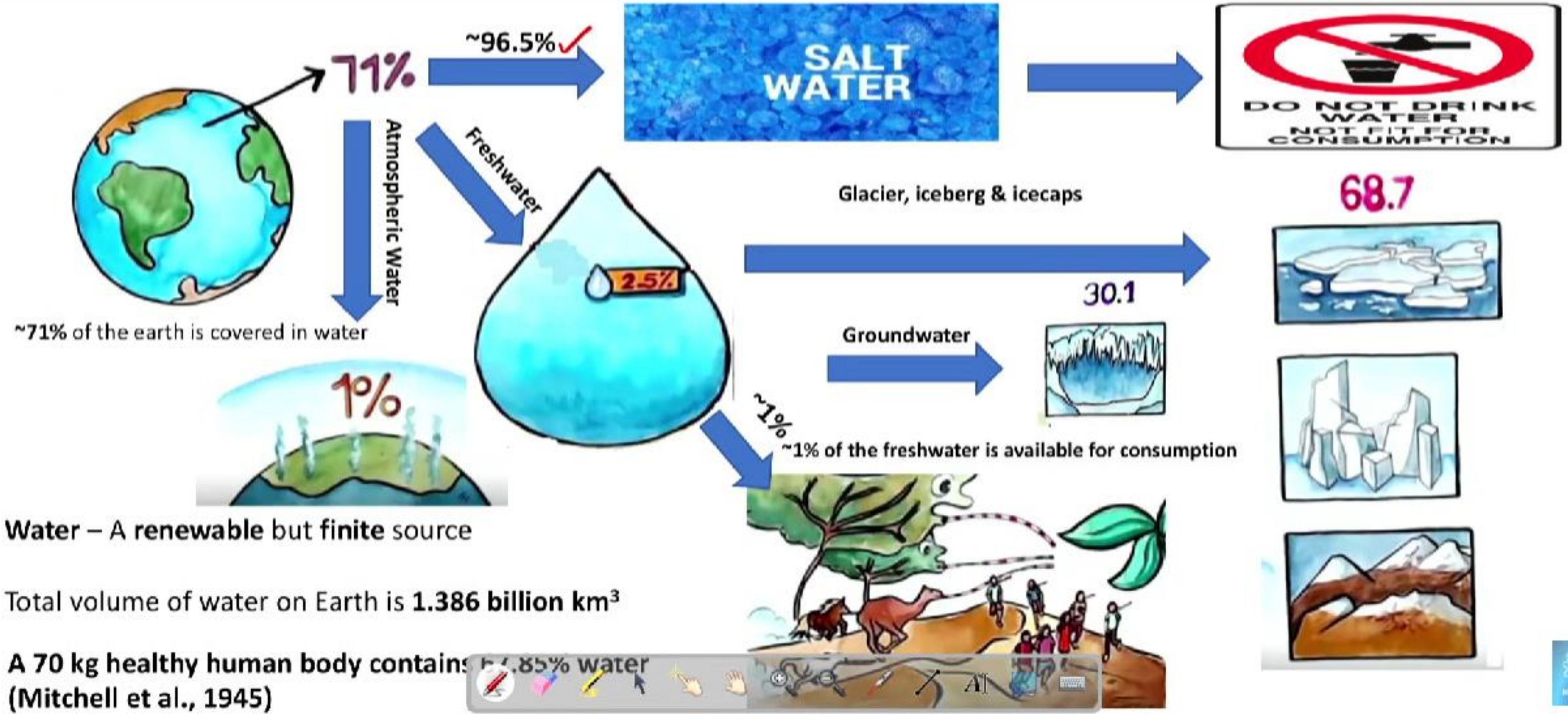
Water Availability & Consumption



Water – A **renewable** but **finite** source

Total volume of water on Earth is **1.386 billion km^3**

A 70 kg healthy human body contains 67.85% water (Mitchell et al., 1945)

