M.Sc. Final Year

Chemistry, MC-08

ENVIRONMENTAL CHEMISTRY

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल

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SYLLABI-BOOK MAPPING TABLE

Environmental Chemistry

Syllabi	Mapping in Book
Unit I **Environmental:** Introduction, Composition of atmosphere, vertical temperature, heat budget of the earth atmospheric system, vertical stability atmosphere. Biochemical cycles of C, N, P, S and O. Biodistribution of elements.	**Unit-1:** Concept of Environmental Chemistry **(Pages 3-39)**
Unit II **Hydrosphere:** Chemical composition of water bodies-lakes, streams, rivers and wetland etc. Hydrological cycle. Aquatic pollution - inorganic, organic, pesticide, agricultural, industrial and sewage, detergents, oil spills and oil pollutants. Water quality parameters dissolved oxygen, biochemical oxygen demand, solids, metals, content of chloride, sulphate, phosphate, nitrate and micro-organisms. Water quality standards. Analytical methods for measuring BOD, DO, COD, F, Oils, metals (As, Cd, Cr, Hg, Pb, Se, etc.), residual chloride and chlorine demand. Purification and treatment of water.	**Unit-2:** Hydrosphere **(Pages 41-89)**
Unit III **Soils:** Composition, micro and macro nutrients, Pollution-fertilizers, pesticides, plastics and metals. Waste treatment.	**Unit-3:** Soils **(Pages 91-108)**
Unit IV **Atmosphere:** Chemical composition of atmosphere - particles, ions and radicals and their formation. Chemical and photochemical reactions in atmosphere, smog formation, oxides of N, C, S and O and their effect, pollution by chemicals, petroleum, minerals, chlorofluorohydrocarbons. Green house effect, acid rain, air pollution controls and their chemistry. Analytical methods for measuring air pollutants. Continuous monitoring instruments.	**Unit-4:** Atmosphere **(Pages 109-148)**
Unit V **Industrial Pollution:** Cement, sugar, distillery, paper and pulp, thermal power plants, nuclear power plants, metallurgy. Polymers, drugs, etc. Radionuclide analysis. Disposal of wastes and their management. **Environmental Toxicology:** Chemicals solution to environmental problems, biodegradability, principles of decomposition, better industrial processes. Bhopal gas tragedy, Chernobyl, Three mile island, Seveso and Minamata disasters.	**Unit-5:** Industrial Pollution **(Pages 149-204)**

CONTENTS

INTRODUCTION

Environmental chemistry is the branch of chemistry that studies the reactions, origins, movement, and effects of all chemical species found in the soil, water, and air environments, as well as the influence of technology on them. It is the scientific investigation of biochemical and chemical processes that occur in natural settings. Environmental chemistry is a research field that encompasses more than just air, water, soil, and chemicals. This field employs a variety of methodologies from biology, genetics, engineering, hydrology, toxicology, and other fields to help find answers to all environmental concerns. Environmental chemistry encompasses features of analytical chemistry, physical chemistry, organic chemistry, and inorganic chemistry, as well as a wide range of other disciplines such as epidemiology, public health, biochemistry, biology, and toxicology.

When there are undesired chemical substances present in the atmosphere, the environment is contaminated. In reality, environmental chemistry is primarily concerned with the investigation of these undesirable chemicals and their consequences. These contaminants lead to pollution, which occurs when contaminants are introduced into the natural environment and cause harm. Any chemical or energy can be a source of pollution. Pollutants are either foreign substances/energies or naturally occurring pollutants that contribute to pollution. We will study the effect of such pollution on water, air, and soil in detail.

This book, *Environmental Chemistry*, has been designed keeping in mind the Self-Instruction Mode (SIM) format and follows a simple pattern, wherein each unit of the book begins with the Introduction followed by the Objectives for the topic. The content is then presented in a simple and easy-to-understand manner, and is interspersed with Check Your Progress questions to reinforce the student's understanding of the topic. A list of Self-Assessment Questions and Exercises is also provided at the end of each unit. The Summary and Key Terms further act as useful tools for students and are meant for effective recapitulation of the text.

UNIT 1 CONCEPT OF ENVIRONMENTAL CHEMISTRY

Structure

1.0 INTRODUCTION

The scientific study of chemical and biological events that occur in natural settings is known as environmental chemistry. It's not to be confused with green chemistry, which aims to eliminate pollution at the source. It is the study of chemical species' sources, reactions, movement, impacts, and fates in the air, soil, and water environments, as well as the impact of human and biological activity on these. Environmental chemistry is an interdisciplinary subject that encompasses atmospheric, aquatic, and soil chemistry, as well as relies significantly on analytical chemistry and being linked to other fields of study. Understanding how the uncontaminated environment functions, which chemicals are present naturally in what concentrations, and with what consequences, is the first step in environmental chemistry. It would be hard to evaluate the effects humans have on the environment through chemical emission without this. In this unit, we will discuss the concept of environmental chemistry and the composition of atmosphere, along with vertical temperature and vertical stability of the atmosphere. It will also focus on the biochemical cycles of C, N, P, S, and O, along with the bio-distribution of elements.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe the concept of environmental chemistry and the composition of atmosphere
- Explain the vertical temperature and vertical stability of the atmosphere
- Discuss the biochemical cycles of C, N, P, S, and O, along with the bio-distribution of elements

1.2 ENVIRONMENTAL CHEMISTRY: INTRODUCTION

Environmental Chemistry deals with the study of the various chemical phenomena taking place in the environment. In a broader perspective, it comprises of the study of the chemical species existing in the various segments of the environment, their sources, pathways, reactions and their consequences on the activities of human beings and other life-forms. Thus, environmental chemistry may be considered as a multi-disciplinary study, involving physical and life-sciences, meteorology, agriculture, public health, engineering, etc. The basic concepts of environmental chemistry is interesting not only to the scientists engaged in various scientific and engineering activities but also to the personnel involved in resource planning and material management. It is now universally realised that any future developmental activity has to be viewed in the light of its ultimate environmental impact. The tremendous increase in industrial activity during the last few decades and the release of obnoxious industrial wastes into the environment, have been of considerable concern in recent years from the point of view of environmental pollution. Environmental pollution on one hand and deforestation and population explosion on the other, are threatening the very existence of life on the earth. This situation can improve only if people from all walks of life realize the importance of environmental protection. Hence, environmental education (which includes basic concepts of environmental chemistry) at all levels of non-formal and formal education, is of paramount importance.

1.2.1 Types of Environment

Environment mainly consist of Atmosphere, Hydrosphere, Lithosphere and Biosphere. Which can be roughly divided as (a) Micro Environment, (b) Macro Environment, (c) Physical Environment and (d) Biotic Environment. Environment can principally be categorized as follows:

1. **Built environment:** Built environment means the human made surroundings that provide the setting for human activity. The built environment includes places and spaces created or modified by people including buildings, parks or green spaces and supporting infrastructures, such as water supply or

energy networks, transportation systems, etc. Built environment is shaped by:

- Climate and Geology
- Economy
- Government
- Culture and Fashion
- Technology
- Customers

2. **Natural environment:** It includes all the living and non-living things occurring naturally on Earth. Natural environment is composed of:
   - **Lithosphere:** It is rigid outermost shell (crust and mantle) of Earth.
   - **Hydrosphere:** It is the part of Earth composed of water (ocean, rivers, lakes, ponds).
     - (i) 97% of Earth's water is in the oceans.
     - (ii) 2% of the water is locked in the polar ice caps and glaciers.
     - (iii) Only 1% is available as fresh surface water from rivers, lakes, streams and ground water fit to be used for human consumption and other uses.
   - **Atmosphere:** It is the gaseous envelope surrounding a planet.
     - (i) It sustains life on the Earth.
     - (ii) It absorbs most of the cosmic rays from outer space and transmits only ultraviolet, visible, infrared radiation (300 to 2500nm) and radio waves (0.14 to 40m).
     - (iii) The atmosphere composed of Nitrogen (78%), Oxygen (21%), Carbon Dioxide (0.04%), Argon (0.9%) and trace gases.
   - **Biosphere:** Earth along with its living organisms and atmosphere which sustains life, i.e., living organisms and their interactions with environment, viz., atmosphere, lithosphere and hydrosphere.
3. **Social environment:** It refers to the immediate physical and social setting in which people live or in which something happens or develops. It includes culture, media, language, social condition, health, profession, living condition, economic capability of the people in a certain area.
4. **Physical environment:** The physical environment is the specific part of the human environment that includes purely physical factors, such as soil, climate, water supply, etc. Fundamentally, the physical environment includes land, air, water, plants and animals, buildings and other infrastructure, and all of the natural resources that provide our basic needs and opportunities for social and economic development. All processes and behaviours take place within specific physical environments. Therefore, a simple definition of any physical environment would be the natural surroundings (whether it is clean or dirty), the living species of flora and fauna, the non-living things within it and how they interact with each other and the environment.
5. **Biotic environment:** Biotic means living, and biotic factors are the living

parts of the ecosystem with which an organism must interact. The biotic factors with which an organism interacts depend on whether it is a producer, a consumer or a decomposer. Fundamentally, the Biotic environment includes the various Biotic components or Biotic factors which can be defined as any living component that affects another organism or shapes the ecosystem. It includes both animals that consume other organisms within their ecosystem, and the organism that is being consumed. Biotic factors also include human influence, pathogens, and disease outbreaks.

1.2.2 Structure of Environment

Environment is both physical and biological.

