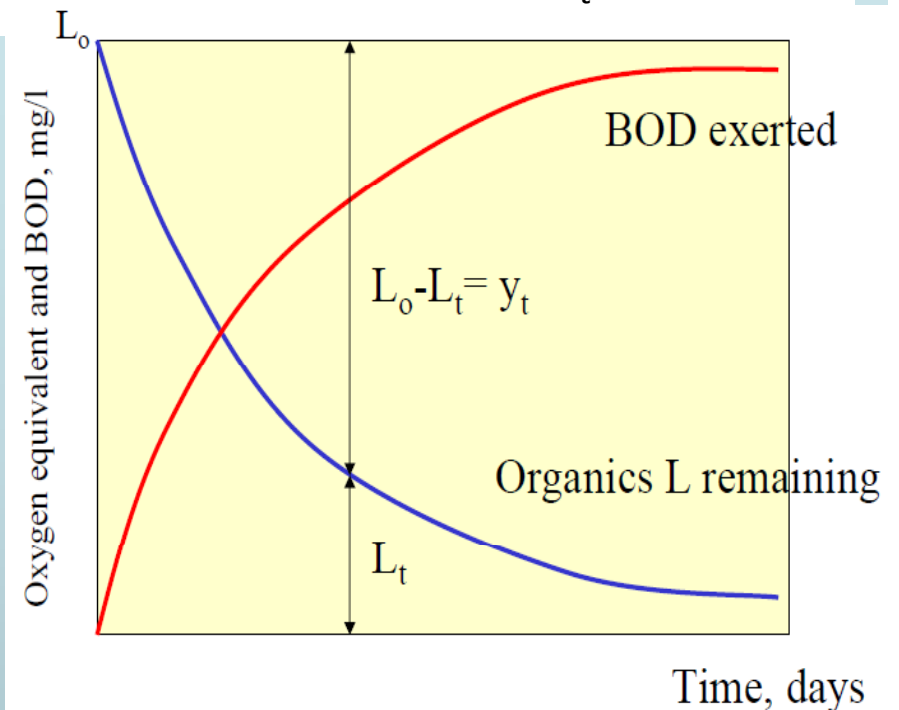
$$L_t = L_0 e^{-kt}$$
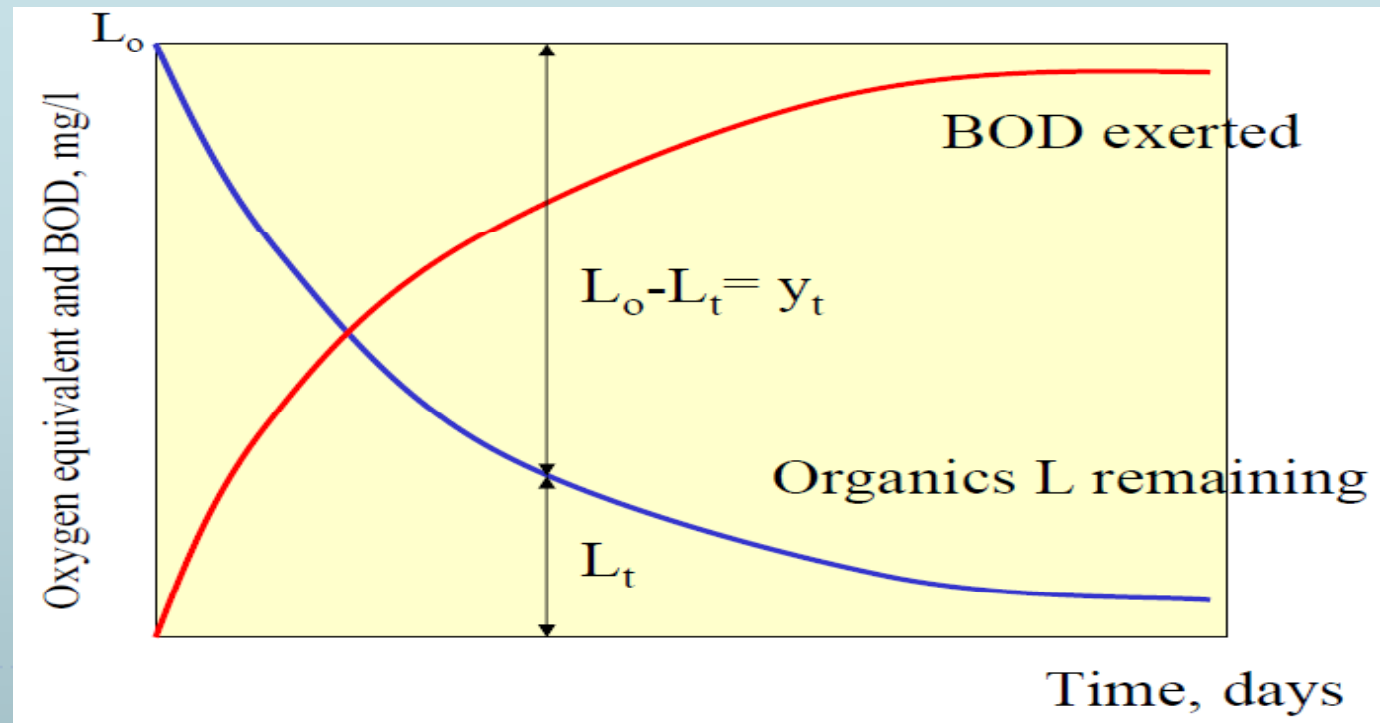
BOD Kinetics

