CHAPTER 23
ENVIRONMENTAL CHEMISTRY

ALTITUDE (In km)

1. Troposphere 0 - 11 km
2. Stratosphere 11 - 50 km
3. Mesosphere 50 - 85 km
4. Thermosphere 85 - 500 km

TEMPERATURE RANGE

1. Troposphere 15 to -56°C
2. Stratosphere -56 to -2°C
3. Mesosphere -2 to -92°C
4. Thermosphere -92 to 1200°C

IMPORTANT CHEMICAL SPECIES

1. Troposphere N_2, O_2, CO_2, H_2O, Ar
2. Stratosphere O_3, N_2, O_2
3. Mesosphere NO^+, O_2^+
4. Thermosphere O_2^+, NO^+, O, O^+

TROPOSPHERE

→ constitutes 10% of atmosphere's height.

→ contains 80% of atmosphere's mass.

CHEMICAL REACTIONS IN ATMOSPHERE

→ Minor gases present in troposphere are SO_x, NO_x

→ Combustion engine of motor vehicles is responsible for producing NO by reacting with N_2 and O_2

$$N_2 + O_2 \rightarrow 2NO$$

→ Incomplete combustion of carbonaceous compound is responsible for producing carbon monoxide

$$\text{Hydrocarbon} + O_2 \rightarrow CO + H_2O + \text{Energy}$$

→ Many chemical reactions occuring in atmosphere are responsible for producing smog.

→ NO_x and SO_x gases are responsible for acid rain

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

$$SO_2 + H_2O + \tfrac{1}{2} O_2 \rightarrow H_2SO_4$$

→ CO_2 is not responsible for acid rain

→ At concentration higher than 750 ppm (0.1% of air), CO may cause loss of consciousness and death occurs quickly.

AIR COMPOSITION

Nitrogen = 78.09%

Oxygen = 21%

Remaining 0.97% = CO_2, He, Ar, Kr, Xe, N_2O

AIR POLLUTANTS

CO_x, NO_x, VOC's, SO_x, O_3

CARBON MONOXIDE

→ results from incomplete combustion of carbonaceous compounds.
→ It is termed as asphyxiating pollution bc it can displace O_2 bound to haemoglobin.
→ The Fe binding sites in haemoglobin bind CO 32 times more tightly than O_2.
⇨ Main Source : Vehicles exhaust

SULPHUR DIOXIDE (SO_2)

→ Main Sources : Combustion of coal, smelting of metals (metallurgy) particularly copper.
→ Sulfur content of Refined Petroleum : Low
Sulfur content of coal : High
→ Sulfur in coal is converted to SO_2 at high temperatures of combustion.
→ lung irritant

NOx AND VOC's

→ VOC's (volatile organic compounds)
→ indirect air pollutants
→ main ingredients in the formation of photochemical smog.
→ Although most damage from smog results from the action of ozone and other oxidants, these oxidants cannot build up without the combined action of NOx and VOCs.
→ Controlling smog formation requires reducing emission of NOx & VOCs
→ NOx sources : Fossil fuel combustion
→ VOC's sources : industrial processes, solvent utilization, on-road and non-road vehicles.

OZONE

→ Ozone at ground level is quite harmful
→ Producing cracks in rubber, destroying plants, causing respiratory distress and eye irritation in humans
→ These effects set in at quite low concentration, around 100ppb

AUTOMOBILE POLLUTANTS AND CATALYTIC CONVERTER

→ Major Pollutants : CO, NO, HC's
→ Three-way catalytic converter to reduce these pollutants
→ The converter has two chambers.

1. Reducing Chamber:
   → NO is reduced to N_2 by hydrogen.
   → H_2 is generated at the surface of a rhodium (Rh) catalyst by action of water or unburned fuel molecules.

$$HC's + H_2O \rightarrow H_2 + CO$$
$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

2. Oxidation Chamber:
   → air is added and the CO and unburned HCs are oxidized to CO_2 and H_2O at surface of Pt/Pd catalyst.

$$2CO + O_2 \rightarrow 2CO_2$$
$$HC's + 2O_2 \rightarrow CO_2 + 2H_2O$$

INDUSTRIAL SMOG

→ combination of smoke and fog
→ Smog causes brownish coloration in atmosphere.
→ Major Products produced by burning of fossil fuels: CO_2, H_2O, smoke (carbon) particles
→ SO_2 is an obnoxious pollutant primarily bcz it gradually reacts further to form SO_3. Then in presence of water or water vapours, droplets of H_2SO_4 are formed which is corrosive
→ Another coal-burning power station pollutant is soot (primarily particles of carbon) which give smoke its persistent dark colour.
→ Incomplete combustion of coal produce CO or soot.
→ CO plays vital role in formation of smog