Physical environment

It includes landforms, water bodies, climate, soil, rocks and minerals. Physical environment refers to geographical climate and weather or physical conditions wherein individual lives. It is categorized into three categories:

- Solid – The Lithosphere
- Liquid – The Hydrosphere
- Gases – The Atmosphere

These three basic environments may be termed as:

A. Lithospheric Environment, such as Mountains, Plateau.

B. Hydrosphere Environment, such as Glacier, Coastal.

C. Atmosphere Environment, such as Wind, Temperature.

A. Lithospheric environment

Lithosphere refers to all the rocks of the Earth. It includes the planet's mantle and crust (outermost layer). The actual thickness of the lithosphere ranges from roughly 40 km to 280 km. It includes mountains, soil, land, and minerals. For example,

1. **Mountains:** Mountain covers 24% of the world's surface. Mountains are important water reservoirs storing water in the form of glaciers, snow, wetlands, lakes and sub-surface deposits. Mountains supply about 50% of total freshwater and they are mountains are important for agriculture, food and biodiversity. Mountains provide diverse and scattered array of habitats in which a large range of plants and animals can be found. Mountain environments have different climates from the surrounding lowlands and hence the vegetation differs as well. The differences in climate results from the principal causes:
    - **Height of Mountains:** Mountains, hills, valleys, etc., are formed due to irregularities in the surface of Earth. Effect of different altitude can be better seen on mountains. With increase in altitude above sea level, there are changes in values of temperature, pressure, wind, velocity, humidity, intensity of solar radiation. Due to these changes vegetation at different altitudes differ much. It affects climate because atmospheric temperature decreases with increasing altitude.

- **Direction of mountains and valleys:** Mountains deflect winds into different directions and capture moisture from wind on certain sides. This may be the reason, why on certain sides and at particular height one may see luxuriant forests, whereas on other sides and at lower levels vegetation is scanty and show xeric tendencies.
- **Exposure of slope:** Exposure of slope to the Sun and wind affects very much the kind of plants growing there. Generally, the slope exposed to the Sun and wind supports vegetation which may be entirely different from that which is less or not at all exposed to Sun or wind.
- **Relief:** It affects climate because they stand in the path of wind system and force air to rise over them. As the air rises it cools, leading to higher precipitation, as it descends it becomes warmer and reduces likelihood of precipitation and creating areas of drier climate.

2. **Soil:** Soil is the thin layer of material covering the Earth's surface. It is any part of Earth's crust in which plants grow. For example, muddy bottoms of ponds, porous rock surfaces, bottoms of lakes, etc. Soil has mineral matter, soil organic matter (humus), soil water, soil atmosphere, biological system. It is thus preferred to call it as a soil complex. The soil has taken thousands of years to form. The whole process of soil formation is divided into two stages:
   - **Weathering:** It is breakdown of bigger rocks into fine, smaller, mineral particles. Two main categories of weathering include:
     (i) Physical, such as wetting, drying, heating, cooling, etc.
     (ii) Chemical, such as hydration, oxidation-reduction, etc.
   - **Pedogenesis:** Modification of the mineral matter through interaction between biological, topographic and climatic effects which lead to the development of any of great variety of potential soil types. It is largely a biological phenomenon.

Soil profile is defined as a vertical section of the soil from the ground surface downwards to where the soil meets the underlying rocks. Soil horizons is a layer parallel to the soil surface, whose physical, chemical and biological characteristics differ from the layers above and beneath. Soil profile consists of 6 main horizons (Refer Figure 1.1):

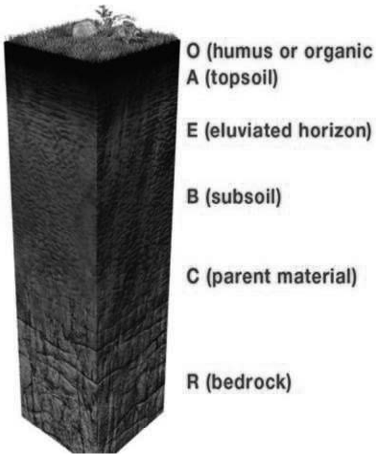


***Fig. 1.1** Horizons of Soil*

3. **Land:** It is all the living organisms and their physical environment on piece of land. Landforms such as hills, valleys, plains, river basins and wetlands include different resource generating areas that the people living in them depend upon. Man needs land for building homes, cultivating food, maintaining pastures for domestic animals, developing industry to provide goods. Land should be used rationally. Land use involves the management and modification of natural environment or wildness into built environment, such as settlements and semi-natural habitats such as fields, pastures and managed woods.

B. Hydrosphere environment

All the water in its various forms, present in all the components of Earth's environment together constitutes the hydrosphere. It includes all liquid and frozen surface waters, groundwater held in soil and rock and atmospheric water vapour. 73% of Earth is covered with water. About 1.4 billion cubic meter of water is liquid and frozen form make up the oceans, lakes and streams, glacier and ground water.

Table 1.1 *Water Masses at Earth's Surface*

Reservoir	Volume (cubic km)	Percent of Total
Oceans	1,338,000,000	96.5
Ice Caps, Glaciers	24,064,000	1.74
Ground Water	23,400,000	1.69
Lakes	176,400	0.013
Soil Moisture	16,500	0.001
Rivers	2,120	0.0002

Table 1.1 illustrates the water masses at the Earth's Surface.

C. Atmospheric environment

Atmospheric environment is the envelope of air surrounding the Earth, including its interfaces and interactions with the Earth's solid or liquid surface. The atmosphere of Earth is composed of Nitrogen (78%), Oxygen (21%), Argon (0.9%), Carbon Dioxide (0.04%) and other gases in trace amounts. Earth's atmosphere consists of a number of layers that differ in properties, such as composition, temperature and pressure.

- Troposphere – 17 km at Equator to 7 km at Poles
- Stratosphere – 15 km to 35 km
- Mesosphere – 35 km to 85 km
- Thermosphere – 85 km to 690 km
- Ionosphere – 85 km to 690 km
- Exosphere – about 690 km to 1000 km

Troposphere

- It is the atmospheric layer in which we live. This layer starts at ground level and extends about 12 km upwards and at an altitude of 8 km at the poles and 18 km at the equator.

- This is where all weather occurs and it’s the air that we breathe.
- The troposphere ends with the Tropopause.
- As one goes upward, the temperature in this layer falls at the rate of 5°C per kilometer, and reaches –45°C at the poles and –80°C over the equator at Tropopause.
- The fall in temperature is called ‘Lapse Rate’.
- The troposphere is marked by temperature inversion, turbulence and eddies.
- Almost all the weather phenomenon like rainfall, fog and hailstorm, etc., are confined to this layer.
- The Troposphere is influenced by seasons and jet streams.

NOTES

Tropopause

- Top most layer of troposphere.
- It acts as a boundary between troposphere and stratosphere.
- This layer is marked by constant temperatures.

Stratosphere

- This layer extends upwards from the tropopause to about 50 km from the Earth’s surface.
- The temperature in this layer remains constant for some distance but then rises to reach a level of 0°C at 50 km altitude.
- This rise in temperature is due to the presence of Ozone (harmful UltraViolet (UV) radiation is absorbed by Ozone).
- This layer is almost free from clouds. So aero planes fly in lower stratosphere, sometimes in upper troposphere where weather is calm.
- Sometimes, cirrus clouds are present at lower levels in this layer.

Ozonosphere

- It lies at an altitude between 30 km and 60 km from the Earth’s surface and spans the stratosphere and lower mesosphere.
- Because of the presence of ozone molecules, this layer reflects the harmful ultraviolet radiation.
- The Ozonosphere is also called chemosphere because a lot of chemical activity goes on here.
- The temperature rises at a rate of 5°C per kilometer through the Ozonosphere.

Mesosphere

- This layer continues up to an altitude of 80 km from the Earth’s surface.
- The temperature gradually decreases with height to -100°C at 80 km altitude.
- Meteorite burn up in this layer on entering from the space.

Thermosphere and ionosphere

- The layer of very rare air lies above the Mesosphere is called the Thermosphere, and is a region in which temperatures again increase with height.
- Temperature rises to hundreds or at times thousands of degrees due to absorption of high energy X-rays and UV radiation from the Sun. However, the air in this layer is so thin that it would feel freezing cold to us.
- Many satellite actually orbit Earth within the Thermosphere.
- Variations in amount of energy coming from the Sun exert a powerful influence on both the height of the top of this layer and the temperature within it. Because of this, top of the thermosphere can be found anywhere between 500 and 1000 km above the ground.
- Temperatures in the upper thermosphere can range from about 500°C (932°F) to 2000°C (3632°F) or higher.
- Between night and day and between the seasons the temperature of the Thermosphere varies. Shortwave radio broadcasts in India from other parts of the world is received by the radio waves which are absorbed and reflected by Ionosphere.

Exosphere

- The region above about 500 km is called the Exosphere.
- It contains mainly oxygen and hydrogen atoms, but there are so few of them that are rarely collide- they follow 'ballistic' trajectories under the influence of gravity and some of them escape right out into space.

Figure 1.2 illustrates the various layers of the atmosphere.

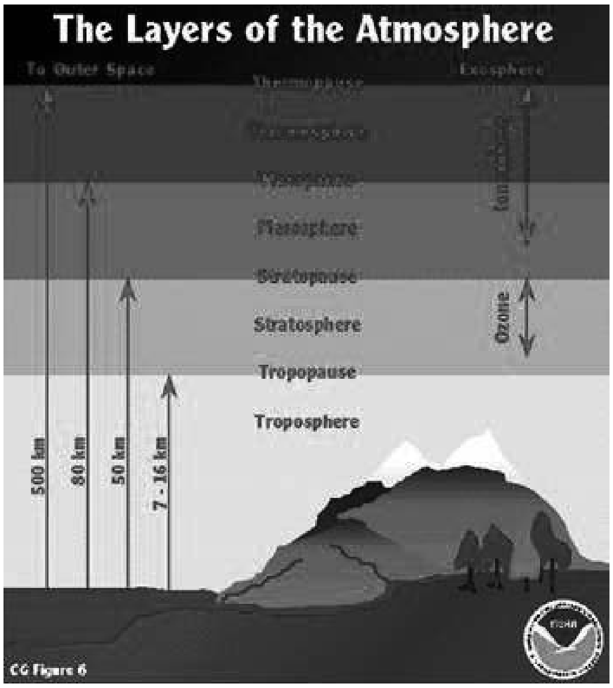


Fig. 1.2 *Various Layers of the Atmosphere*

Besides atmosphere it also includes other factors also such as light, temperature and wind.

Biotic/Biological environment

Biotic environment is the environment comprising of living organisms which interact with each other and their Abiotic environment. The biological environment consists of plants and animals and they constitute the biosphere. On the basis of their role in the ecosystem Biotic factors are grouped into three major groups, these groups are producers or autotrophs, consumers or heterotrophs, and decomposers or detritivores. Three different types of organisms are discussed below:

Producers

These are also known as autotrophs (‘auto’ for ‘self’ and ‘trophs’ for ‘food’), are green plants (organisms that make their own food) which contain chlorophyll with the help of this they trap solar energy and change it to chemical energy of carbohydrate using inorganic materials namely water and carbon dioxide and energy sources. There are two major classes of producers:

- Photoautotrophs are the most common type of producer on Earth today. These producers harness energy from sunlight to power their life functions. Green plants, green algae, and some bacteria are photoautotrophs. Most photoautotrophs use a pigment, such as chlorophyll, to catch photons from the Sun and harvest their energy. They then package that energy into a form that all life forms can use, and use it to create proteins, sugars, lipids, and more essential materials for life. In most ecosystems, plants – which are producers that are multicellular, highly complex, and very efficient at turning sunlight into fuel for living organisms – form the bottom of the energy pyramid. All other organisms depend on the energy plants harvest from the Sun to survive.
- Chemoautotrophs are rare in most ecosystems. They obtain energy from chemicals such as hydrogen, iron, and sulfur, which are not common in most environments. Nonetheless, they can still play an important role in ecosystems because of their unusual biochemistry. Some Methanogens microorganisms that make Methane are chemoautotrophs. Methane, a greenhouse gas which is much more powerful than carbon dioxide, may play a major role in regulating the planet’s temperature. Other chemoautotrophs can produce similarly powerful chemicals with their unique metabolisms.

Consumers

These organisms lack chlorophyll and cannot make their own food, therefore eat other living organisms in order to obtain energy. They, also called ‘heterotrophs,’ (‘hetero’ for ‘other’ and ‘trophs’ for ‘food.’). Herbivores who eat plants, carnivores who eat animals, and omnivores who eat both plants and animals, are all heterotrophs. Some autotrophs subsequently evolved symbiotic relationships with consumers, such as angiosperms – plants which produce nectars and fruits to attract animals, who ultimately help them to reproduce. Carnivores feed on herbivores or on other carnivores.

- Secondary Carnivores – Feed on Herbivores
- Tertiary Consumers – Feed on Other Carnivores
- Omnivores – Feed on Both Producers and Consumers
- Scavengers – Feed on Dead or Decaying Organisms

Decomposers

They break down the dead organic materials of producers (plants) and consumer (animals), which can then be used again by other organisms. Decomposers include soil bacteria, fungi, worms, flies, and other organisms. They are distinct from consumers, because consumers usually consume other organisms while they are still alive. Decomposers, on the other hand, metabolize waste products that might not be of interest to consumers, such as rotting fruit and dead animals. In the process they break down these dead things into simpler chemicals that can be used by heterotrophs to thrive and produce more energy for the ecosystem as a whole. The decomposers are known as saprotrophos. Examples include:

- Producers – Green Plants
- Consumers – Herbivores – Goat, Deer, etc.
- Carnivores – Lion, Tiger, etc.
- Omnivores – Man, Bear, etc.
- Decomposers – Bacteria and Fungi

Check Your Progress

1. Define environmental chemistry.
2. What elements shape built environment?
3. What are the features of the atmosphere layer Tropopause?

1.3 COMPOSITION OF ATMOSPHERE

The atmosphere is divided into five distinct layers characterized by the slope of its temperature profile: (*i*) Troposphere (*ii*) Stratosphere (*iii*) Mesosphere (*iv*) Ionosphere/Thermosphere and (*v*) Magnetosphere/Exosphere

Troposphere

This region extends from the earth (about 8-10 km at the polar latitude, 12 km at the moderate latitude and 18 km at the equator). The troposphere accounts for about 80 per cent of the atmospheric mass. The vertical temperature gradient of the troposphere is 5° per km in the lower and 7° per km in the upper regions of the troposphere. The upper region of the troposphere is separated by the lower region of the stratosphere in a narrow range called the Tropopause.

The uppermost region of the troposphere is almost transparent to the sun's rays. The sun's rays are mostly absorbed by the earth's surface due to various materials present in it. Some of the absorbed solar energy radiates as heat waves from the lower region of the troposphere to the middle and finally to the upper troposphere. Thus, there occurs a gradual decrement in temperature with height. Again, the non-uniform heating of the ground surface of the earth, due to uneven distribution of materials, ascending and descending air currents so produced result in turbulence and mixing of air mass. This mixing helps air to maintain a good quality since it rapidly disperses pollutants. The temperature in the troposphere region varies from ground temperature to – 56°C with altitude. The average pressure on the earth's surface is 1,014 millibars, close to 1 atmosphere (atm). With increased height the air pressure decreases. Natural happenings like rains, storms, thunder showers, etc., are found in this layer only. Because of climatic changes, this layer has tremendous effect on the eco-system.

All living beings live in the troposphere. Although, they are surrounded by air they cannot see it, but only feel it when it blows or when they breathe. Air has no colour, odour or definite shape, the composition (per cent by volume) of clean air being: nitrogen 77.2 per cent, oxygen 20.6 per cent, carbon dioxide 0.04 per cent, water vapour varies from place to place, inert gases 0.94 per cent and other traces approximately 0.03 per cent.

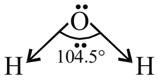
- **Nitrogen (N_2):** It is a colourless, tasteless and odourless gas. It is a diatomic gas. The structure is $(: N \equiv N :)$. At room temperature it is inert and only at higher temperature it shows some chemical reactivity. It dilutes the effect of oxygen and controls combustions. It is very essential for plant and animal life as it forms amino acids and proteins.
- **Oxygen (O_2):** It is a diatomic gas. It is a colourless, tasteless and odourless gas. The structure is $(:\ddot{O} = \ddot{O}:)$. Pure oxygen is very necessary for most forms of life. Oxygen helps in combustion, oxidation and respiration of all living beings. Plants in all ecosystems release about 8 moles of oxygen per year per square meter of the earth's surface during photosynthesis. This amount of oxygen is utilized by plants and heterotrophic organisms in respiration, so that there is a balance between the amount of oxygen production and utilization.
- **Carbon dioxide (CO_2):** It is a colourless gas with faint pungent smell with a resonance hybrid of three structures.

  $$O^- - C = O^+ \longleftrightarrow O = C = O \longleftrightarrow O \equiv C^+ - O^-$$

  It is very essential for photosynthetic activity. The biochemical formula of this process is given as

  $$H_2O + CO_2 + \text{solar energy} \xrightarrow[\text{of plants}]{\text{chlorophyll}} (CH_2O)_n + O_2$$

  In this process CO_2 and H_2O is consumed and carbohydrate $(CH_2O)_n$ is produced and O_2 is released. CO_2 has a unique property of absorption of infrared radiation of the solar spectrum keeping the earth warm. CO_2 has a linear structure $(\overset{\leftarrow}{O} = C = \vec{O})$, thus the net dipole moment is zero. However, in the infrared region here, it is vibration, rather than the rotation which gives rise to a dipole change. The symmetric stretching $\overset{\leftarrow}{O} = C = \vec{O}$ (1330 cm^{-1}), anti-symmetric stretching $\overset{\leftarrow}{O} = \overset{\leftarrow}{C} = O$ or $\vec{O} = \vec{C} = O$ (2349 cm^{-1}) and bending mode of vibration $\overset{\uparrow}{O} = \underset{\downarrow}{C} = \overset{\uparrow}{O}$ (667 cm^{-1}) of CO_2 is as given. The anti-symmetric bending vibration gives rise to net dipole change and the molecules become infrared active.

- **Water vapour (H_2O):** It has got tetrahedral structure , but due to lone pair-lone pair electron repulsion, there is a decrease in bond angle and becomes 104.5° instead of 109°28", which attributes to a tetrahedral structure. Water vapours are responsible for the formation of clouds and rains.
- **Inert gases (Helium [He], Neon [Ne], Argon [Ar], Krypton [Kr], Xenon [Xe] and Radon [Rn]):** They are zero or 18 group elements in the periodic table. They undergo very few chemical reactions under drastic conditions and are therefore known as noble gases. Neon gas is very effective in formation of chlorophyll. These gases are generally required to create inert atmosphere.

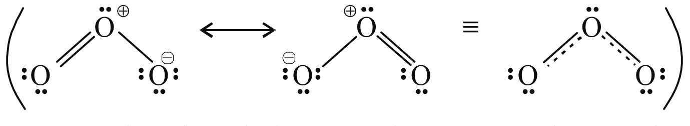
Stratosphere

The layer above the tropopause is called the stratosphere. Its thickness is about 50 km above the earth surface and it consists of a rich layer of ozone. The short wavelength ultraviolet energy (190nm – 380nm) is absorbed by ozone and oxygen, causing the air to be heated and simultaneously this layer acts as a shield to protect life on earth from the harmful effect of this radiation. The temperature in this region continues to increase with height and at 50 km, attains a maximum of –2°C.

Stratosphere is therefore, a stable layer of very dry air with composition of ozone, oxygen and atomic oxygen. The atomic oxygen which is produced has less residence period as it combines with molecular oxygen to form ozone and hence, it has less contribution to heating effect on the stratosphere unlike its role in thermosphere/ionosphere. Pollutants that finds their way into the stratosphere may remain there for many years before eventually drifting back to the troposphere and are then finally removed by settling or precipitation. The upper region of the stratosphere is separated from the lower region of the mesosphere by a narrow range called the stratopause.

Ozone

It is a pale blue gas and has a strong odour. When inhaled, it causes headaches and large quantities of it prove fatal. Ozone molecules are considered to be the resonance hybrid of two structures—



The O – O – O bond angle in ozone is 116.8° and O – O bonds are of equal length (127.8 pm).