- The oxygen equivalent remaining i.e. L_t is not the parameter of primary importance

- However, the amount of oxygen used or consumed in the degradation of organics i.e. BOD_t or y_t is important and can be found out from the L_t value

- Mathematically, the BOD exerted i.e. y_t is:

$$y_t = L_0 - L_t$$

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

$$y_t = L_0\left(1 - e^{-kt}\right)$$

- The value of y_t approaches L_0 asymptotically, indicating that the total or ultimate BOD (y_u or BOD_u) is equal to the initial oxygen equivalent i.e. L_0

BOD Kinetics

- The final equation is:

$$BOD_t \equiv y_t = L_o(1 - e^{-kt})$$

- The value of BOD reaction constant i.e. k determines the speed of the BOD reaction without influencing the magnitude of BOD_u

- Values of k range from about 0.1 to 0.5 d^{-1} depending on the nature of organic matter

- The value of k for any given organic compound is temperature dependent and the change in k with temperature can be approximated by the van't Hoff-Arrhenius model:
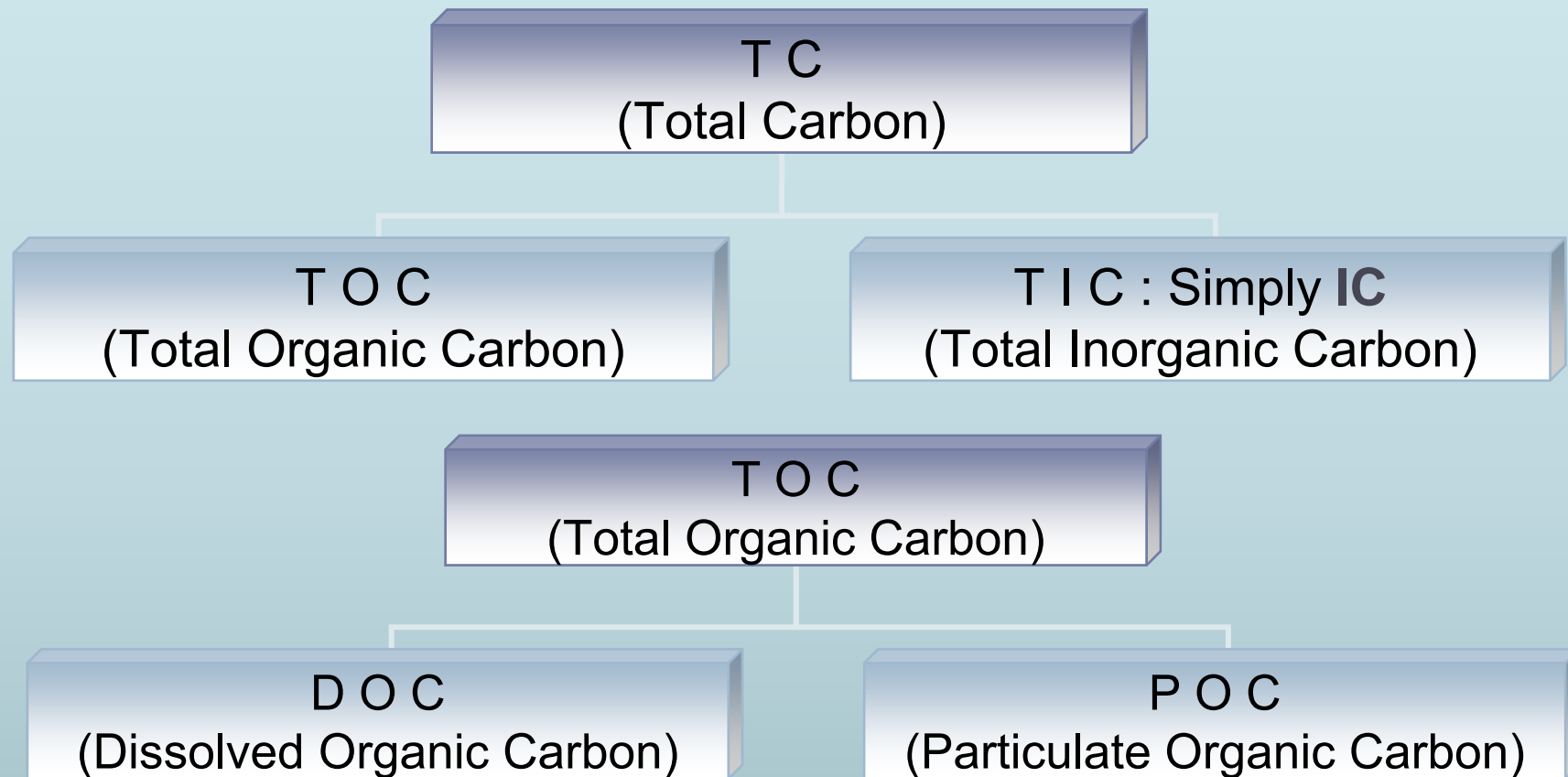
$$k_T = k_{20}\theta^{T-20^0} \qquad (\theta = 1.047)$$