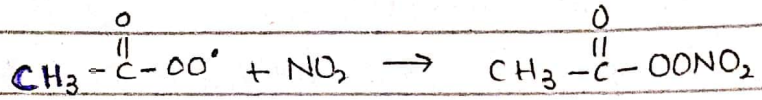
PHOTOCHEMICAL SMOG

→ The smog consisting of high concentration of photochemical oxidants (O_3, NO_2) is known as photochemical or oxidizing smog.
→ characterized by an accumulation of brown, hazy fumes, containing ozone (O_3) and other oxidants.
→ Photochemical smog can form when large quantities of automobile and industrial exhausts are trapped to exposed to sunlight.
→ Major contributors : HC's, NO, O_3 and other oxidants
→ NO_2 absorb visible light of bluish region (400nm) and gives brownish tint in air

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

↑ Photochemical cycle

→ HC's react with O_3 to form peroxyacetyl radical and it reacts further with NO_2 to form peroxy acetyl nitrate (PAN)



→ Initiation of cycle depends on formation of organic radicals.

→ Extent of smog formation depend on reactivity of HC's with O_3 radical.

GLOBAL WARMING

Heating effect due to increased concentration of CO_2

GREEN HOUSE EFFECT

→ Increase in temp due to increase in concentration of CO_2

→ Green House Gases:

1) 50% contributing gas is CO_2

2) Other 50% → CH_4, CFC's, SO_2, NO_x

→ CO_2 is colourless gas and doesnot absorb visible radiation

→ In green house effect, CO_2 allow sunlight to enter but prevents I.R radiation from escaping.

ACID RAIN

→ Normal Rain pH : 5.6

→ Acid pH is less than 5.6

→ HNO_3 and H_2SO_4 make rain water acidic

→ Heavy metals e.g Cu, Hg, Pb are dissolved by acid rain producing various toxic effects.

OZONE LAYER

→ Formation of ozone requires O and O_2.

→ O_2 molecules in stratosphere absorb solar radiations and split into oxygen atoms.

→ The oxygen atoms combine with O_2 to form ozone.

$$O + O_2 \rightarrow O_3$$

→ In atmosphere ozone layer occurs as a band at intermediate altitutedes, b.w 25 and 30 km.

→ At Low Altitudes: Ample O_2 molecules, Few Oxygen Atoms

→ At High Altitudes: More oxygen atoms, Few O_2 molecules

→ At Intermediate Altitudes: Optimum Conditions

→ Ozone is destroyed by:

1. Solar Radiation

$$O_3 + h\nu \rightarrow O_2 + O$$

2. When O_3 encounters free oxygen atom

$$O_3 + O \rightarrow 2O_2$$

→ Concentration of O_3 depends on relative rates of the formation and destruction reactions.

DEPLETION OF OZONE LAYER

→ Chlorofluorocarbons, CFC's (Freon) and bromine-containing halons.

→ CFCs have been widely used as refrigerants, blowing agents for plastic foams, propellants for aerosol sprays and solvents for cleansing micro-electronic components.

→ The halons are used as fire extinguishers.

→ CFC's and halons are non-toxic and non-flammable

→ CFC's and halons are not subjected to halons (Either in flame or biochemical reaction)

→ CFC's and halons are destroyed in troposphere as follows:

$$R\text{-}X + uv \rightarrow R^{\cdot} + X^{\cdot}$$
$$X^{\cdot} + O_3 \rightarrow XO^{\cdot} + O_2$$
$$XO^{\cdot} + O_3 \rightarrow X^{\cdot} + 2O_2$$

→ Big hole in ozone layer was observed over Antarctica

→ Now hydrofluoro carbons (HEFC's) and hydrofluoric carbons (HFC's) are used as alternative of CFC's and halons.

→ But OH^{-} radical reacts with HCFC's and HFC's in troposphere.

→ Chlorofluorocarbons (CFCs) are anthropogenic compounds (pollutant)

→ Water is purified naturally by distillations, sand filtration, charcoal filtration, reverse osmosis and by uv light

WATER POLLUTION

Types of Water Pollutants:

1. Suspended solids and sediments
2. Dissolved solids

1. SUSPENDED SOLIDS AND SEDIMENTS

may be:

a) Filtrable solids

b) Colloidal Particles

Colloidal particles can be detected by passing a beam of light through the water and observing the scattering of light

2. DISSOLVED SOLIDS

→ may either be organic or inorganic
→ The total amount of organic substances can be estimated from the amount of oxygen or any other chemical (oxidizing agent) needed to oxidize these substances to CO_2 and H_2O
→ The dissolved inorganic materials are mostly salts.
→ Above 500 ppm, the salts make water unfit for drinking.
→ Common Salts: carbonates, bicarbonates, sulphates and sulphides of Ca and Mg
→ Hardness of water depends primarily on Ca^{+2} and Mg^{+2} ion content

SOURCES OF WATER POLLUTION

1. INDUSTRIAL EFFLUENTS

Metals that are released by various industries to pollute water, include arsenic, mercury, lead & cadmium.