Oxygen in the upper atmosphere absorbs ultraviolet radiation and changes to atomic oxygen. Atomic oxygen thus produced, is combined with molecular oxygen to form ozone

$$(O_2) \xrightarrow{\text{UV Rays}} O + O$$

$$O_2 + O \rightarrow O_3$$

$$2O_3 \xrightleftharpoons{\text{Ultraviolet Rays}} 3O_2$$

Ultraviolet rays harmful to animals (including man) are absorbed by oxygen to form ozone and the ozone thus formed prevents the remaining ultraviolet rays to reach the earth's surface.

Mesosphere

This is the region above the stratosphere and extends up to a height of 85 km above the earth's surface. Concentration of ozone is very low in this region and decreases rapidly with increase in height. Thus, there is a decrease in absorption of solar radiation and temperature falls to – 92°C. The dominant chemical species found in this region are O_2 and NO. It has the highest clouds which often are visible in clear weather. Meteors and upward convection air currents cause these clouds. This layer is also responsible for reflecting all sound waves moving upwards from the earth. So beyond this layer, a valley of silence prevails. The upper region of the mesosphere is separated from the lower region of the thermosphere by a narrow range called the mesopause.

Nitric oxide (NO)

It is a colourless gas. Nitric oxide is paramagnetic, having an odd electron. It is a resonance hybrid of two structures.

$$\left(:\dot{N} = \ddot{O}: \longleftrightarrow \overset{\ominus}{:\ddot{N}} = \overset{\oplus}{\dot{\ddot{O}}}:\right)$$

Thermosphere/Ionosphere

The region immediately above the mesopause, where the temperature rises very rapidly with increasing altitude is known as the thermosphere. It extends up to 500 km above the earth surface. The most dominant chemical species in this region are O_2, NO and atomic oxygen (O). They absorb uv-radiation, x-rays and γ-rays and undergo ionization. The maximum temperature in this region is about 1200°C. The heating of the thermosphere is mainly due to the absorption of solar energy by atomic oxygen (O). Within the thermosphere, is a relatively dense band of charged particles (O_2^+, NO^+,O^+ and electrons) called the ionosphere. The ionosphere is high electrical conductor as it contains charged particles produced from NO as well as from hydrogen, oxygen, helium, ozone, etc.

Appreciable levels of positive ions, such as O_2^+, O^+, NO^+ exist in this region with considerable residence times. The charged species mainly form due to the absorption of UV radiation. During the nights when UV radiations are not present, the positive ions combine with the free electrons and form neutral species. Before the induction of satellites, the ionosphere was important for world wide communication due to its ability to reflect short radio waves back to earth.

Magnetosphere/Exosphere

Very little is known about this layer. It exists above the ionosphere and extends approximately up to 2000 km above the earth. This layer is almost airless and empty. It probably contains hydrogen gas in ionized state. It has very high temperature and merges into airless dark black interplanetary space.

Table 1.2 *Characteristics of the various regions of atmosphere*

Region	*Height above the earth's surface*	*Temperature (°C)*	*Major chemical species*
Troposphere			
Polar latitude	0 – 10	15 to – 56	N_2, O_2, CO_2, H_2O(vapour)
Moderate latitude	0 – 12		
Equator	0 – 18		
Stratosphere			
Polar latitude	10 – 50	– 56 to – 2	O_3, O_2, O
Moderate latitude	12 – 50		
Equator	18 – 50		
Mesosphere	50 – 85	– 2 to – 92	O_2, NO
Thermosphere/Ionosphere	85 – 500	– 92 to 1200	O_2^+, NO^+, O^+
Magnetosphere/Exosphere	500 – 2000	≥ 1200	H_2^+

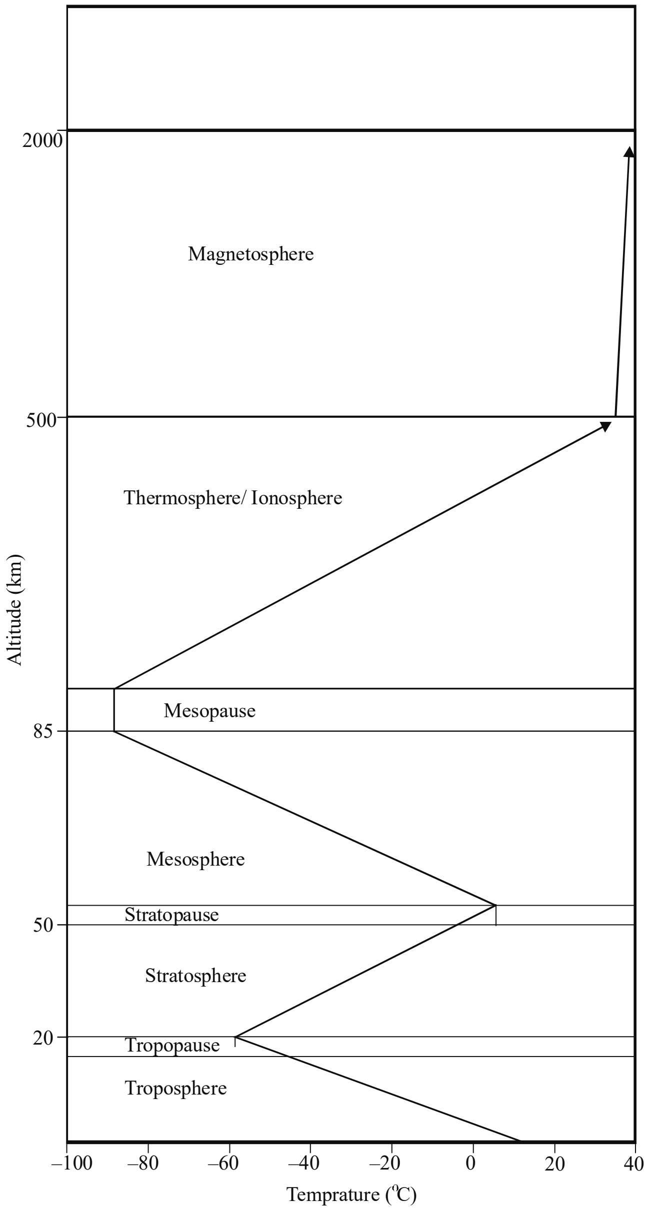


Fig. 1.3 *Temperature Profile Curve of the Atmosphere*

1.3.1 Vertical Temperature

The vertical temperature profile of the coupled surface-atmospheric system indicates a balance between radiation, convective and dynamical heating/cooling. In weather forecasting and climate modelling, vertical temperature profiles are commonly utilised. The average vertical temperature profile is calculated by averaging atmospheric temperatures across all latitudes and over the course of a year. This plot is referred to as a standard atmosphere. Four separate layers are suggested by the average vertical temperature profile.

The average atmospheric temperature in the first layer, known as the troposphere, drops progressively from roughly 290K (63°F; 17°C) at the surface to around 220K (-64°F; -53°C) at a height of about 6.2 mi (10 km). The tropopause, which is just above the cruising altitude of major commercial jet aircraft, is located at this altitude. The lapse rate, or temperature decline with height, is essentially constant throughout the troposphere, at 43.7°F (6.5°C) every 0.6 mi (1 km). The lapse rate abruptly drops to extremely low levels at the tropopause. The temperature of the atmosphere remains rather steady for the following 12 miles (20 kilometres), then begins to climb with increasing altitude up to about 31 miles (50 km). The stratosphere is the area where temperatures are rising. Temperatures near the top of the layer, known as the stratopause, are nearly as warm as those on the surface. The mesosphere is situated between 31 and 50 miles (50 and 80 kilometres), where atmospheric temperature begins to drop with altitude and reaches an extremely cold low of 180 degrees Kelvin (-93 degrees Celsius) at the top of the layer (the mesopause), about 50 miles (80 kilometres). The thermosphere is characterized by high gas temperatures and is located above the mesopause. Depending on how active the sun is, gas temperatures in the very high thermosphere (approximately 311 mi (500 km) above Earth's surface) can range from 500–2,000K (441–3,141°F; 227–1,727°C).

These data, however, are a little deceiving. The energy of the motion of gas molecules is measured by temperature. Despite their high energy, the molecules in the thermosphere are in extremely small numbers, less than one millionth of those found on Earth's surface. Because such a limited number of energetic gas molecules are unable to transfer much of their heat energy, a person in the thermosphere would feel much more like the freezing cold of space.

1.3.2 Heat Budget of the Earth Atmospheric System

The heat budget of the Earth is the balance of incoming and outgoing heat. To maintain constant conditions, the budget must be balanced so that the incoming heat equals the departing heat, just like any other budget. The heat budget of the atmosphere is made up of 48% solar radiation, with 14% originating from shortwave entering solar radiation and 34% coming from outgoing long-wave terrestrial radiation.

The rate at which the earth and its atmosphere receives energy from space, is equal to the rate at which energy is being returned to space and is known as 'global energy balance'.

To calculate global energy, three separate regions namely the earth, its atmosphere and the outer space need to be considered.

The incoming solar radiation striking the earth surface is $S\pi R^2$. Surface area of earth being $4\pi R^2$, the total radiation striking per unit surface area becomes

$$\frac{S\pi R^2}{4\pi R^2} = \frac{S}{4} = \frac{1370 \text{ W/m}^2}{4} = 342 \text{ W/m}^2$$

The albedo being 31 per cent, the amount of solar radiation reflected back will be

$$\frac{S\pi R^2 \alpha}{4\pi R^2} = \frac{S}{4}\alpha = \frac{1370}{4} \times \frac{31}{100} \text{ W/m}^2 = 107 \text{ W/m}^2$$

It is estimated that out of 107 W/m^2, 77 W/m^2 is reflected off the atmosphere and remaining 30 W/m^2 are reflected off the earth's surface.

The solar energy which is not reflected is absorbed by the surface of earth and its atmosphere. The absorbed energy per unit surface area becomes

$$\frac{S\pi R^2(1-\alpha)}{4\pi R^2} = \frac{S}{4}(1-\alpha) = 342\ (1-0.31) = 235 \text{ W/m}^2$$

Out of 235 W/m^2, 67 W/m^2, are absorbed by the atmosphere and remaining 168 W/m^2, by the surface of the earth.

If the global temperature does not change with time, then the rate at which energy is received by earth and its atmosphere, must be radiated back. Out of 342 W/m^2, 107 W/m^2, is reflected back into space, hence, the absorbed 235 W/m^2 radiation must be radiated back into the space. If the earth's surface was at 254 K, it would radiate 235 W/m^2 to balance the incoming energy. But it is known that greenhouse gases absorb most of the outgoing radiation, hence, required energy balance would not be realized.

Therefore, to achieve necessary energy balance, enough energy should be forced out through the atmosphere, *i.e.*, the temperature of the earth's surface must be higher than 254 K.

Supposing earth as black body radiator, the amount of radiation per unit surface area, having surface temperature of 288 K, becomes

$$\frac{\sigma 4\pi R^2 T_s^4}{4\pi R^2} = \sigma T_s^4 = 5.67 \times 10^{-8} \text{ W/m}^2\text{ K}^4 \times (288\text{K})^4 = 390 \text{ W/m}^2$$

(T_s is the surface temperature of earth)

Atmospheric Window

The incoming solar energy just outside the earth's atmosphere has wavelength less than 3 μm ($\lambda_{max} = 0.5$ μm), while the outgoing energy radiated by the earth has essentially a wavelength greater than 3 μm ($\lambda_{max} = 10.1$ μm). In an attempt to pass through the atmosphere, it is affected by various atmospheric gases as well as by aerosols. It is known that a molecule absorbs energy only when the frequency of its oscillation matches with the frequency of radiation. Thus, most of the long wavelength energy radiated by the earth is absorbed by gases like H_2O (water vapour), CO_2 ,CH_4, N_2O and O_3 (greenhouse gases). However, radiant energy having wavelength between 7 to 12 μm, is not absorbed by any atmospheric gases due to frequency mismatch. As a result, the radiated energy (40 W/m^2) in the frequency range of 7 to 12 μm easily escapes to the space. This relatively clear sky, for this outgoing energy is referred to as the 'atmospheric radiation window'.

Out of 390 W/m^2, only 40 W/m^2 passes directly through the atmosphere, mostly through the atmospheric window between 7 and 12 μm. The remaining 350 W/m^2 is absorbed by the greenhouse gases in the atmosphere. The atmosphere then radiates 324 W/m^2 back to the surface and (169 + 26 = 195) 195 W/m^2 to the space.

Heat transfer also occurs from the surface to the atmosphere by convective heating as well by evaporation and condensation of water. Convection transfers 24W/m^2 to the atmosphere and condensation of water vapour provides 78W/m^2 of latent heat.

If the model is internally self consistent, the rate of energy gain must be equal to the rate of energy loss in all of the three regions: the space, the atmosphere and the earth's surface.

	Rate of energy gain (W/m^2)	*Rate of energy loss (W/m^2)*
Earth's surface	168 + 324 + 30 = 522	78 + 24 + 30 + 390 = 522
Atmosphere	67 + 78 + 24 + 350 = 519	169 + 26 + 324 = 519
Space	107 + 169 + 26 + 40 = 342	

The model thus, shows the necessary balance.

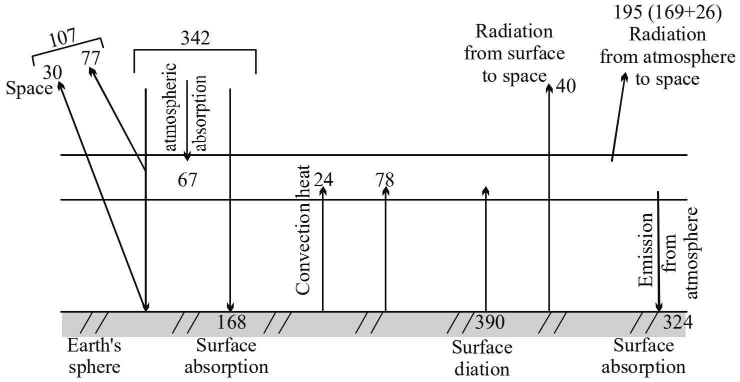


Fig. 1.4 *Global Average Energy Flow between the Atmosphere and the earth's Surface*

1.3.3 Vertical Stability of Atmosphere

Turbulence and cloud formation are mostly caused by vertical motion in the atmosphere. The strength of vertical motion is largely influenced by the atmosphere's vertical stability. Vertical motion is more difficult to achieve in a stable atmosphere than in an unstable one. The atmosphere is said to be neutrally stable when it neither resists nor facilitates vertical motion.

When air is warmer than its surroundings, it rises. Air does not rise because it is warmer; it rises because warm air is less dense and thus more buoyant than cold air. As distinct air masses dominate a region, the vertical temperature profile of the atmosphere changes. The rate of change of temperature with height (the environmental lapse rate) and hence the stability of the atmosphere at that moment in time can be determined if the temperature profile is known.

Check Your Progress

4. What is the thickness of Stratosphere layer?
5. What is the dominant chemical species found in Mesosphere?
6. What is the heat budget of the Earth?
7. What happens to vertical motion in stable, unstable, and neutrally stable atmosphere?

1.4 BIOCHEMICAL CYCLES OF C, N, P, S, AND O

The mineral cycling is also termed as biogeochemical cycle or nutrient cycle as it describes about the occurrence and regulation of the biogeochemical or nutrients Carbon, Nitrogen and Phosphorus in the ecosystem. Fundamentally, the movement of chemical substance through Biotic (Biosphere) and Abiotic (Lithosphere, Atmosphere, and Hydrosphere) compartments of Earth is called biogeochemical cycle.

- Energy flows through an ecosystem and is released as heat, but chemical elements are recycled.
- The ways in which an element or compound moves between its several biotic and Abiotic forms and locations in the biosphere is called a biogeochemical cycle.
- It is a movement of nutrients and other elements between living and non-living beings.
- All life depends upon basic source of energy Sun.
- Life on Earth comprises of a diversity of living organisms.
- These living organisms exist and survive in a diversity of associations. Such survival encompasses the presence of systemic flows, such as flows of energy, water, and nutrients.
- Cyclic movement through the tissues of plants and animals maintains balance of the chemical elements.
- The cycle starts by absorbing the chemical elements by the organism and is returned to the air, water, and soil through decomposition.
- These cycles are largely energized by solar insolation.

The nutrient cycle can be divided into two pools:

(1) The reservoir pool, which is the large, slow-moving non-biological component.

(2) The cycling or labile pool, which is a small but active portion that is exchanged between the organisms and their environment.

The principles of biogeochemical cycle can be illustrated through five examples:

(1) Nitrogen Cycle, which is an example of a very complex, well-buffered, gaseous type cycle.

(2) Phosphorus Cycle, which is an example of a simpler, less well-buffered, regulated cycle.

(3) Sulphur Cycle, which illustrates the links between air, water and the crust of the Earth, the key role played by microorganisms and the complications caused by industrial air pollution.

(4) Carbon Cycle, the Carbon is the most important element of the protoplasm. It is the major constituent of carbohydrates, proteins, fats and nucleic acid of the cells of an organism. Therefore, the Carbon is generally considered as the basis of life. Carbon constitutes 49% of the dry weight of organisms.

(5) Hydrologic Cycle, which are crucial to life and are being increasingly affected by the activities of human beings.

There are two types of Biogeochemical Cycles, namely the Gaseous Cycle and the Mineral Cycle.

(1) Gaseous Cycle: In this type of cycle, the element that exists there in gaseous phase constitutes the major reservoir of atmosphere. Examples include the Carbon, Oxygen and Nitrogen cycles.

(2) Mineral/Sedimentary Cycle: In this type of cycle, the major reservoir is the lithosphere from which the elements are released by weathering. Examples include the Phosphorus, Sulphur and Iodine cycles.

1.4.1 Carbon Cycle

Carbon is a fundamental part of the Earth system. Through Carbon Cycle, the Carbon is exchanged among the biosphere, lithosphere, hydrosphere and the atmosphere of the Earth. In oceans carbon is present as carbonates and bicarbonates, that also dissolve to generate Carbon Dioxide or CO_2 and it is present as CO_2 in air. In soil (Lithosphere), the Carbon is present as fossil fuels. Figure 1.5 illustrates the basic Carbon cycle flow diagram.

Steps of Carbon Cycle

The steps of carbon cycle are:

1. **Entry of Carbon in the Atmosphere:** Carbon enters the atmosphere from respiration (breathing) and combustion (burning) as Carbon Dioxide.
2. **Absorption of Carbon Dioxide by Producers:** By producers (for example, plants) the Carbon Dioxide is absorbed to make carbohydrates in photosynthesis. These producers then release Oxygen.
3. **Passing of the Carbon Compounds in the Food Chain:** Animals feed on the plants, thus passing the Carbon compounds along the food chain. Most of the Carbon these animals consume however is exhaled as Carbon

Dioxide. This is through the process of respiration. The animals and plants then eventually die.

4. **Carbon Returned to the Atmosphere:** Decomposers eat dead organisms (dead animals and plants) present in the ground, so the Carbon is then returned to the atmosphere as Carbon Dioxide which was in their bodies. The decomposed plants and animals may then be available as fossil fuel in the future for combustion. The Carbon cycle is closely connected to ecosystems because plants and animals are an integral part of the Carbon cycle. The Carbon cycle will change as ecosystems change under a changing climate.
5. **Ocean Intake:** Carbon Dioxide is continuously being dissolved in the seas and oceans through the process of diffusion. Once dissolved, this Carbon Dioxide may get converted into carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-) or may remain as it is in the marine waters. Marine plants use dissolved Carbon Dioxide for photosynthesis and certain marine organism's convert carbonates into Calcium Carbonate. The Corals and Oysters use this Calcium Carbonate to make their Shells. Their shells deposit on the sea floor when these organisms die and finally turn into sedimentary rocks.
6. **Weathering of Rocks:** Some Carbon Dioxide or CO_2 that is present in the dissolved state in water gets converted into Calcium Carbonate ($CaCO_3$) in limestone and other carbonate rocks. Weathering of carbonate containing rocks or treatment of their minerals gives out Carbon Dioxide. When acid rain falls on these rocks, then Carbon Dioxide is released.

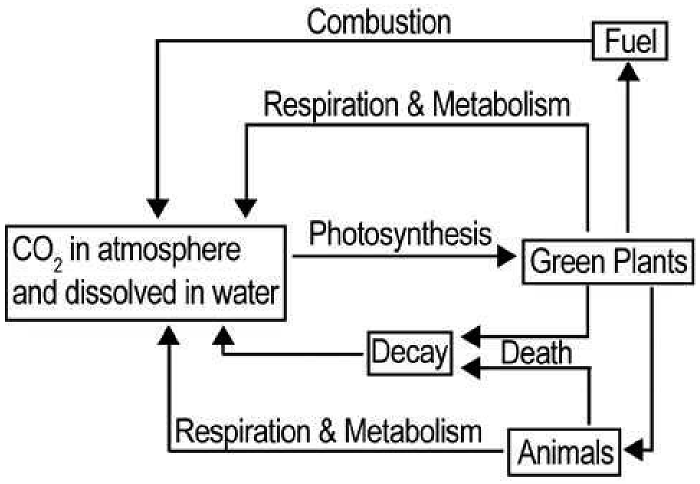


Fig. 1.5 *Basic Carbon Cycle Flow Diagram*

Types of Carbon Cycling

In general, depending on how long it takes to occur the Carbon cycle can be divided into two types: short term and long term.

1. **Short term:** In short term cycling the movement of Carbon across reservoirs only takes relatively short time (minutes, hours, days, months, or years) and in this type of cycling annual changes occur within the atmosphere, terrestrial ecosystems, and the marine ecosystem.

2. **Long term:** This type of Carbon cycling takes thousands to millions of years to occur. The excess Carbons from the short term cycling are stored into the 'long term' reservoir until they are removed after a long time.

Importance of Carbon Cycle

In general, the Carbon cycle is essential for living organisms and biological systems. Discussed below are some of them.

1. **Essential for life:** All living organisms are made up of Carbon or one way or another and it is very essential for life.
2. **Important for the maintenance of the balance in the ecosystem:** Due to the movement of Carbon in various reservoirs balance in ecosystems is maintained. If ever imbalance in ecosystem happens serious environmental disasters like global warming may occur.
3. **Critical to food chain:** The Carbon migrate to the consumers that eat producers. Consumers that eat other consumers as well receive the Carbon from their food as well through food chain and food webs.
4. **Important for climate regulation:** The process of Carbon cycle determines the amount of Carbon Dioxide and Methane in the atmosphere and these two gases significantly contribute to global warming.

The level of greenhouse gases increases, when there is a huge amount of Carbon released into the atmosphere and therefore trapping more heat in the Earth. Hence, if we understand how Carbon cycle occurs in the environment it paves the way for the development of the understanding for world climate.

Human impact on the carbon cycle

The Carbon cycle is a natural process, and has been ongoing throughout Earth's history. As the reservoirs are linked (either directly or indirectly), a change in any of the Carbon reservoirs causes changes in the others. Actions by humans have resulted in the removal of Carbon from Carbon sinks (such as, the oil and coal deposits), directly adding it to the atmosphere. Besides unconcerned (by natural or human processes) it maintains a stable concentration in the atmosphere, biosphere, hydrosphere, and lithosphere. The two main human impacts on the Carbon cycle are:

1. Burning of fossil fuels

Carbon is released into the atmosphere due to burning of coal and oil at a faster rate than it is removed. As a result of this the concentration of Carbon Dioxide in the atmosphere increases. Petroleum refining, paper, food and mineral production, mining and the production of chemicals are the primary industrial activities that emit Carbon Dioxide and affect the Carbon cycle. However, humans are heavily reliant on fossil fuels, and extract it from the lithosphere in great quantities. Burning coal, oil, natural gas, and other fossil fuels, for example for industrial activity and power generation, removes the Carbon from the fossil fuels and emits it as CO_2 into the atmosphere.

NOTES

2. Land use and deforestation

Large amounts of Carbon are stored in living plants (C.1,000 Gigatonnes). Therefore, land use changes, especially the clearance of forests which are very densely inhabited by plants, and therefore contain a large amount of Carbon, can influence the Carbon cycle in two ways. Firstly, the removal of vegetation eliminates plants which would otherwise be capturing Carbon from the atmosphere through photosynthesis. Secondly, as dense forests are replaced by crops/pasture land/ built environments, there is usually a net decrease in the Carbon store, as smaller plants store far less Carbon than large trees. Deforestation also allows much more soil to be eroded, and Carbon stored in the soil is rapidly taken into rivers.

Carbon sequestration

Removal as well as storage of Carbon Dioxide from the air by plants is called Carbon sequestration. Amount of Carbon Dioxide removed from the atmosphere and stored by the plants is affected by agricultural and forestry methods. These sinks of Carbon Dioxide can be farms, grasslands or forests. These sinks of Carbon Dioxide affect the Carbon cycle by decreasing the amount of Carbon Dioxide in the air.

Increasing atmospheric CO_2 and CH_4 along with other greenhouse gases causes higher global air temperatures which in turn increases decomposition in soil, thereby releasing more CO_2 to the atmosphere. Increases in global temperature also affect ocean temperatures, modifying oceanic ecosystems and having the potential to disrupt the oceanic Carbon cycle, limiting the ocean's ability to absorb and store Carbon.

1.4.2 Nitrogen Cycle

Nitrogen circulates among atmosphere, terrestrial, and marine ecosystems and get converted into multiple chemical forms and the conversion of Nitrogen can be carried out through both biological and physical processes. Figure 1.6 illustrates the Nitrogen cycle in an ecosystem.

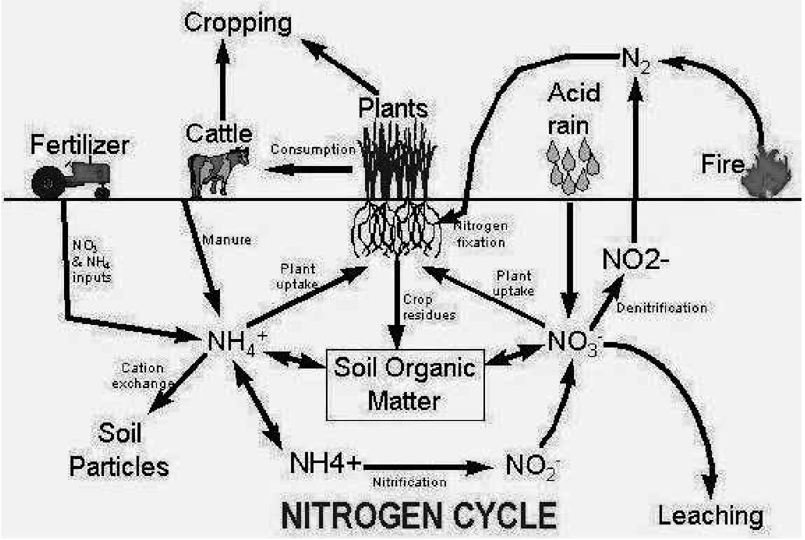


Fig. 1.6 Nitrogen Cycle

Forms of Nitrogen

In the environment chemical forms of Nitrogen is present in wide variety including organic Nitrogen, Ammonium (NH_4^+, Nitrite ($NO_2^"$), Nitrate ($NO_3^"$), Nitrous Oxide (N_2O), Nitric Oxide (NO) or inorganic Nitrogen gas (N_2). Organic Nitrogen may be in the form of a living organism, 'Humus' or in the intermediate products of 'Organic Matter Decomposition'.

Steps of Nitrogen Cycle

The Nitrogen cycle consists of the following stages:

(i) Fixation of Nitrogen, N_2 to NO_3^- or NH_4.

(ii) Assimilation, here the NH_3 and NO_3^- are incorporated into the Biological Tissues.

(iii) Ammonification, Organic Nitrogen Compounds to NH_3.

(iv) Nitrification, NH_3 to NO_3^-.

(v) Denitrification, NO_3^- to N_2.

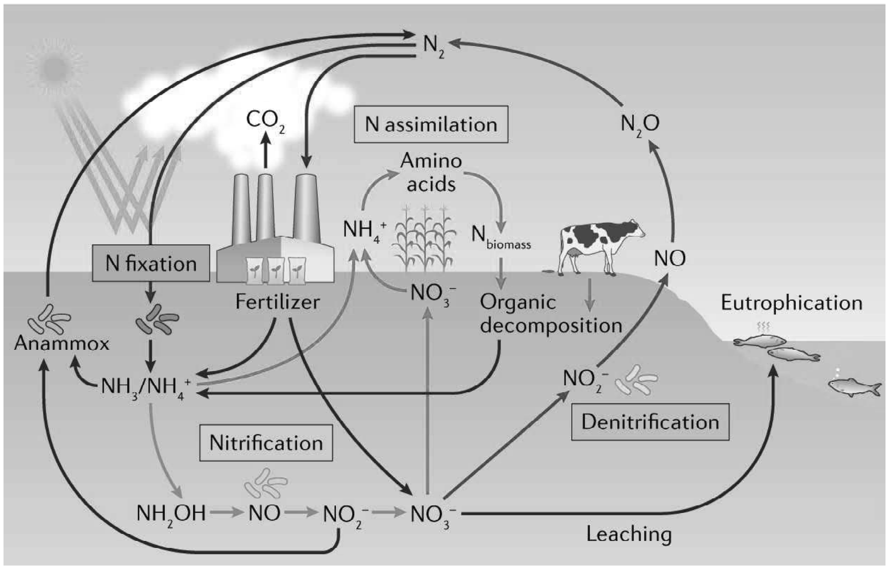


Fig. 1.7 *Nitrogen Fixation*

(i) **Nitrogen Fixation:** This is the first step of the Nitrogen cycle, as shown in Figure 1.7. Nitrogen fixation can be of two types: Atmospheric Fixation (involves lightening), Industrial Nitrogen Fixation (manufacturing Ammonia under high temperature and pressure condition).