COD *vs* BOD

❑ COD does not distinguish between biodegradable and non-biodegradable organic matter whereas BOD only measures biodegradable organic matter

❑ COD is not specific to oxygen-consuming organics or inorganic whereas BOD is specific to oxygen-consuming organic or inorganic compounds

❑ COD and BOD do not necessarily measure the same types of oxygen consumption

❑ COD determination requires less time (2-3 h) as compared to BOD determination (5 d)

Total Organic Carbon (TOC)

▸ TOC is a general measure for organic pollutants mass in water/wastewater (similar to COD function, but more precise)

▸ The amount of carbon bound or organic fraction of carbon in water/wastewater

```
                    T C
                (Total Carbon)
                 /          \
        T O C                  T I C : Simply IC
  (Total Organic Carbon)      (Total Inorganic Carbon)

                    T O C
                (Total Organic Carbon)
                 /          \
        D O C                  P O C
  (Dissolved Organic Carbon)  (Particulate Organic Carbon)
```

Nutrients: Nitrogen

- ❑ Nitrogen forms found in water (expressed as mg-N/L):
  - ▪ Dissolved gaseous N_2
  - ▪ Dissolved free (unionized) ammonia (NH_3)
  - ▪ Ionized ammonia (NH_4^+)
  - ▪ Nitrite ion (NO_2^-)
  - ▪ Nitrate ion (NO_3^-)
  - ▪ Organic nitrogen
- ❑ In surface water samples, nitrogen is present mainly as nitrate (NO_3^-), which is the most oxidized form of nitrogen
- ❑ In groundwater samples nitrogen may be present as both nitrate (NO_3^-) and nitrite (NO_2^-)
- ❑ In raw wastewater samples, and in water contaminated with domestic and industrial wastes, nitrogen is mainly present as ammonical nitrogen (NH_4^+-N or NH_3-N), and organic nitrogen (Org.-N)
- ❑ Total Kjeldahl Nitrogen (TKN) = NH_4^+-N + Org.-N and expressed in mg NH_4^+-N/L
- ❑ Depending on pH (at 9.3) of water system, free and ionized ammonia are in equilibrium according to the following equation:

$$NH_4^+ \rightarrow NH_3 \uparrow + H^+$$

Nutrients: Phosphorous

❑ Phosphorous is mainly found in water as soluble mineral phosphate ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}), soluble organic P and particulate P. Organic P can be mineralized into soluble mineral phosphate by bacteria.

❑ Sources of phosphorous in wastewater are: detergent, fertilizer and animal waste

❑ Phosphorous in water/wastewater is expressed as mg PO_4^{3-}-P/L

❑ Excessive amount of nutrients i.e. N and P in water leads to algae formation → Algal bloom → Eutrophication

Routine Water Quality Analysis

▸ A "routine" water quality analysis usually includes all the major constituents (except carbonic species).

▸ All the minor constituents (also regarded as trace constituents) are also to be expected.

▸ Checking the *ion balance* or *charge balance* is a good practice to eliminate gross errors induced in the routine water quality analysis.

▸ Errors mainly arise as a result of:
  ▸ Improper sample storage (including sealing of container and buffering)
  ▸ Failure to measure rapidly changing *on-site* parameters in the field (pH, alkalinity, etc.)
  ▸ Poor or no filtration for removal of suspended solids.

▸ An error of less than 10% is generally acceptable in analysis

  ▸

Example of Routine Water Quality Analysis: *Ion Balance and Error Analysis*

Problem Statement: Results are shown below from a routine water quality analysis being run on a water sample -

Constituents	Concentration (mg/L)	Constituents	Concentration (mg/L)
Ca^{2+}	55.0	HCO_3^-	250.0
Mg^{2+}	18.0	SO_4^{2-}	60.0
Na^+	98.0	Cl^-	89.0
pH = 7.7			

Perform the *ion balance* or *charge balance* based on the analysis results and estimate the percent error induced in the analysis. Also, construct a representative bar diagram of the *ion balance* or *charge balance*.

Example of Routine Water Quality Analysis: *Ion Balance and Error Analysis*

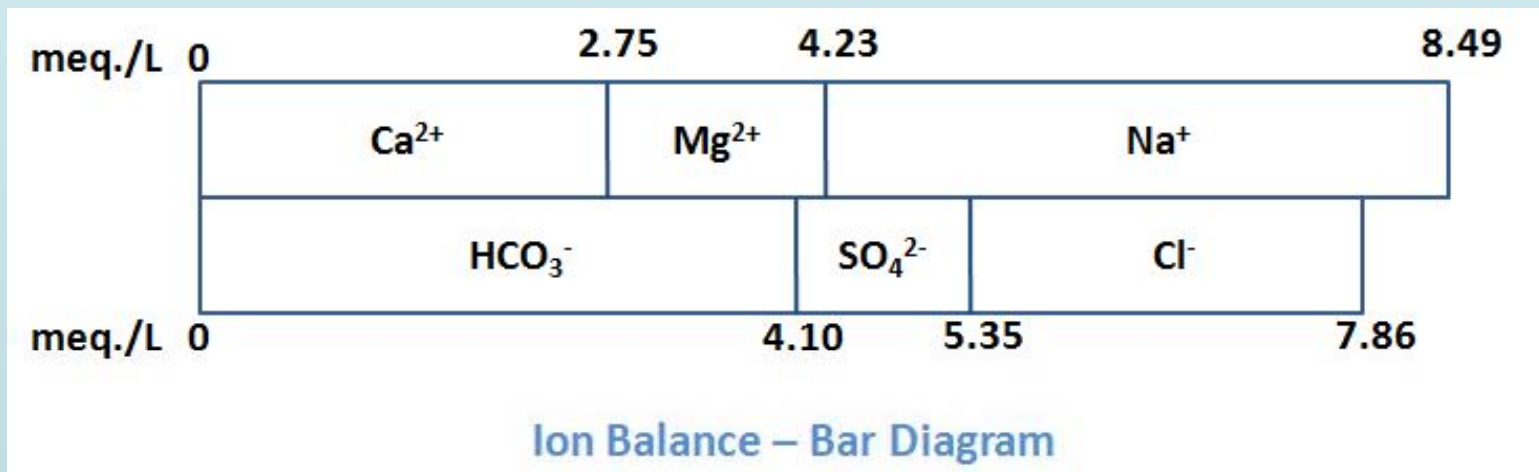*Solution:* The ion balance or charge balance based on the analysis results -

Ion	Cations			Ion	Anions		
	Conc. (mg/L)	Eqv. (mg/meq.)	Eqv. Conc. (meq./L)		Conc. (mg/L)	Eqv. (mg/meq.)	Eqv. Conc. (meq./L)
Ca^{2+}	55.0	40/2	2.75	HCO_3^-	250.0	61/1	4.10
Mg^{2+}	18.0	24.3/2	1.48	SO_4^{2-}	60.0	96/2	1.25
Na^+	98.0	23/1	4.26	Cl^-	89.0	35.5/1	2.51
Total Ions			**8.49**				**7.86**