(i). ARSENIC

→ Smelting of gold, lead, copper, iron and nickel ores can be a source of arsenic pollution
→ Arsenic in drinking water is a slow poison
→ It decolourizes the skin (keratoses) which leads to cancer.

(ii) MERCURY

→ Mercury's toxicity is associated with almost entirely with eating fish.

→ Sulphate reducing bacteria in sediments generate methyl mercury and release it into the water above, where it is absorbed by fish from the waters passing across their gills or from their food supply.

→ The polsoning of mercury causes numbness of limbs, blurring and even loss of vision and loss of hearing and muscle coordination

(iii) LEAD

→ Leaded paints, leaded gasoline and lead solder (to seal food and drinks in cans) are main sources of lead pollution.

→ Once absorbed in the body, lead enters the blood stream and moves from there to soft tissues.

→ Higher exposures produce anemia

→ Lead inhibits the enzyme involved in biosynthesis of haemoglobin

(iv) CADMIUM

→ Cadmium inputs to soils and ultimately to surface waters, are mainly from airborne deposition and from commercial phosphate fertilizers which contain Cd as natural constituent of phosphate ore.

→ Chronic exposure to cadmium causes heart and lung disease (including lung cancer at high levels), immune system suppression, and liver and kidney diseases.

2. DOMESTIC ACTIVITIES

→ soaps and detergents
→ Phosphates used in detergent formulation affect water quality
→ eutrophication

3. AGRICULTURAL WASTES

→ fertilizers, herbicides and pesticides
→ Fertilizers increase level of nitrate ions in ground water.
→ The main nitrate hazard is "blue baby syndrome", a condition of respiratory failure in babies having excessive nitrate in their diet.

THERMAL POLLUTION

→ The cooling of power plants and other machinery by circulating water, raises the temperature of water. This is called thermal pollution.
→ The high-temperature water, when mixed with cold water, increases solubility of many pollutants (organic and inorganic), salts, ions, causing the water to be more easily polluted, thus affecting quality of water and making it unfit for drinking and public use.

PARAMETERS OF WATER

Drinking water should qualify following qualities or parameters:

1. odorless, tasteless and colorless
2. Free from turbidity causing agents such as suspended Solids, dissolved solids, excess of chlorides, sulphates, phosphates etc
3. Turbidity, not more than 10 ppm
4. Free from bacteria causing diseases
5. Slightly alkaline (pH = 7 - 8.5)

Water Quality Parameters

1. Biological Oxygen Demand (BOD)

In BOD, the amount of dissolved oxygen is determined by adding bacteria to water.

2. Chemical Oxygen Demand (COD)

In COD, amount of dissolved oxygen is determined by adding chemical oxidizing agents to water

3. Determination of Total Organic Carbon (TOC)
4. Total Dissolved Solids (TDS)
5. Total Suspended Solids (TSS)
6. pH and Alkalinity
7. Colour, odour etc

WASTE WATER TREATMENT

1. FILTRATION

Coarse objects are removed by running the water through screens / filters.

2. REMOVAL OF COLLOIDAL PARTICLES

→ A Flocculating agent (a substance that forms large gelatinous particles) is added.

→ Common flocculating agent is aluminium sulfate $Al_2(SO_4)_3$, often referred to as alum.

→ Some lime $Ca(OH)_2$ is generally also added so that ppt of $Al(OH)_3$ which has the desired gelatinous form, is produced

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_{3\ ppt} + 2CaSO_4$$

→ This ppt traps both inorganic solid particles and bacteria in the large curd like particles.

→ These particles are then easily removed by filtration through a sand-bed or charcoal.

3. CHLORINATION

→ Water is treated with chlorine to kill remaining bacteria and other microbes.

→ $H_2O + Cl_2 \rightarrow H^+ + Cl^- + HOCl$

→ HOCl is weak acid and partially dissociates

$$HOCl \rightarrow H^+ + OCl^-$$

$$HOCl \rightarrow [O] + HCl$$

→ It is this nascent oxygen [O] that gives taste and odour to water.

→ Air is sometimes blown through water i-e water is aerated to improve its odour and taste

→ A fluoride compound is added in some plants, to help fight tooth decay.

GREEN CHEMISTRY

→ Paul Anestas of America enunciated twelve principles of Green chemistry in 1994.

→ Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that minimizes the use and generation of hazardous substances.

ATOM ECONOMY

$$\% \text{ Atom Economy} = \frac{\text{Formula weight of product}}{\text{Sum of formula weight of all reactants}} \times 100$$

Good Atom Economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment)