CHAPTER 1

Introduction

MODULE 1.1

Introduction

Environmental Chemistry deals with the origins, transport, reactions, effects and fates of chemical species in the water, air, terrestrial and living environments. It overlaps with different branches of chemistry such as organic chemistry, analytical chemistry, physical chemistry, photochemistry, geochemistry and biological chemistry and also includes many widely different fields such as physics, life sciences, agricultural sciences, medical sciences, public health and sanitary engineering.

Environmental Segments:

The environment consists of various segments such as **atmosphere, hydrosphere, lithosphere and biosphere.** Before explaining the chemistry that is taking place in these segments one by one, a brief out line about their importance will be discussed.

Atmosphere:

The following points highlight the vital role played by atmosphere in the survival of life in this planet.

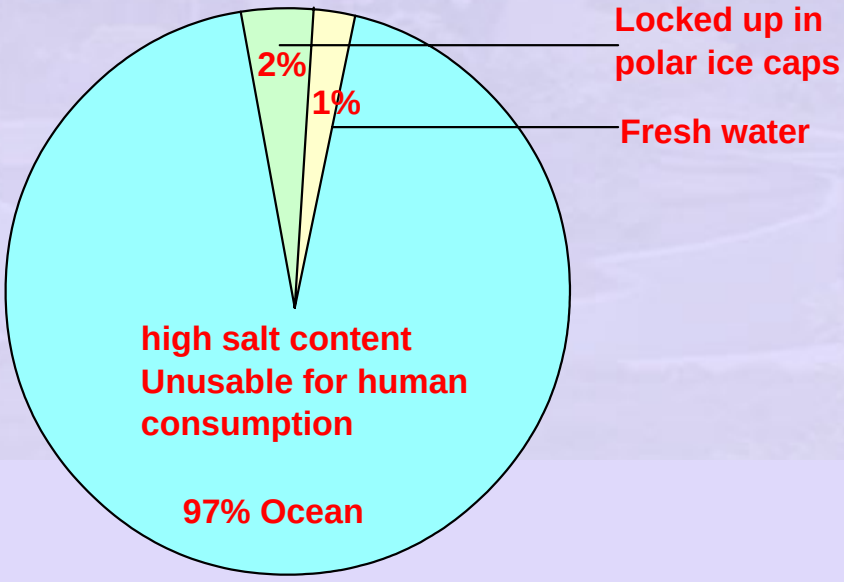
- *The atmosphere is the protective blanket of gases which is surrounding the earth. It protects the earth from the hostile environment of outer space.*
- *It absorbs IR radiations emitted by the sun and reemitted from the earth and thus controls the temperature of the earth.*
- *It allows transmission of significant amounts of radiation only in the regions of 300 – 2500 nm (near UV, Visible, and near IR) and 0.01 – 40*

meters (radio waves). i.e it filters tissue damaging UV radiation below 300 nm.

- *It acts as a source for CO_2 for plant photosynthesis and O_2 for respiration*
- *It acts as a source for nitrogen for nitrogen fixing bacteria and ammonia producing plants.*
- *The atmosphere transports water from ocean to land.*

Hydrosphere:

The hydrosphere is a collective term given to all different forms of water. It includes all types of water resources such as oceans, seas, rivers, lakes, streams, reservoirs, glaciers and ground waters. The distribution of earth's water supply is shown in fig 1.



(Fig 1 Distribution of earth's water supply)

As can be seen, only 1% of the total water supply is available as fresh water in the form of rivers, lakes, streams and ground water for human

consumption and other uses. The extent of the use of available fresh water for various purposes is shown in the following figure 2.

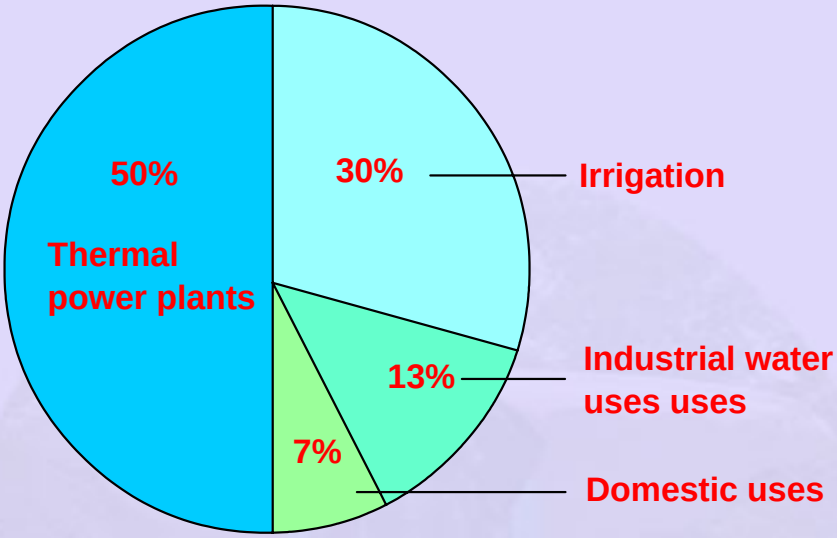


Fig 2 Major use of fresh water

The major problem with global water supply is it's non-uniform distribution, since people in areas with low precipitation often consume more than people in regions with more rainfall.

Lithosphere:

- *The earth is divided in to layers as shown in fig: 3*
- *The lithosphere consists of upper mantle and the crust*.

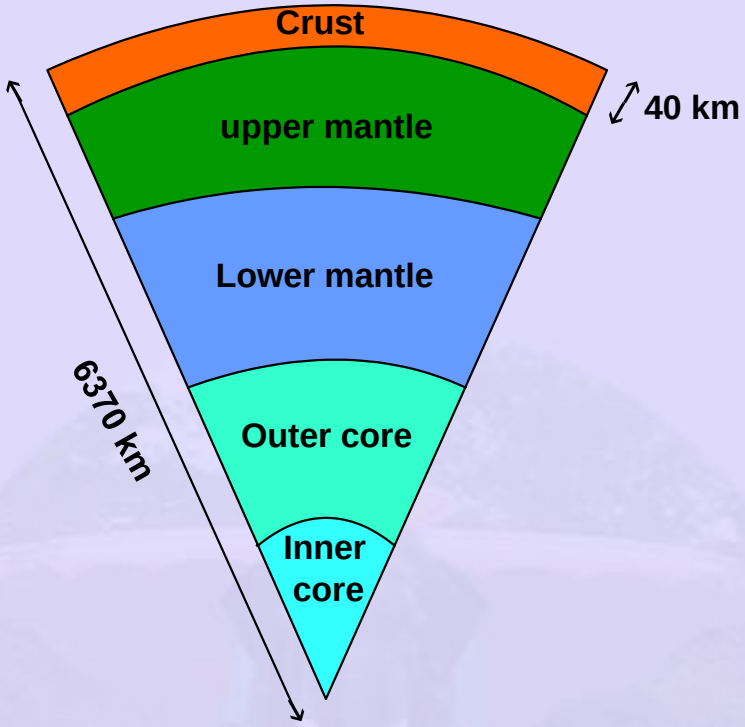


Fig 3 Layers of earth

The crust is the earth's outer skin that is accessible to human.

The crust consists of rocks and soil of which the latter is the important part of lithosphere.

Biosphere:

- *The biosphere refers to the realm of living organisms and their interactions with the environment (VIZ: atmosphere, hydrosphere and lithosphere)*
- *The biosphere is very large and complex and is divided into smaller units called ecosystems.*
- *Plants, animals and microorganisms which live in a definite zone along with physical factors such as soil, water and air constitute an ecosystem.*
- *Within each ecosystems there are dynamic inter relationships between living forms and their physical environment*

- *These inter relationships manifest as natural cycles.**(hydrologic cycle, oxygen cycle, nitrogen cycle, phosphorous cycle and sulphur cycle)**,*
- *The natural cycles operate in a balanced manner providing a continuous circulation of essential constituents necessary for life and this stabilizes and sustains the life processes on earth.*

Natural Cycles Of The Environment:

Hydrologic cycle:

The hydrologic cycle involves a continuous exchange of water between sea, atmosphere, land and living animals through massive evaporation of water from the ocean, cloud formation and precipitation as outlined in figure 4, and in the following paragraph.

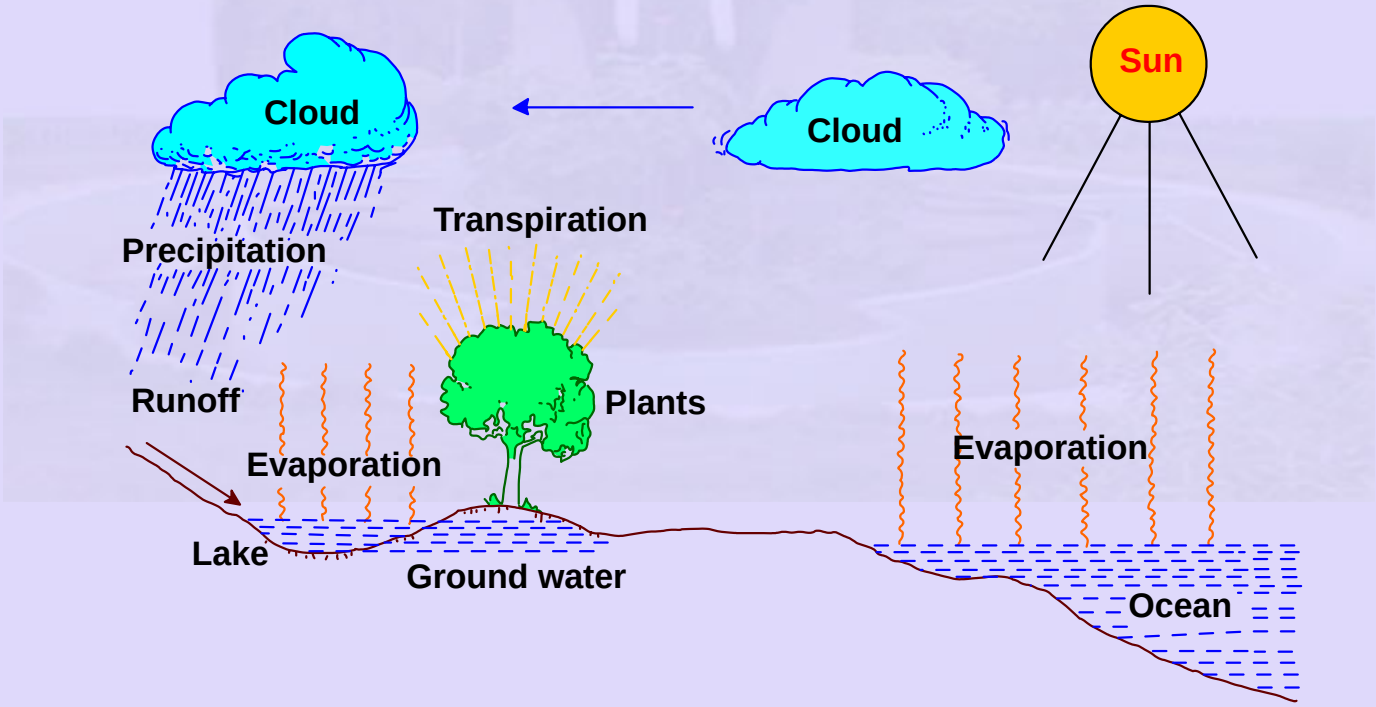


Fig 4 Hydrologic cycle

(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from Fundamentals of Environmental Chemistry, S.E.Manahan, p.374,1993)

- *The land surface and water surfaces on earth lose water by evaporation by solar energy.*
- *Normal evaporation of water from ocean exceeds precipitation by rain into seas by 10% .*
- *This 10% excess which precipitates on land balances the hydrological cycle.*
- *Some of the precipitated rain seeps into the soil as ground water.*
- *Ground water moves up by capillary action and there by maintains a continuous supply of water to the surface layer of soil.*
- *The water from the surface layer of the soil is absorbed by plants, which in turn is returned to atmosphere through transpiration.*
- *Surface water or runoff flows into streams, rivers, lakes and catchment areas or reservoirs.*
- *Animals also take water which is also returned to the atmosphere through evaporation.*
- *Thus there is always a balanced continuous cycling of water between earth's surfaces and atmosphere.*

Oxygen cycle:

The exchange of oxygen between different segments of the environment such as atmosphere lithosphere, hydrosphere and biosphere is shown in fig 5.

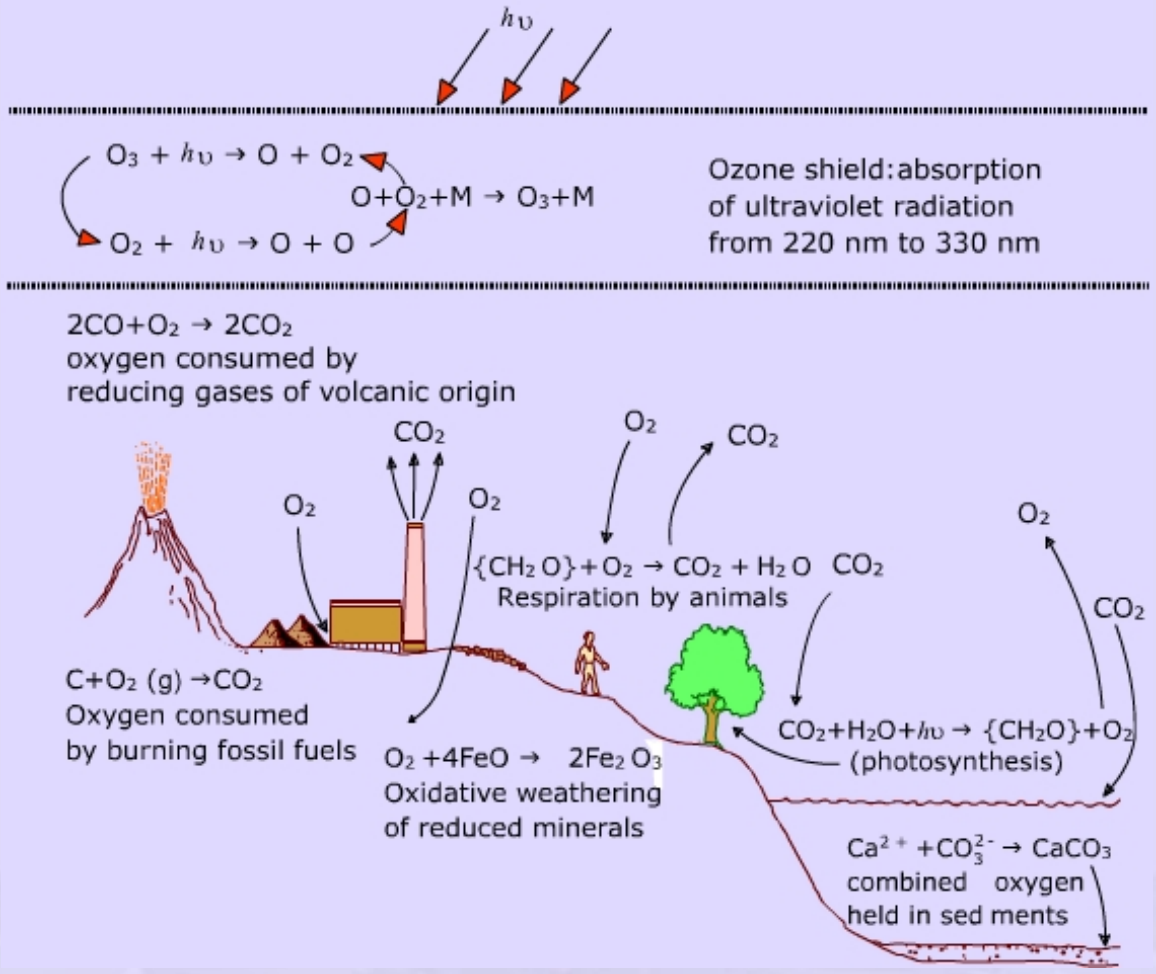


Fig 5 Oxygen cycle

(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from Fundamentals of Environmental Chemistry, S.E.Manahan, p.561,1993)

The importance of oxygen in atmospheric chemistry, geo chemical transformation and life processes is outlined in the following paragraph.

- *Atmospheric oxygen contributes largely to the processes on the earth's surface. Atmospheric oxygen participate in energy producing reactions such as burning of fossil fuels,*

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{.....(1)}$$

(In natural gas)

- *Atmospheric oxygen is utilized by aerobic organism in the degradation of organic material*

$$[CH_2O] + O_2 \xrightarrow{\text{Organism}} CO_2 + H_2O \quad \textbf{.....(2)}$$

- *Oxygen is consumed by some oxidative weathering processes of minerals*

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \quad \textbf{.....(3)}$$

- *Photosynthesis by plants return the oxygen to the atmosphere.*

$$CO_2 + H_2O \xrightarrow[h\upsilon]{\text{plants}} CH_2O + O_2 \quad \textbf{.....(4)}$$

- *A form of oxygen containing species O_3 occurring in the rarified region of the atmosphere (stratosphere) absorbs harmful UV radiation and serves as radiation shield.*
- *All the molecular oxygen now in atmosphere is thought to have originated through the action of photosynthetic organisms, which shows the importance of photosynthesis in the oxygen balance of atmosphere.*

Nitrogen cycle:

Nitrogen cycle refers to the incorporation of N_2 from the atmosphere into living matter and chemically bound nitrogen in soil, water and then back into the atmosphere again. Fig.6 shows some of the most important microorganism mediated chemical reactions involving nitrogen components in aquatic and soil environments.

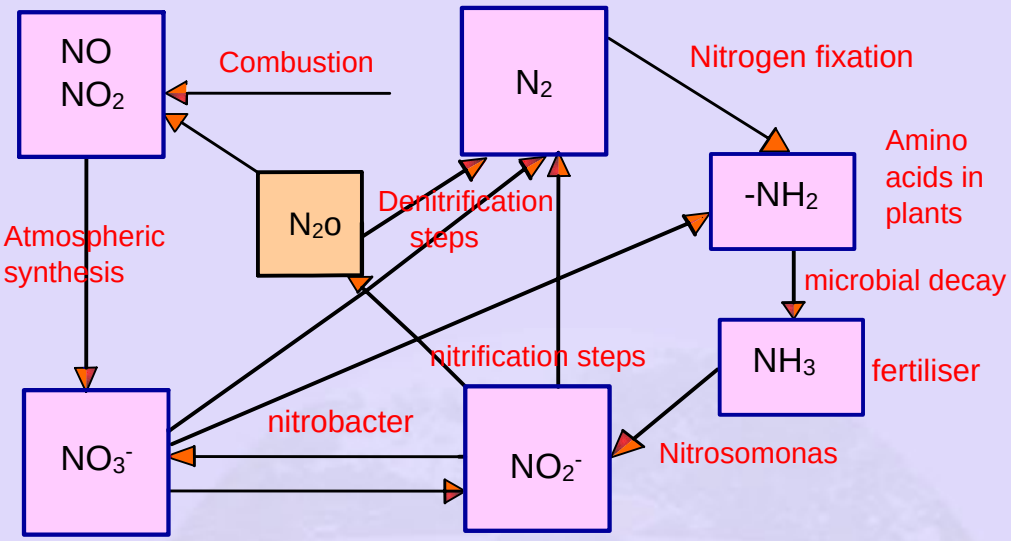


Fig 6 Nitrogen cycle

Nitrogen fixation:

In this step the atmospheric nitrogen is chemically bound to form ammonia by bacteria and algae.

$$3(CH_2O) + 2N_2 + 3H_2O + 4H^+ \rightarrow 3CO_2 + 4NH_4^+ \text{ .....} \textbf{\textit{(5)}}$$

(bacteria and algae)

Biological nitrogen fixation is mediated by organisms like *Rhizobium* that live a symbiotic relation with nodules on the roots of particular species of plants.

These organisms are capable of catalysing the conversion of atmospheric nitrogen into forms usable by plants.

Nitrification:

It is the conversion of N(-III) to N(V) catalysed by ***Nitrosomonas*** and ***Nitrobacter***

$$2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O \quad \text{.....(6)}$$

Ammonium ion present in water or soil is subjected to oxidation in an aerobic environment. The optimum pH for nitrification is between 6.5 and 8, and the reaction rate decreases significantly when the pH falls below 6.

Nitrification is important in nature, since nitrogen is absorbed by plants primarily as nitrate. Even when nitrogen is applied in the form of ammonium salts as fertilisers, the ammonia is microbially oxidized to nitrate so that it can be assimilated by plants

Nitrate Reduction:

This refers to the reduction of nitrogen in chemical compound by microbial action to lower oxidation states in the absence of free oxygen

$$2NO_3^- + \{CH_2O\} \rightarrow 2NO_2^- + H_2O + CO_2 \quad \text{.....(7)}$$

$$2NO_2^- + 3\{CH_2O\} + 4H^+ \rightarrow 2NH_4^+ + 3CO_2 + H_2O \quad \text{.....(8)}$$

In the absence of dissolved oxygen (e.g: in water logged soils) *Bacterium denitrificans* mediates the reaction(8) to produce ammonium ion.

Denitrification:

There are several types of denitrification reactions. One of these is the reduction of nitrate to form nitrogen gas. The process involves several steps. A number of heterotrophic bacteria including species of *Pseudomonas* and *Anchromobacter* mediate these processes. In this process N_2 gas is produced from chemically fixed nitrogen

$$4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \text{ .....} \textbf{(9)}$$

By this natural microbial mediated process N_2 gas is returned to the atmosphere.By all these processes the nitrogen cycle is balanced and thus the N_2 concentration in the atmosphere is relatively kept constant.

Phosphorous cycle:

- *For the growth and maintenance of animal bones and teeth phosphates are necessary.*
- *Organophosphates are essential for cell division involving the production of nuclear DNA and RNA.*
- *The major inorganic phosphorous includes soluble $H_2PO_4^-$ and HPO_4^{2-} and insoluble $Ca_5(OH)(PO_4)_3$, $Fe_3(PO_4)_2 8H_2O$.*
- *Terrestrial plants absorb inorganic phosphate salts from the soil and convert these into organic phosphate.*
- *Animals obtain their phosphate by eating plants.*
- *Plants and animals after their death return the phosphate to the soil.*
- *The microorganisms present in the soil convert them into soluble inorganic phosphate, a process known as **mineralisation** or biodegradation.*
- *Biodegradation also deactivates highly toxic organophosphate compounds, such as phosphate ester insecticides.*
- *In water phosphorous solubility is controlled by the availability of iron and aluminium under acid conditions and calcium under alkaline conditions; each of these metals form insoluble phosphates. When the pH is slightly acidic, phosphorous has its maximum solubility and under these conditions $H_2PO_4^-$ is the predominant species.*

Sulphur cycle:

In the atmosphere, oxidation reactions convert lower oxidation state species into sulphate. In hydrosphere and soil, sulphur is present in many inorganic and organic forms exhibiting oxidations states from -2 to + 6. The sulphur cycle involves interconversion among a number of sulphur species. The major microbially mediated process in this cycle are the following.