Estimation of the percent error induced in the analysis:

$(8.49 - 7.86) \times 100 / 7.86 = 8\% < 10\%$ (Acceptable)

Example of Routine Water Quality Analysis: *Ion Balance and Error Analysis*

Solution: The representative <u>bar diagram</u> of the *ion balance* or *charge balance* -

Ion Balance – Bar Diagram

Ion	Cations			Ion	Anions		
	Conc. (mg/L)	Eqv. (mg/meq.)	Eqv. Conc. (meq./L)		Conc. (mg/L)	Eqv. (mg/meq.)	Eqv. Conc. (meq./L)
Ca^{2+}	55.0	40/2	2.75	HCO_3^-	250.0	61/1	4.10
Mg^{2+}	18.0	24.3/2	1.48	SO_4^{2-}	60.0	96/2	1.25
Na^+	98.0	23/1	4.26	Cl^-	89.0	35.5/1	2.51
Total Ions			8.49				7.86

MICROBIOLOGICAL PARAMETERS

- There are several types of organisms like viruses, bacteria, fungi, protozoa, algae, worms (hook worm, tape worm, blood worm, etc.) which find their way into aquatic environment, and are of environmental significance.

- These organisms can be grouped into following three categories based on their natural habitat:

- *Aquatic organisms:* These are generally present in surface waters. Water is their natural habitat and hence are also referred as natural organisms by water supply engineers. These are natural flora and fauna, and are not pathogens or disease causing organisms. However, these may cause colour, taste, odour, clogging, corrosion, etc. problems. *Example:* pseudomonas, algae, etc.

- *Soil organisms:* Soil is their natural habitat. They enter in to aquatic environment through soil-water contact. These can't survive in water for a long time. *Example:* Aerobacter aerogens.

- *Intestinal organisms:* These organisms are the natural habitats of warm-blooded animals and are discharged in large numbers in feces. These enter in aquatic environment when fecal matter or sewage comes in contact with water or discharged into water bodies. Many pathogenic organisms like clostridum, entrococci, streptococci, salmonella, shigella, viruses, etc. are present in sewage. These organisms do not live longer outside their natural habitat. If they reach a host before they die, they are likely to cause diseases. *Coliform organisms, which generally, do not cause disease are also present in large number in sewage.*

MICROBIOLOGICAL PARAMETERS

Selection of Microbiological Parameter(s)

The selection of microbiological parameters for water quality analysis is guided by following limitations:

1. There are many pathogens or disease causing organisms. The questions arises as to which pathogen we should check or we should check for all pathogens. Measurability or its ease is an important attribute. Performing test in reasonable time and available resources is a major factor for routine analysis. One can think of microscopic examinations, but is not feasible. Many organisms look alike but produce different types of disease. Even otherwise microscopic examination is not a feasible proposition for routine analysis.

2. Number of pathogens in treated water is small and hence testing becomes difficult.

3. Tests available are destructive→ Not for organisms but for the sample.

4. The pathogens are very specific to the environment (host).

MICROBIOLOGICAL PARAMETERS

Selection of Microbiological Parameter(s): **Indicator Organisms**

In order to overcome the aforementioned difficulties, we use *indicator organisms* which indicate the possible presence of pathogens. The desirable properties of the indicator organisms are as follows:

▸ They should always be present along with the pathogens i.e. source of pathogens and indicator organisms should be same.

▸ They should be present in large number compared to pathogenic organisms.

▸ They should be easily measurable →Time, resources (money) and skill.

▸ They should have same or more resistance to various water treatment operations, particularly disinfection.

MICROBIOLOGICAL PARAMETERS

Selection of Microbiological Parameter(s)

Coliform Group

Coliform group of bacteria as a whole are universally accepted indicator of fecal pollution and suggests potential presence of pathogens responsible for infections transmitted by the fecal oral route, because they are present in high number in the feces of the warm-blooded animals including human beings. All persons, sick or not, excrete them in large numbers.

▸ Presence of indicator organisms is a *necessary condition, but not a sufficient condition*, for the presence of pathogens (healthy persons will not harbour pathogens).

▸ Major members of the coliform group:

Escherichia Coli → *E. Coli* or *B. Coli* (Bacillus Coli)

Klesbiella → 100% Fecal origin

Enterobacter → Also called fecal coliform

Citrobacter → Non-pathogen but in high concentration cause diarrhea in infant.