Hydrological Cycle

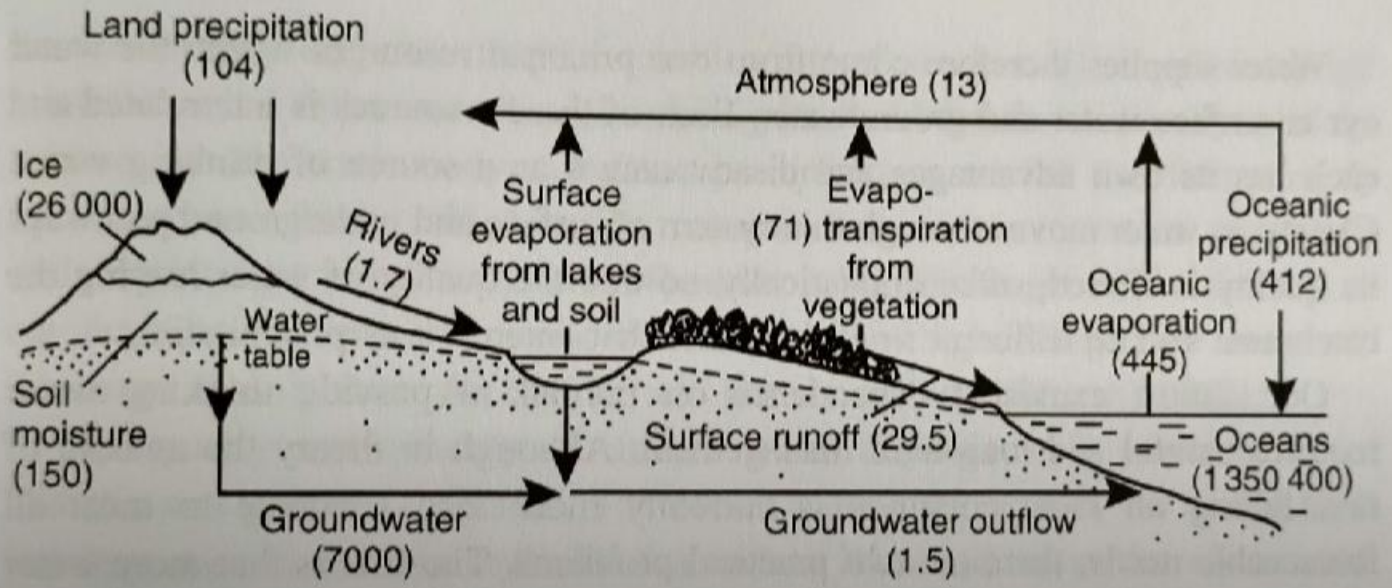


Figure 4.1 Hydrological cycle showing the volume of water stored and the amount cycled annually. Volumes expressed in 10^3 km^3.

Hydrological Cycle

- Water is considered a renewable resource, as it can be replenished after use by hydrological cycle
- All water sources are interconnected by constant motion of water molecule via hydrological cycle
- This flow of water through the earth's environment constitutes the water cycle also known as the hydrological cycle
- It keeps the volume of water in particular water reservoir remains more or less constant under natural conditions, unless over exploitation by man.
- It ensures the continuity and availability of water in the environment

Hydrological Cycle

- The driving force for the cycle is the solar energy from the sun
- The three basic process involved in the cycle are:
  - evaporation
  - condensation
  - precipitation
- The other major processes include
  - transpiration
  - convection
  - freezing
  - melting
  - runoff
  - groundwater fl

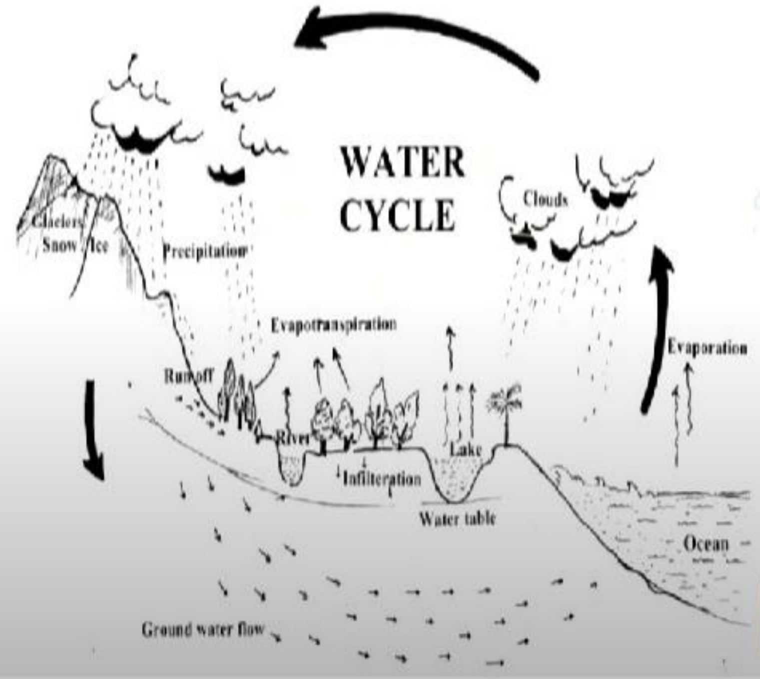


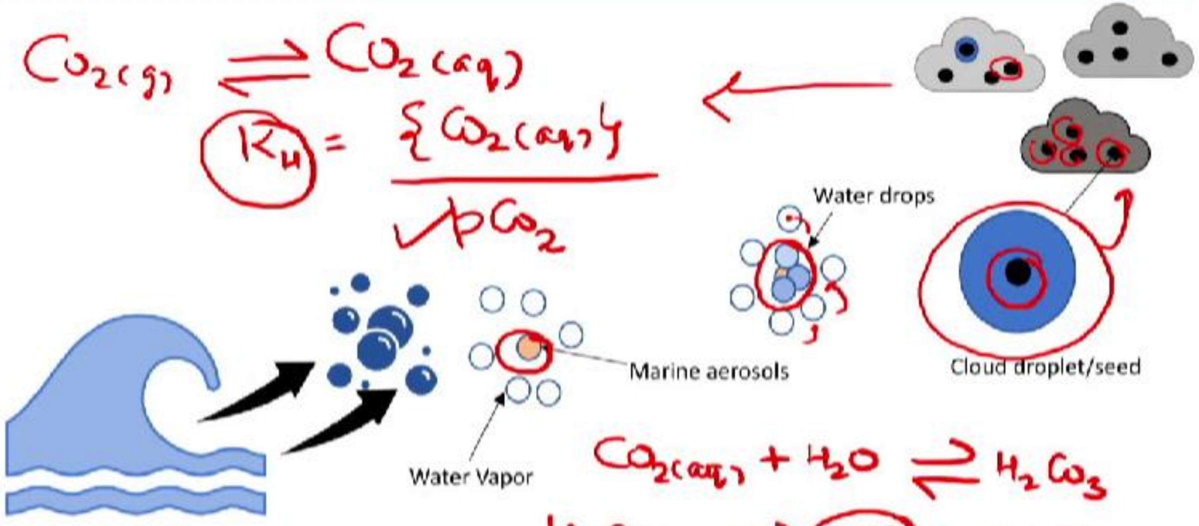
Figure 2. Glo ater cy

Natural Water Composition: Rain

Constituent	Concentration (mg/L)
Na^+	1.98
K^+	0.3
Mg^{2+}	0.27
Ca^{2+}	0.09
Cl^-	3.79
SO_4^{2-}	0.58
HCO_3^-	0.12
pH	5.7

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$

$$K_H = \frac{\{CO_{2(aq)}\}}{pCO_2}$$



$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$\boxed{pH < 5.7}$

- Rainwater is largely derived from the sea
- Marine aerosols formed due to the breaking of bubbles
- The droplets dehydrate to form chloride and sulphate aerosols
- The aerosols become nucleation centre for moisture to condense and form clouds

River Water Composition

- River water composition is largely determined by three factors

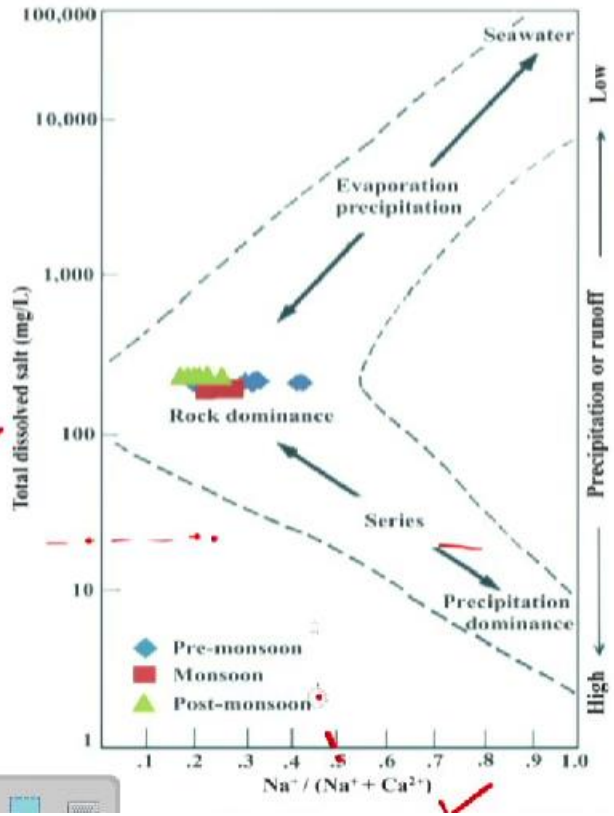
a) The salts in rain water (Precipitation dominance)

b) The weathering and erosion of continental material (Rock dominance)

Ca^{2+} CO_3^{2-}

c) Evaporation due to solar heating (Evaporation precipitation dominance)

- Gibbs (1970) developed a diagram by plotting TDS vs $Na^+/(Na^+ + Ca^{2+})$ to explain the dominance of the above-mentioned factors



River Water Composition

Constituent	Concentration (mg/L)
Na^+	6.3
K^+	2.3
Mg^{2+}	4.1
Ca^{2+}	15
Fe	0.67
Al	0.01
Cl^-	7.8
SO_4^{2-}	11.2
HCO_3^-	58.4
SiO_2	13.1

Garrels & MacKenzie (1971)

- 95-99% of total dissolved solute in any natural water are the seven ions 4 cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and 3 anions (Cl^-, SO_4^{2-}, HCO_3^-)
- Usually Ca^{2+} is almost always greater in concentration than Mg^{2+} (exception seawater) and Na^+ is almost always greater than K^+

What would be the composition of lake water?

Seawater Composition

Component	Concentration (g/L)
Na	10.76
K	0.399
Ca	0.412
Mg	1.294
Cl	19.35
Sulphate	2.712
Total Alkalinity (eq/L)	2.3E-3
pH (units)	8.1

Water Chemistry, Brezonik & Arnold, Oxford University Press, 2011

- High TDS due to evaporation/crystallization and deposition of weathered minerals
- Ca and carbonate concentration has decreased over the course of the rivers
- Na and Cl concentrations build-up, relatively Mg also

Groundwater (GW) Composition

- Depends on geochemical condition in the sub-surface region
- Typically, high on divalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} etc.
- DO not present enough; aeration required before consumption
- Bicarbonate ions present in higher concentration than other water systems

Constituent	Concentration (mg/L)
Na^+	8.5
K^+	1.3
Mg^{2+}	19.4
Ca^{2+}	80
Cl^-	35
SO_4^{2-}	8.2
HCO_3^-	207.4
SiO_2	14
pH	7.48

Water Chemistry, Brezonik & Arnold, Oxford University Press, 2011

Water Pollution

- Water pollution: The release of substances into water bodies at such a concentration that interferes with the beneficial use of water or with natural functioning of the ecosystem
- It is any change in physical, chemical or biological properties of water that can make it unfit for consumption and can have harmful impact on living beings and the environment
- Water pollution is mostly anthropogenic
- It is one of the leading causes of deaths in most developing countries

https://www.britannica.com/science/water-pollution

- **Water Quality Parameters**
  - **Chemical**
    - **Organic**
    - **Inorganic**
  - **Physical**
  - **Biological**
  - **Physiological**

- Water quality parameters provide us a parametric basis to classify a water sample as polluted or fit for various applications
- Not all applications require same water quality

Chemical Oxygen Demand (COD)

Org. matter $+ O_2 \longrightarrow CO_2 + H_2O$

$Hg^{2+} + Cl^-$

$HgCl^+$

$HgCl_2$

- COD is an indirect method of estimating the organic pollutant level in a water sample

H_2SO_4 $Cl^- \rightarrow Cl_2$ $4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$ $\frac{32}{4} = 8$ mg/meq O_2

- It is defined as the amount of oxygen needed to completely oxidize the organic matter to CO_2 and H_2O in a given volume of sample expressed as mg of O_2 needed per L of the sample. Higher the amount of oxygen needed, higher would be the organic loading in the sample. Fe^{2+}

Ferrous Ammonium Sulphate

$Fe^{2+} \rightarrow Fe^{3+}$

- The standard method for determining COD is to conduct a titrimetric dichromate (0.25 N $K_2Cr_2O_7$) test $Cr^{+6} \rightarrow Cr^{3+}$

COD in the discharge effluent to receiving water bodies should not exceed 250 mg/L according to Indian standard

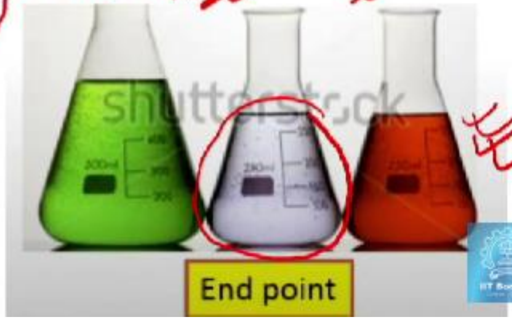


Image Courtesy: Dr. Manjunath Channegowda, Asst. Prof. Chemistry, RVCE

Biochemical Oxygen Demand (BOD)

$L = L_0(1-\exp(-k_d t))$, BOD_0, L_0, k_d

Biodegradable Org. matter + O_2 $\xrightarrow{\text{Aerobic bacteria}}$ $CO_2 + H_2O$

L = Biodeg. Org. matter

$L = L_0 \exp\{-k_d t\}$

$y = \Delta = L_0(1-\exp(-k_d t))$
$= DO_i - DO$

- The amount of dissolved oxygen needed (i.e. demanded) by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period.

DO initial Dissolved Oxygen

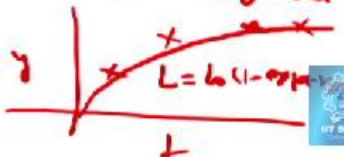
- The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20°C and is often used as a surrogate of the degree of biodegradable organic pollution of water
- First order rate kinetic has been observed for BOD degradation by bacteria
- The data for DO consumption is then curve fitted to the model and constants are obtained

$$y = BOD_0 * (1 - e^{-k_d t})$$

- Some common biodegradable pollutants are proteins, fats, carbohydrates, alcohols, esters etc
- Permissible level of BOD in effluent discharge for inland surface water <30 mg/L and for drinking water supply <2 mg/L

Dissolved Oxygen after 5 days = Amount of biodegr. Org. matter degraded

t	$y = DO_i - DO$
1	✓
2	
3	✓
4	
5	
6	✓
7	✓ y



$CO_{2(g)} \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$

Dissolved Oxygen

$O_{2(g)} \rightleftharpoons O_{2(aq)}$

$K_H = \frac{\{O_{2(aq)}\}}{pO_2}$

- One of the most important parameters that determine the quality of a river
- Important for sustaining life in aquatic environment

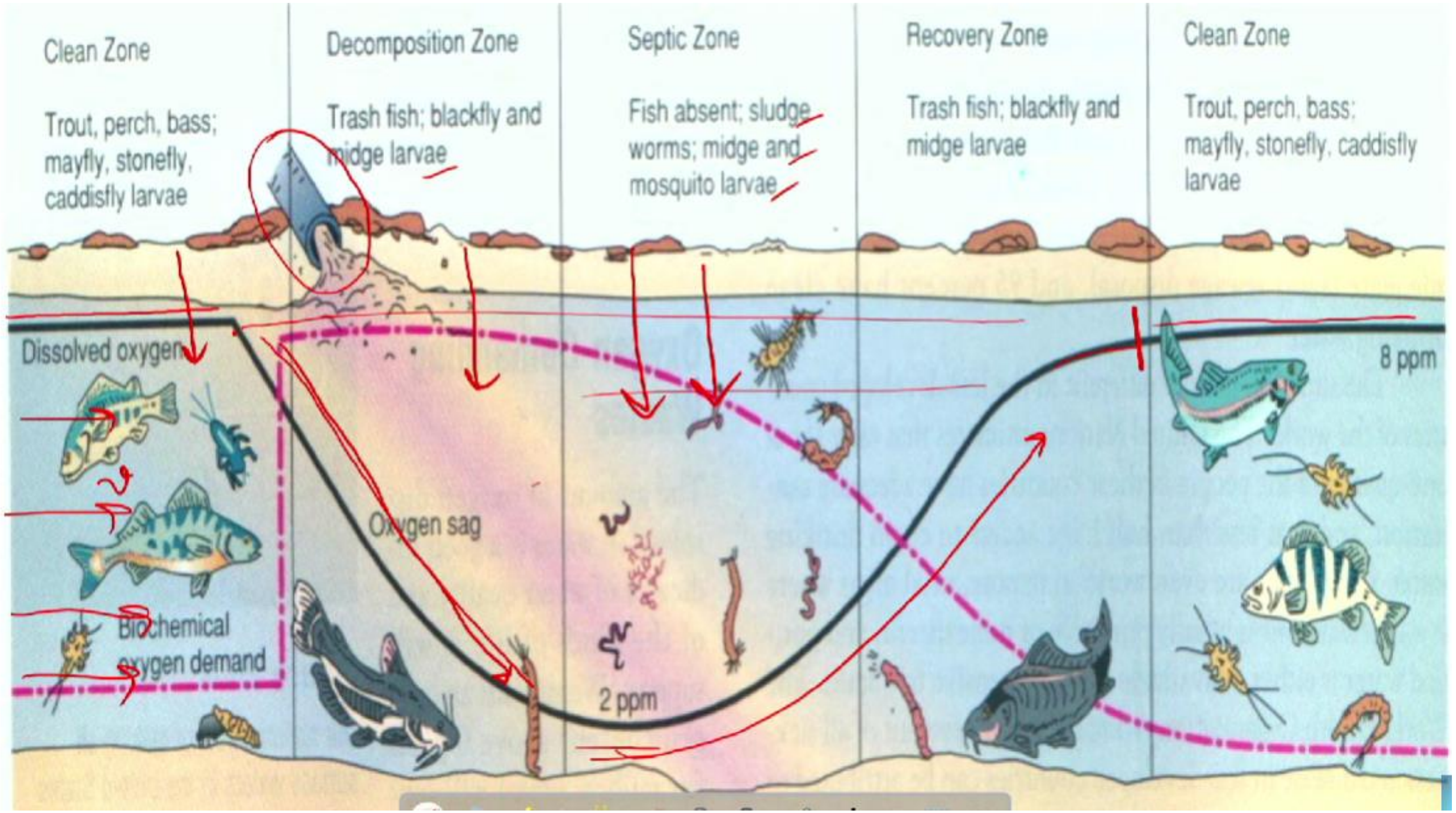
$O_{2(aq)}$

- DO levels in a healthy stream should be in the range of 7-9 mg/L
- Below 5 mg/L most fish particularly trout do not survive
- Decrease in DO levels creates anaerobic conditions, which can lead to the generation of gases like methane, carbon dioxide, hydrogen sulfide and ammonia

Reduced environment

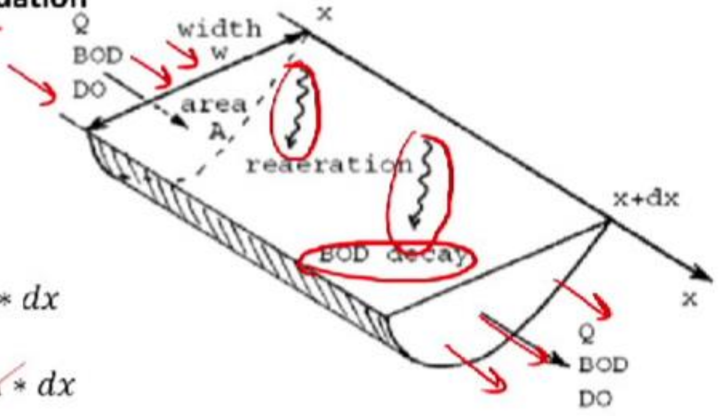
$\mu_{sea} > \mu_{river}$ Background salt ↳ Ionic strength

- Which one will have higher DO concentration: a sea or a river?
- You have two jars of water – jar a is at temperature 20°C throughout but jar b was first heated to 80°C and then cooled to 20°C immediately. In which jar a freshwater fish would be more comfortable?



Clean Zone
Trout, perch, bass; mayfly, stonefly, caddisfly larvae
Decomposition Zone
Trash fish; blackfly and midge larvae
Septic Zone
Fish absent; sludge worms; midge and mosquito larvae
Recovery Zone
Trash fish; blackfly and midge larvae
Clean Zone
Trout, perch, bass; mayfly, stonefly, caddisfly larvae
Dissolved oxygen
Oxygen sag
Biochemical oxygen demand
2 ppm
8 ppm

Streeter-Phelps Equation



DO advected at the boundaries = DO$_{in}$ by re-aeration – DO$_{lost}$ by BOD degradation

DO$_{in}$ by re-aeration = k_a*(DO$_{sat}$ – DO)

v & H/depth of the channel

DO$_{out}$ by BOD degradation = k_d*BOD$_0$ e$^{(-kdt)}$

$$v * A[DO + dDO - DO] = k_a[DO_{sat} - DO] * A * dx - k_d BOD_o e^{-k_d t} * A * dx$$

$$v * \cancel{A}[\cancel{DO} + dDO - \cancel{DO}] = k_a\underbrace{[DO_{sat} - DO]}_{Y\,=\,\text{deficit}} * \cancel{A} * dx - k_d BOD_o e^{-k_d t} * \cancel{A} * dx$$

$$v * \frac{dDO}{dx} = k_a y - k_d BOD_o e^{-k_d * \frac{x}{v}}$$

https://www.dartmouth.edu/~cushman/courses/engs43/River-oxygen-erosion.pdf

$$since \ \frac{dDO}{dx} = -\frac{dy}{dx} \rightarrow \boxed{v * \frac{dy}{dx} = -k_a y + k_d BOD_o e^{-k_d * \frac{x}{v}}}$$

Streeter-Phelps

Inorganic Water Quality Parameters

- Inorganic pollutants include inorganic acids, alkalis, salts, anions, cations, free chlorine, ammonia etc.
- They are added a result of industrial effluents, sewage, household cleansers and surface run-off from urban and agricultural field etc. nutrients N & P
- They affect the physical and chemical quality of water.
- Desirable residual chlorine 1 mg/L (inland SW), 0.2 mg/L (drinking water), chloride 250 mg/L (DW), Fe 0.3 mg/L (DW), nitrate 45 mg/L (DW) fluoride 1.9 mg/L (DW)
- Ammoniacal nitrogen (ISW); 50 mg/L as N, Kjeldahl nitrogen: 100 mg/L as N; dissolved phosphate: 5 mg/L

Pollutant	Examples
Acids	Phosphoric acid, sulfuric acid, hydrochloric acids etc.
Alkalis	Sodium hydroxide, lime etc.
Cations	Calcium, magnesium, sodium, potassium, ammonium, iron, manganese, aluminium, mercury, lead etc.
Anions	Phosphates, sulphates, chlorides, nitrites, nitrates, cyanides, carbonates, bicarbonates etc.