- **Atmospheric Fixation:** In this process the Nitrogen is broken down into Nitrogen Oxides by energy of lightning and is then used by plants. It is a natural phenomenon.
- **Industrial Nitrogen Fixation:** In this process by direct combination of Nitrogen and Hydrogen, the Ammonia is produced and later, it is converted into various fertilizers, such as Urea. It is a man-made alternative that aids in Nitrogen Fixation by the use of Ammonia.

- **Biological Nitrogen Fixation:** Nitrogen cannot be used directly from the air. It can be transformed in usable form and other compounds that are more readily usable by Bacteria like Rhizobium and Blue-Green Algae (BGA). These microbes fix Nitrogen compounds in soil. Biological organisms, such as Bacteria, BGA, etc., converts small part of atmospheric Nitrogen (Nitrogen gas) into biologically acceptable Nitrogenous compound (NH_3) and the process is called Biological Nitrogen Fixation.
- **Non-Biological Nitrogen Fixation:** During lightening and thundering, the atmospheric Nitrogen reacts with Oxygen to produce Nitrogen Oxide and this Nitrogen Oxide gets dissolved with rain water and fall to the ground, reacts with minerals in soil to form Nitrates and Ammonium salts.
- **Haber's Process:** Ammonia is formed by reaction of Nitrogen and Hydrogen at high temperature termed as Haber's process.

$$\mathbf{N_2 + O_2 \xrightarrow{\hspace{3em}} NO_2}$$

(ii) Nitrification: This is a two-step process in which NH_3/ NH_4^+ is converted to NO_3^- (Nitrates). First NH_3 is converted to NO_2^- by soil bacteria, such as *Nitrosomonas* and *Nitrococcus*, and then the NO_2^- is converted to NO_3^- by another bacterium, *Nitrobacter*. These bacteria gain energy through these conversions.

(iii) Assimilation: Plants can absorb Nitrogen through their roots once it has fixed in the soil. This process of absorption of Nitrogen is known as assimilation.

(iv) Ammonification: It is the process of conversion of organic Nitrogen into Ammonia. Some bacteria that are present in the soil help to break down organic remains of plants and animals to release Ammonia into the soil. Microorganisms use these dead and waste matter as food and they release Ammonia into the soil.

(v) Denitrification: This process occurs in the deep layers of soil and it is reverse of Nitrification. The anaerobic bacteria present in the soil convert NO_3^- into N_2 and other gaseous compounds like NO_2. This occurs because in deep layers of soil, Oxygen is not available and the soil bacteria use these Nitrogen compounds instead of Oxygen.

Importance of the Nitrogen Cycle

The importance of the Nitrogen cycle can be understood through following points.

- Plants and animals could not live without Nitrogen.
- The Nitrogen cycle helps to bring the Inert Nitrogen from the air into the biochemical process in plants and then to animals.
- Nitrogen cycle is absolutely essential for them because plants need Nitrogen to synthesise chlorophyll, which plants use in photosynthesis to make their food and energy.

- Bacteria help degrade decomposing animal and plant matter during the process of Ammonification. This helps in naturally cleaning up the environment.
- Nitrates and Nitrites are released into the soil which helps in enriching the soil with nutrients needed for cultivation due to Nitrogen cycle.
- Animals obtain the Nitrogen and Nitrogen compounds from plants because plants use Nitrogen for their biochemical processes. Nitrogen is needed as it is an integral part of the cell composition. Animals are also able to utilise the Nitrogen present in the air due to the Nitrogen cycle.

Impact of Humans on Nitrogen Cycle

Humans are greatly impacting the Nitrogen cycle. One way in which this is occurring is by the mass production and use of Nitrogen-based fertilizers. Plants must take in Nitrogen to produce proteins for cellular processes. Fertilizer contains Nitrogen and is widely used on farms to increase and improve the growth of crops. However, fertilizer often ends up in excess, which occurs when heavy rainwater collects on the soil and runs into bodies of water. This greatly increases the amount of Nitrogen that ends up areas of water as well as in soil, which can be harmful to ecosystems. Another way humans affect the Nitrogen cycle is by the burning of fossil fuels, known as combustion. Fossil fuels contain Nitrogen that, when burned, is released into the atmosphere in the form of Nitrous Oxides. Nitrous Oxides are the key components of Acid Rain, a type of pollution that is harmful to forests and bodies of water.

1.4.3 Phosphorus Cycle

Movement of Phosphorus through the Lithosphere, Hydrosphere, and Biosphere is called Phosphorus cycle. Various weather conditions (for example, rain and erosion) help to wash the Phosphorus found in rocks into the soil because of that Phosphorus cycle is extremely slow. In the soil, the organic matter (for example, plants and fungi) absorb the Phosphorus to be used for various biological processes. Phosphorus cycle is faster through plants and animals than it does through rocks and sediments.

The Phosphorus cycle, unlike those of Carbon and Nitrogen cycles lacks an atmospheric component. In rock formations and ocean sediments Phosphorus is most commonly found as Phosphate salts. Phosphate salts usually dissolve in soil water that are released from rocks through weathering and will be absorbed by plants. By eating plants or plant-eating animals absorb Phosphate.

Aquatic and soil compartments are involving in global Phosphorus cycle. Phosphorus is one of the nutrients of major importance to biological systems because it is a basic constituent of Nucleic Acids, Phospholipids and numerous Phosphorylated compounds. Figure 1.8 illustrates the Phosphorus cycle.

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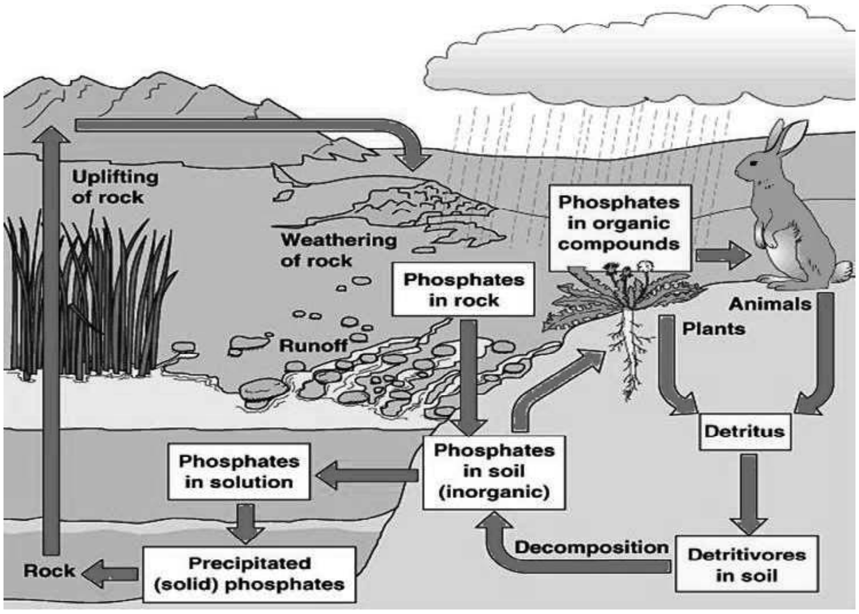

Fig. 1.8 *Phosphorus Cycle*

Steps of Phosphorus Cycle

The steps in the phosphorus cycle are:

1. **Weathering:** It is the first step of the Phosphorus cycle. In this step Phosphorus is extracted from the rocks by weathering, the Phosphorus is being washed into the soil due to rain and other sources of erosion.
2. **Absorption by Plants and Animals:** Plants, fungi, and microorganisms grow by absorbing Phosphorus present in the soil. Phosphorus can be leached into the water systems and plants can absorb Phosphorus from the water directly and grow. Besides the plants, animals also obtain Phosphorus from drinking water and eating plants.
3. **Return to the Environment via Decomposition:** Phosphorus is returned back to the environment via the water or soil after the death of plants and animals, by decomposition. Plants and animals in these environments can then use this Phosphorus. After that, the element will end up in rock formations or sediments, where it will remain for millions of years. Phosphorus is again released into the soil through weathering and absorbed by the plants in the end and the Phosphorus cycle starts over. Figure 1.9 illustrates the Phosphorus cycle on land while Figure 1.10 illustrates Phosphorus cycle in water.

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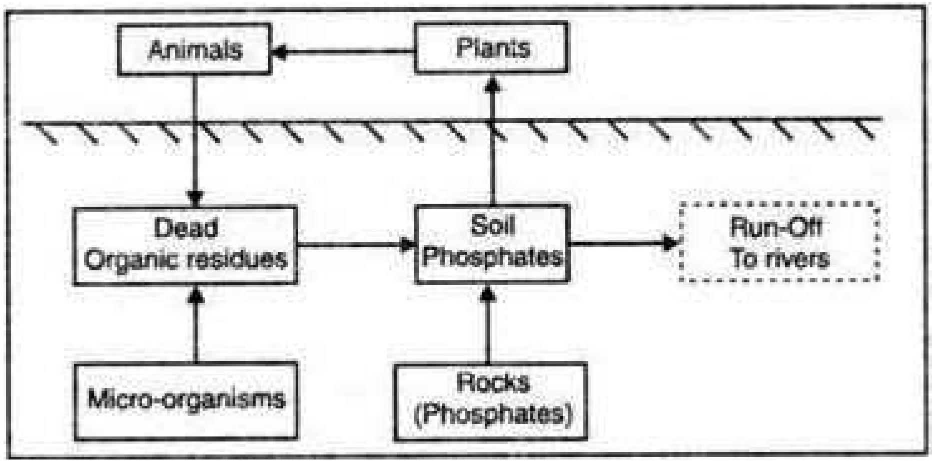

