Unit

14

Environmental Chemistry

- **Environmental chemistry** deals with the study of various chemicals and biochemical phenomena that take place in various segments of environment.
- The physical and biochemical world around us is called environment.

Earth's Environment

Lithosphere
- Crust of the earth
- Mainly consists of rocky material
- Thickness 35 km – 60 km

Hydrosphere
- Surface and ground water resources
- 70% of earth's surface – oceans

Atmosphere
- Cover of gases surrounding earth
- Extends from earth's surface to 1000 km

Biosphere
- Part of other three spheres where life exists.

Troposphere | Stratosphere or ozonosphere | Mesosphere | Thermosphere

Regions of the atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/Species present
(i) Troposphere	0 – 10 km	Decreases from 15 to – 56°C	N_2, O_2, CO_2, H_2O vapour
(ii) Stratosphere (or ozonosphere)	10 – 50 km	Increase from – 56 to – 2°C	N_2, O_2, O_3, O-atoms
(iii) Mesosphere	50 – 85 km	Decreases from –2 to – 92°C	N_2, O_2^+, NO^+
(iv) Thermosphere	85 – 500 km	Increases from – 92 to 1200°C	O_2^+, O^+, NO^+, e^-.

TYPES OF ENVIRONMENTAL POLLUTION

1. Air Pollution

- Air pollution occurs when the concentration of a normal component o f the air or a new chemical substance added or formed in air builds up to undesirable properties causing harm to humans and other animals, vegetation and materials.

  Some common air pollutants and their sources are:

Pollutants	Major sources
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agriculture and slash matter, volcanic eruption, forest fires.
NO, NO_2	Combustion of fuel, interaction of N_2 and O_2 of the atmosphere at high temperatures.
Hydrocarbons	Combustion of fuel in automobiles, refineries, anaerobic bacterial decomposition of organic matter, natural gas.
Pesticides	Application of pesticides and their volatilization from soil, water treated surfaces and industrial units producing pesticides.
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.

Reactions Occurring in Atmosphere

- Many chemical and photochemical reactions are occuring in atmosphere in which main constituents such as oxygen, nitrogen, carbon dioxide, etc., are involved.

Reactions Occurring in Troposphere

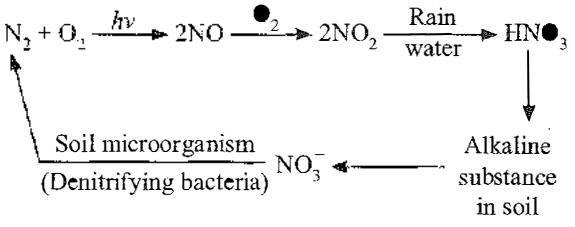
- The carbon dioxide and water present in atmosphere are used by green plants in the presence of sunlight to form glucose. The process is termed as photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2$$

- Oxygen released in photosynthesis is also utilised in the degradation of organic material by aerobic organisms.

$$\text{Organic matter} + O_2 \xrightarrow[\text{organisms}]{\text{Aerobic}} CO_2 + H_2O$$

- Chemical reactions such as hydrolysis, oxidation, etc., involving oxygen occur at the surface of the earth.
- Electrical disturbances in the atmosphere initiates reactions between nitrogen and oxygen.



- Some of the gaseous components of the atmosphere like water vapours, carbon dioxide, nitrous oxide and methane allow the solar radiation to pass through, but do not allow the terrestrial radiation to escape.

Reactions Occurring in Stratosphere

- The principal chemical species present in the stratosphere are N_2, O_2, O_3 and some H_2O. The far ultraviolet radiation (wavelength < 190 nm) are filtered before these reach the stratosphere. Ultraviolet radiations (> 190 nm and < 340 nm) are removed in the stratosphere due to the following reactions,

$$O_2 \xrightarrow[\lambda < 240\ nm]{UV} O + O$$

- The highly reactive O atoms combine with oxygen molecules to form ozone.

$O + O_2 + M \longrightarrow O_3 + M$ (Exothermic reaction)

where M is some inert substance such as N_2.

- Ozone absorbs UV light between 200 and 300 nm.

$$O_3 \xrightarrow{UV} O + O_2$$

$$O_3 + O \longrightarrow 2O_2$$

- Hence, a cycle of ozone formation and destruction exists. Thus, the stratosphere acts as a shield against UV radiations which can induce skin cancer, cause genetic mutations and destroy crops and other forms of vegetation at the earth's surface.

Reactions Occurring in Upper Atmosphere

- In upper atmosphere (*viz.*, mesosphere, thermosphere and ionosphere) ultraviolet radiations cause photochemical reactions giving rise to excited atoms, ions and electrons.
- Some reactions are given below :

$$O_2 + h\nu \xrightarrow{135 - 176\ nm} \underset{\text{Oxygen atoms}}{O + O}$$

$$O_3 + h\nu \xrightarrow{308\ nm} \underset{\text{Oxygen ion}}{O^+ + O_2 + e^-}$$

- In the upper part of atmosphere, these species survive for long as the density of the atmosphere is low.

Effects of Air Pollution

Acid rain : The term "acid rain" is used to describe all precipitations – rain, snow, fog, dew which are more acidic than normal.

Rain water normally has a pH of 5.6 due to dissolution of CO_2 present in the atmosphere.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

When this pH falls below 5.6, the rain water becomes acidic. It is caused due to presence of acidic gases into the atmosphere. The common ones are sulphur dioxide and nitrogen oxides which are changed in the atmosphere into sulphuric acid and nitric acid by combining with oxygen and water.

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

Harmful effects of acid rain

- It causes extensive damage to buildings and statues made of marble, limestone, slate, etc. due to the reaction

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

- It is toxic to vegetation and aquatic life.
- It corrodes water pipes resulting in the leaking of the heavy metals such as Fe, Pb and Cu into the drinking water which have toxic effects.

Smog : The phenomenon which occurs due to the condensation of fog on the carbon particles present in the smoke due to combustion of fuels.

Thus, smog = smoke + fog

Smog is of two types :

Classical smog	Photochemical smog
• Observed first in London (1952) so also known as London smog.	• Observed first in Los Angeles (1950) so, also known as Los Angeles smog.
• Produced from oxides of sulphur, particulates and high humidity.	• Produced from oxide of nitrogen, particulates and hydrocarbons.
• Usually formed during winter season.	• Occurs in warm, sunny and dry climate.
• Also called reducing smog as it contains SO_2 and C.	• Also called oxidising smog due to high concentration of oxidants.
• Causes bronchitis, asthma, irritation to E.N.T.	• Causes high irritation to eyes and lungs, cracking of rubber.

Greenhouse Effect and Global Warming

- The energy trapping phenomenon by infrared active gaseous molecules and vapour (called greenhouse gases such as CO_2, CH_3, O_3, CFCs and water vapours) present in the atmosphere is termed as **greenhouse effect**.
- Earth absorbs energy from sunlight entering the atmosphere and emits energy out to space in the form of infrared rays. The incoming sunlight, which is radiation with a shorter wavelength, travels unobstructed through the atmosphere (unless hitting a cloud) because this short wave radiation is at a wavelength that is not in the absorption range of atmospheric gases. On the other hand, the outgoing radiation emitted by the surface is at wavlength that is the absorption range of many atmospheric gases, including carbon dioxide, methane, and water vapour.
- These radiations are thus locked in the earth's atmosphere. This results in the steady increase of temperature of the earth resulting in **global warming**.

Consequences of Global Warming

- Melting of Polar ice caps, thus raising the level of water in seas and oceans.
- Increase in infectious diseases like dengue, malaria, sleeping sickness, etc.
- The moisture content of soil would decrease due to increase in temperature and cause reduce in soil fertility.

Ozone layer and Its depletion

Reactions of Ozone :

With Nitric oxide (NO) : NO is introduced directly into the stratosphere in the form of exhaust of the engine of supersonic transport planes. O_3 gets depleted as shown by the following reactions :

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_2 \xrightarrow{h\nu} O + O$$

$$NO_2 + O \longrightarrow NO + O_2$$

Thus NO is regenerated in chain reaction.

II. **With Chlorofluorocarbons (CFCs) :** CFCs are commonly known as freons and introduced into the atmosphere from aerosol sprays, refrigerating equipments. They undergo photochemical decomposition and destroy ozone as shown by the following sequence of reactions :

$$CF_2Cl_2 \xrightarrow{h\nu} \dot{C}F_2Cl + Cl^{\bullet} \text{ (free radical)}$$

$$CFCl_3 \xrightarrow{h\nu} \dot{C}FCl_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

Chlorine free radical is regenerated in course of reaction. It has been found that one molecule of CFC (or one $Cl^{\bullet}$ atom) can destroy more than one thousand O_3 molecules in the stratosphere.

Ozone Depletion and Its Harmful Effects

- At higher altitudes stratosphere consists of a layer of ozone (O_3) which acts as an umbrella or shield for harmful ultraviolet radiations coming from sun and thus protect us from their harmful effect such as skin cancer. Gradual depletion of this protective ozone layer has been caused by nitric oxide and chlorofluorocarbon. In most part of the stratosphere, $ClO^{\bullet}$ reacts with nitrogen dioxide (NO_2) and hydrocarbons.

$$ClO^{\bullet} + NO_2 \rightarrow ClONO_2$$

$$Cl + CH_4 \rightarrow \dot{C}H_3 + HCl$$

In Antarctica, in winters, there are special types of clouds called **Polar Stratospheric Clouds (PSCs)** composed of either nitric acid trihydrate ($HNO_3 \cdot 3H_2O$).

(Type I PSC) or ice (Type II PSC). These clouds convert chlorine nitrate and HCl into HOCl and Cl_2 through the following reactions.

$$ClONO_2 + H_2O \xrightarrow{\text{Hydrolysis}} HOCl + HNO_3$$

$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3$$

- During spring, the sun shines over Antarctica and HOCl and Cl_2 formed in above reactions undergo photolysis to form reactive chlorine atoms which destroy the ozone layer.

$$HOCl + h\nu \longrightarrow {}^{\bullet}OH + Cl^{\bullet}$$

$$Cl_2 + h\nu \longrightarrow 2Cl^{\bullet}$$

- It will result in
  - ⇒ Skin cancer
  - ⇒ Eye damage such as cataracts
  - ⇒ Immune system damage, damage of plants and crops, disturbance of heat balance of earth.

Water Pollution

- Water pollution may be defined as any change in its physical, chemical or biological properties or contamination with foreign materials that can adversely affect human beings or reduce its utility for the intended use.

Major water pollutants and their sources are :

Pollutants	Major sources
Natural wastes	Leaching of minerals, silt from soil erosion, falling of organic matter from banks, etc.
Organic chemicals	Pesticides, surfactants, detergents, industrial wastes.
Metals (Hg, As, Pb, Cd, etc.)	Nuclear power plants, mining, metal plating industries.
Man made wastes	Sewage, domestic waste, soaps and detergents, waste from animal sheds and slaughter houses, run off from agricultural fields, industrial wastes, oil pollution.

Effects of Water Pollution

- High concentrations of fluoride are poisonous and are harmful to bones and teeth at levels over 10 ppm.
- Excess nitrate in drinking water can lead to blue baby syndrome.
- Excess sulphate (> 500 ppm) have a laxative effect.

Biochemical Oxygen Demand (BOD)

- $BOD = \frac{\text{Number of milligrams of } O_2 \text{ needed}}{\text{Number of litres of sample}}$

  To determine BOD, water sample is first saturated with oxygen and then incubated at constant temperature for five days.

Chemical Oxygen Demand (COD)

- In COD determination, a known quantity of water sample is oxidised by acidified $K_2Cr_2O_7$. The unused amount of dichromate is determined by back titration. The amount of oxygen used in oxidation is calculated from consumed concentration of $K_2Cr_2O_7$.

Soil Pollution

- Soil pollution is the addition of such chemical substances (in an indefinite proportion) which deteriorates the quality, texture and mineral content of the soil and disturbs the biological balance of the organisms in it and has lethal effect on the plant growth.

  Some major soil pollutants and their sources are:

Pollutants	Major sources
Industrial wastes	Waste products from paper, sugar, chemical industries dumped into the soil.
Agriculture wastes	Chemicals such as fertilizers, pesticides, etc. used for killing insects, fungi and weeds.
Soil conditioners	Used to protect soil fertility but contains several toxic metals like Pb, As, Hg, Cd, etc.
Farm wastes	Wet slurry, faecal wastes are seeped into the soil.
Radioactive pollutants	Dumping of nuclear wastes into the soil.

GREEN CHEMISTRY

- "Green Chemistry", can be defined as the design, development and implementation of chemical of products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment.
- Chemical products should be designed to affect their desired function while minimising their toxicity.
- The use of auxiliary substances (*e.g.*, solvents, separation agents, etc.) should be reduced.
- A raw material or feedstock should be renewable.
- Catalytic agents as selective as possible should be used.

Examples of Green Chemistry

- Halons are greenhouse gas compounds, used in fire fighting and other applications. Pyrocool Technologies have synthesized a halon substitute.
- Substitutes to CFC's such as HFC–134a (CF_3CH_2F) have been discovered which are considered to be more friendly to environment.
- Switching from air (78% nitrogen) to pure oxygen eliminates NO production and also saves fuel by more efficient burning.
- The current commercial method of producing ibuprofen is a stunning application of green chemistry.

Control of Environmetal Pollution

- **Waste management :** Environmental pollution can be controlled to a certain extent by managing the waste disposal in a proper way.
- **Recycling :** A large amount of disposed waste material can be reused by recycling the waste. Thus it reduces the land fill and converts waste into usable forms.
- **Sewage treatment :** It can be done by following methods:
  - **Incineration :** Incineration is a waste treatment technology that involves the combustion of organic materials and/or substances. Incineration of waste materials converts the waste into ash, flue gases, particulates, and heat, which can in turn be used to generate electricity.

    Incinerators reduce the volume of the original waste by almost 95%.
  - **Digestion :** The sewage sludge can undergo anaerobic digestion when microorganisms degrade wastes in absence of oxygen.

    $$\underset{\text{Organic Waste}}{2(CH_2O)} \longrightarrow CO_2 + CH_4$$
  - **Dumping :** Dumping of sewage sludge into land is increasing because it contains compounds of N and P which act as fertilizers for soil.