By USEPA Environmental-Protection-Agency - Algae bloom in Reflecting Pool, Washington, DC 2007 Potomac River, Chesapeake Bay watershed, USEPA photo by Eric

Inorganic Water Quality Parameters
Alkalinity

- Ability to resist changes in pH with respect to the addition of a strong acid is called alkalinity or acid neutralizing capacity of a water sample
- Alkalinity in natural water samples is largely attributed to the carbonate species (HCO_3^-, CO_3^{2-}) and OH^- silicates, borates, phosphates, bisulfide
- Alkalinity provides buffering capacity to aqueous system. Higher the alkalinity, higher the buffering capacity against pH changes
- Alkalinity is determined either using titrimetric method or measuring the alkalinity contributing species in a sample
- Mathematically, alkalinity is determined as

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] = \text{meq of alkalinity}$$

- Alkalinity is expressed as mg/L as $CaCO_3$

$\frac{100}{2} = 50$

$50 \frac{mg}{1\,meq} CaCO_3$

$\times 50 \frac{mg}{meq}$

Water Hardness

- Water hardness is due to the presence of divalent ions like Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+} etc. dissolved in water
- Presence of hardness causes taste, scaling issues during the water usage
- It is not that we should consume water completely devoid of hardness
- For drinking purpose, 60-120 mg/L a $CaCO_3$ is desirable

Description	Hardness (mg/l of $CaCO_3$)
Extremely soft	<17
Soft to moderately hard	17.1-60.0
Moderately hard	60-120
Hard	120-180
Very hard	>180
Too hard for ordinary domestic use	Over 250

Types of Water Hardness

- **Carbonate/Temporary Hardness:** This refers to hardness whose effects can be removed by boiling the water in an open container. Such waters have usually percolated though limestone formations and contain bicarbonate (HCO_3^-) of calcium and magnesium along with small amounts of carbonate (CO_3^{2-}) as the principal negative ions.
- Both calcium and magnesium bicarbonates decompose when water is boiled. Boiling the water promotes the reaction by driving off the carbon dioxide gas.
- $2\ HCO_3^- \rightarrow CO_3^{2-} + CO_2$
- The CO_3^{2-} reacts with Ca^{2+} or Mg^{2+} ions, to form insoluble calcium and magnesium carbonates which precipitate out, thus removing the calcium and magnesium ions from the water, and so removes the hardness. Therefore, hardness due to bicarbonates is said to be temporary.

Types of Water Hardness

- **Non-carbonate/Permanent Hardness:** Water containing other anions such as chloride or sulfate cannot be removed by boiling, and are said to be "permanently" hard.
- When measuring hardness, we typically consider total hardness which is the sum of all hardness compounds in water, expressed as a calcium carbonate equivalent. Total hardness includes both temporary and permanent hardness caused by calcium and magnesium compounds.

mg of $CaCO_3$ / L

Total Dissolved Solid/ salt

- On basis of salt quantity, water can be classified into fresh water and salt water (or ocean/sea water).
- Salinity of oceans is expressed as the amount of salt in 1000 g of water (referred to as 'parts per thousand' or ppt.)
- Most of the oceans have a salinity between 34 ppt and 36 ppt (35‰ - 36‰).
- Water with a salinity of less than 1 percent of that of the oceans (0.35‰) is defined as fresh water.
- **Total dissolved solids** (**TDS**) is a measure of the dissolved combined content of all inorganic and organic substances present in a liquid in molecular, ionized, or micro-granular (colloidal sol) suspended form.

Fresh:	<1,000 ppm TDS
Brackish:	1,000-5,000 ppm TDS
Highly Brackish:	5,000-15,000 ppm TDS
Saline:	15,000-30,000 ppm TDS
Sea Water:	30,000-40,000 ppm TDS
Brine:	40,000-300,000+ ppmTDS

Kohli et al., ePG Paathshaala, MHRD

Physical Water Quality Parameters: Color

- **Color**: It affects the aesthetic appearance of water body. It may or may not pose harm to health
- Harmful color producing chemical includes various dyes, toxic colored compounds of iron and chromium etc. Color is also produced by pigments like that of microalgae.
- Color is measured in Platinum-Cobalt units (Pt-Co) or Hazen units
- Spectrophotmetric technique is also used at wavelength of 455 nm to measure the color of water sample
- Desirable limit: 5 Hazen unit

Physical Water Quality Parameters : Turbidity

- The cloudiness or haziness in water sample due to colloidal particles which do not settle in standing water.
- Greater turbidity means presence of greater amount of pollutants in water, but absence of turbidity does not mean that water is unpolluted
- Turbidity is measured by focusing a beam of light on water sample, the particles then scatter this light beam focused on them. The instrument called nephelometer measures the intensity of light scattered at 90^0. More the particles, more the scattering. The sample is measured against a standard water sample. The units of turbidity from a calibrated nephelometer are called Nephelometric Turbidity Units (**NTU**).
- Desirable turbidity: 5 NTU

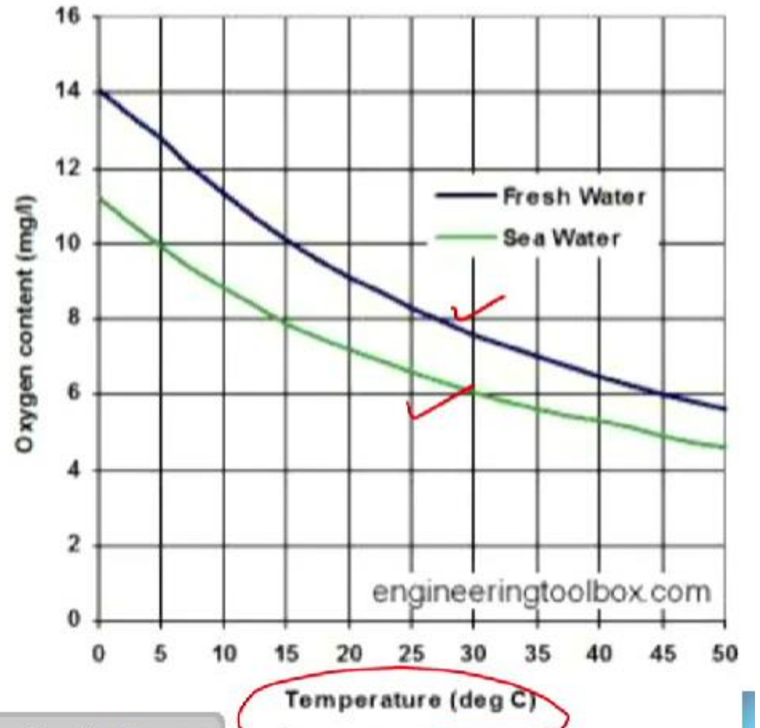
Physical Water Quality Parameters

- **Total Suspended Solids**: Coarse and insoluble matter suspended in water. Natural suspended matters which are not harmful for health include silt, clay, sand and rock particles etc. The suspended matter of sewage and industrial origin are particularly harmful to health.
- **Froth:** Froth formation occurs due to presence surfactants like soaps, detergents, fatty acids and saponins etc. these lower the surface tension of water. Sodium lauryl sulfate and Sodium lauryl ether sulfate are common surfactants found in personal care products. Blowing agents like gases (e.g. carbon dioxide), baking powder, isocyanate etc. help in foam formation.

https://www.wwdmag.com/instrumentation/suspended-solids-monitors/article/10939708/what-is-total-suspended-solids-tss

Physical Water Quality Parameters: Temperature

- **Thermal Pollution**: It is increase in temperature of water body due to discharge of heated water or wastewater into the watercourse.
- Waste heat is mainly discharged into water by nuclear and thermal power plants, and by industries involving water as coolant in industrial manufacturing.
- Increased water temperature leads to depletion of oxygen and increased respiration
- Temperature of effluent should not exceed more than 5⁰C of the receiving water body



Physiological Water Quality Parameters

- These broadly include taste and odour

	Pollutants	Characteristics
Taste	Synthetic detergents	Mouldy taste
	Phenols	Phenolic taste
	Chlorophenols	Intense, objectionable taste
	Aromatic nitro derivative	Bitter almond taste
Odour	Indole, skatole	Unpleasant fecal odor
	Methyl/dimethyl amines	Fishy odour
	Organo sulfur (methyl/ethyl mercaptans)	Putrid smell
	Hydrogen sulfide	Rotten egg smell
	Organo phosphorus	Fishy smell

Biological Water Quality Parameters

- The biological pollution occurs due to introduction and growth of micro and macro organisms in water body, which adversely affect the quality of water, human health and ecosystem.
- Various biological pollutants include bacteria, algae, weeds, viruses, protozoa and worms.

Biological Pollutants	Examples
Bacteria	E. coli, Salmonella, S. typhi, Vibrio cholera, Clostridium botulinum etc.
Algae	Various macro and micro algae, some produces toxins
Viruses	Hepatitis A virus, Poliovirus etc.
Protozoa	Entamoeba histolytica, Naegleria fowleri, Cryptosporidium parvum, Cyclospora cayetanensis, Giardia lamblia etc.
Worms	Round worms, tape worms, flukes etc.
Weeds	Hydrilla, potamogeton, ceratophyllum etc.