Sulphate reduction to sulphide by bacteria such as *desulfovibrio:*

In an organic rich reducing aqueous environment, sulphate is readily reduced to species in the -2 or less commonly, o oxidation states:

$$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \quad \textbf{.....(10)}$$

The toxic and odiferous H_2S may cause serious problem with water quality.

Sulfide oxidation by bacteria such as *thiobacillus* :

Sulphide is unstable under aerobic conditions and is easily oxidised via a variety of pathways. The sulphide might have been formed during the decomposition of organic matter or might have been present as sulphide mineral in the sediment or soil.

$$2H_2S + 4O_2 \rightarrow 4H^+ + 2SO_4^{2-} \quad \textbf{.....(11)}$$

The acid tolerant sulphur-oxidising *bacteria thiobacillus* produce and thrive in, environmentally damaging acidic waters, such as acid mine water. The reaction simultaneously produces hydronium ions and is thus an acidifying process.

Degradation of organic sulphur compounds:

The degradation of sulphur-containing organic compounds by bacterially mediated processes can result in the production of strong-smelling noxious H_2S and other volatile organic sulphur compounds such as methyl thiol CH_3SH and dimethyl sulphide CH_3SSCH_3. Thus the above reactions give a brief outline of the major microbially mediated processes in the sulphur cycle.

Before going into the details of the various sections of Environmental Chemistry, it is essential to understand the following terms, which will be used often in the course of our discussions

Commonly Used Terms:-

Pollutant:

If the concentration of a substance already present in nature is increased to unrequired ratio due to human activity, which ultimately has a detrimental effect on the environment either by reducing the quality of life or affecting the health then it is known as a pollutant.For example, sulphur dioxide, carbon monoxide, lead, mercury, excess heat, sound etc. are all called as pollutants.

Contaminant:

A contaminant is a substance that does not occur in nature, but is introduced by human activity into the environment. A contaminant is called a pollutant when it exerts detrimental effect on human health. It is also a pollutant.

Receptor:

A receptor may be any thing which is affected by the pollutant. For

example,man is a receptor of contaminated water because cholera and gastroenteritis are caused by it.

Sink:

It is the medium, which interacts and retains the long lived pollutant. The oceans are the sinks for atmospheric carbon dioxide. Ground water and subsoil water act as sinks for pesticides employed in agriculture.

Dissolved Oxygen (DO):

Oxygen dissolved in water is vital for aquatic life. The optimum value for dissolved oxygen in a good quality water is 4-8mg/L. It is consumed by oxidation of organic matter/ reducing agent etc. present in water.Water which has DO value less than 4 mg/L is termed as polluted and is unfit for human or aquatic animal consumptions.

Chemical Oxygen Demand (COD):

It is an index of the organic content of water, since the most common substance oxidized by the dissolved oxygen in water is organic matter, which has a biological origin, such as dead plants etc. The COD of a water sample is determined by the chemical oxidation of the organic matter by $K_2Cr_2O_7$ in 50% H_2SO_4. This method includes other reducible inorganic species that may be present in water such as NO_2^- , $S_2O_3^{2-}$, S^{2-} etc., and hence this method does not truly reflect the organic content in water. However since this method is rapid, it is widely used.

Biological Oxygen Demand (BOD):

The capacity of the organic matter in the sample of natural water to consume oxygen is called its BOD. It is determined experimentally by

determining the dissolved oxygen (DO) at the beginning and at the end of a 5-day period in a sealed sample. The BOD gives the measure of oxygen utilized or consumed in the period as a result of oxidation of dissolved organic matter present in the water sample.

Threshold limit value (TLV):

This value indicates the permissible level of a toxic pollutant in atmosphere to which a healthy industrial worker can be exposed during an eight-hour day without any adverse effect. TLV of a pollutant is found by experimentation on animals, medical knowledge and experience and environmental studies.

Now let us discuss the various segments of our environment in detail one by one. In the first instance let us discuss about the atmosphere and atmospheric chemistry.