Fig. 1.9 *Phosphorus Cycle on Land*

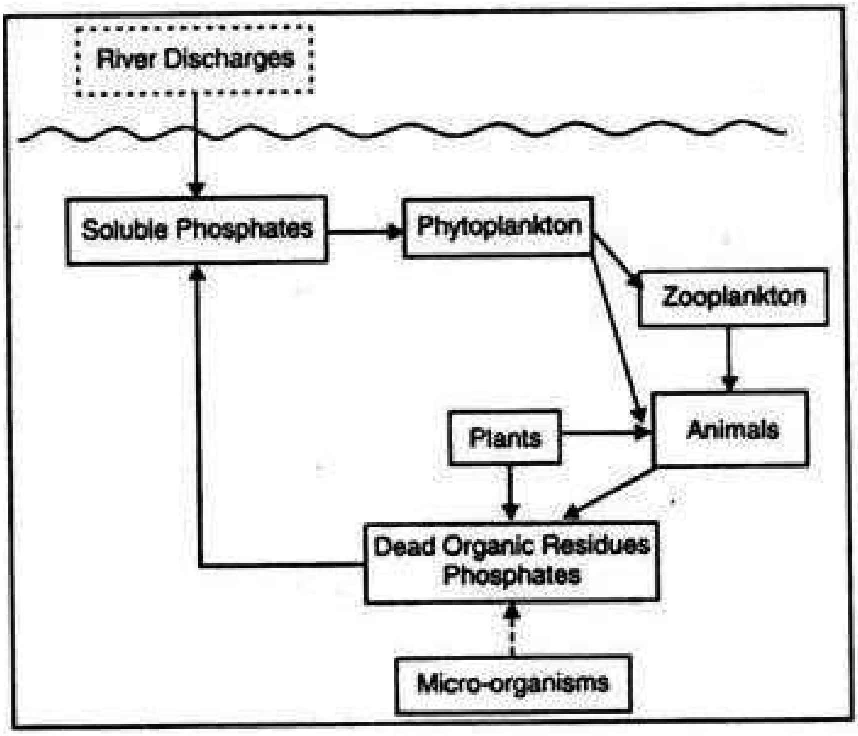

Fig. 1.10 *Phosphorus Cycle in Water*

Impact of Humans on Phosphorus Cycle

Global Phosphorus cycle changes significantly through various activities, such as misuse of Phosphorus fertilizers, shipping of Phosphorus minerals, as well as shipping of food from farms to urban settings where it is lost as effluent by humans. This has led to increased levels of Phosphorus in water bodies as pollutants, resulting in Eutrophication. Eutrophication has devastating effects on water ecosystems as it induces anoxic conditions. Nutrients that are stored in plants and rocks originally are quickly washed away by heavy rains, causing the land to become unproductive due to deforestation and/or forest fire. Much of the Phosphate found in waterways is provided by agricultural runoff. Fertilizers present in the soil are often not absorbed by all the crops, causing excess fertilizer runoff and increasing Phosphate levels in rivers and other bodies of water. At one time the use of laundry detergents contributed to significant concentrations of Phosphates in rivers, lakes, and streams, but most detergents no longer include Phosphorus as an ingredient.

1.4.4 Sulphur Cycle

Sulphur exists in gaseous (as oxides) and solid (compounds) both forms. It is an important constituent of proteins and amino acids. Because it exists in both gas & sold its cycle may be gaseous/sedimentary both. It occur in nature in the form of inorganic and organic deposits from where it releases by weathering and decomposition. The main sources of sulphur in atmosphere are combustion of fossil fuels, volcanic eruptions, surface of ocean and gaseous release. The main source of sulphur reaction in atmosphere is H_2S, which oxidises to SO_2.

$$H_2S + 2O_2 \qquad SO_4^{-2} + 2H^+$$

$$2H_2S + 3O_2 \qquad 2H_2O + 2SO_2$$

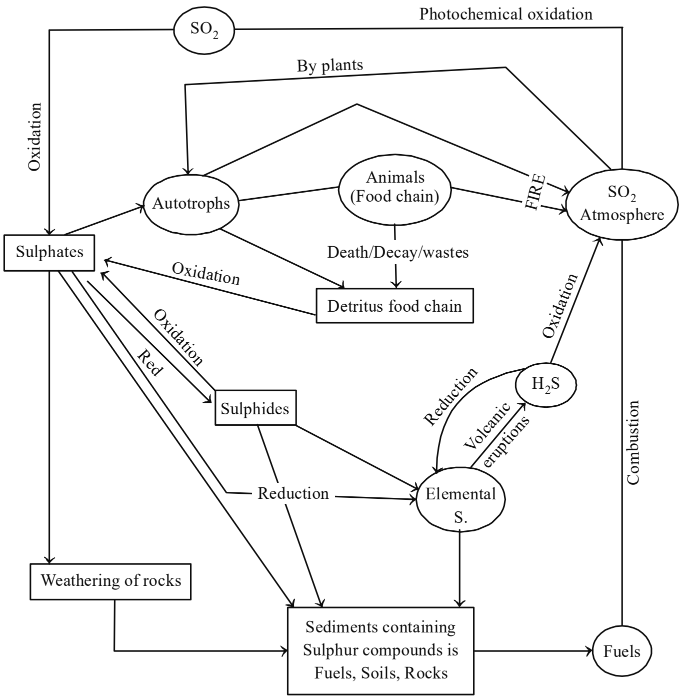

Fig. 1.11 *Sulphur Cycle*

The –SH group of amino acids also gets separated from rest of the molecules as H_2S. This again oxidised to SO_2. SO_2 present in the atmosphere is soluble in water and in carried back to earth thing rain in the form of H_2SO_4/H_2SO_3. Sulphur in the form of SO_4^{-2} absorbed by plants where it is incorporated in to certain organic molecules such as amino acids and proteins. Through decay, excretion & death of livings go back to soil and also in the bottom of ponds & sea. Bacteria may also cause oxidation of sulphur to SO_4.

$$2S + 3O_2 + 2H_2O \qquad 2SO_4^{-2} + 4H+$$

Sulphates can also be reduced to sulphide by some bacteria under certain conditions. This happens in the organic phase of sulphur cycle. From the Figure 1.11 we may get the complete idea about the sulphur cycle.

1.4.5 Oxygen Cycle

The flow of oxygen through the atmosphere (air), Biosphere (plants and animals), and Lithosphere (the earth's crust) is referred to as the oxygen cycle. The oxygen cycle shows how free oxygen is produced accessible in each of these regions and how it is utilised. The oxygen cycle is the biogeochemical cycle of oxygen atoms in ions, oxides, and molecules between different oxidation states via redox reactions inside and between the planet's spheres/reservoirs. Because it is a major product or reactant of many biogeochemical redox reactions within the cycle, the word oxygen in the literature usually refers to the most common oxygen allotrope, elemental/diatomic oxygen (O_2). The oxygen cycle's processes are classified as biological or geological, and they are rated as either a source (O_2 production) or a sink (O_2 consumption).

Biological production

Photosynthesis, which produces sugars and free oxygen from carbon dioxide and water, is the primary source of atmospheric free oxygen:

$$6\,CO_2 + 6H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

Plant life on land as well as phytoplankton in the oceans are examples of photosynthesizing organisms. Prochlorococcus, a microscopic marine cyanobacterium identified in 1986, is responsible for up to half of the open ocean's photosynthesis.

Abiotic production

Photolysis, in which high-energy UV radiation breaks down atmospheric water and nitrous oxide into component atoms, is another source of atmospheric free oxygen. Free hydrogen and nitrogen atoms escape into space, leaving O_2 in the atmosphere:

$$2\,H_2O + \text{energy} \longrightarrow 4\,H + O_2$$
$$2\,N_2O + \text{energy} \longrightarrow 4\,N + O_2$$

Biological consumption

Respiration and decay, methods by which biological life and microorganisms consume oxygen and release carbon dioxide, are the primary ways free oxygen is lost from the atmosphere.

Check Your Progress

8. Why is Nitrogen cycle important?
9. What are the main sources of sulphur in atmosphere?
10. Which organism is responsible for open ocean's photosynthesis?

1.5 BIODISTRIBUTION OF ELEMENTS

About more than 90 elements are found in the earth's crust out of which a mere 9 elements (*viz.*, Al, Fe, Ca, Mg, O, Si, Na, K and Ti) only account for over 99% by weight. The remaining 81 elements together, which account for hardly 0.14% by weight, constitute the so called "trace elements". These elements, notwithstanding their low abundance in nature, play a vital role in plant and animal nutrition. These elements occur in living tissues in such minute amounts (or traces) that their precise concentration could not be measured by the early workers with the analytical techniques then available. This is another reason why the term "trace elements" was used to describe them. The term "trace elements" has remained in popular use still, despite the fact that today, virtually all these elements can be estimated with great accuracy and precision with the help of modern analytical gadgets, such as neutron activation analysis, chromatography, x-ray fluorescence spectrometry, atomic absorption spectrometry, flameless AAS, polarography, etc.

1.5.1 Mechanism of Distribution

In order to clearly understand and appreciate the role played by the trace elements in the environment, it is necessary to study the mechanism by which these elements attained the present level of distribution within the earth. The trace elements are mobilized by the following three types of mechanisms:

- **Primary dispersion:** Trace elements are mobilized in the 'primary environment' by a process called 'hypogene mobility' (or igneous activity) whereby the liquid magma formed deep under the earth at high temperature and pressure, crystallizes and distributes the elements among the various rock types in a definite pattern. In the course of primary dispersion, the elements get concentrated in certain type of geological concentrations, known as ores. These ores fall under the following three main geochemical categories of the elements:
    (a) Siderophile elements, which are concentrated in iron deposits and in the iron-nickel core of the earth. For example: Fe, Co, Ni, Cr, Pt, etc.
    (b) Chalcopile elements, which are concentrated in sulphide deposits. For example: Sb, As, Cu, Cd, Pb, Hg, etc. These elements, though rare in overall abundance, are commercially important because they tend to accumulate in easily accessible sulphide deposits.
    (c) Lithopile elements, which are concentrated as silicate deposits. For example: Ca, Mg, Cr, V, alkali metals, etc.
- **Secondary dispersion:** After the deposition of the rocks by the primary dispersion, the elements are then mobilized in the secondary environment by supergene mobility which occurs at relatively lower temperatures and pressures by the weathering process. This mobilization is strongly influenced by Eh, pH and the stability of the minerals. The factors which ultimately bring about the breakdown of the minerals during the weathering process are mechanical, chemical and biological in nature.

- **Tertiary dispersion:** This is caused by human activities in which the elements are re-distributed in such a manner that some of them pose pollution problems. In fact, what man is really doing is extracting metals that are present in high concentrations in the form of ores in some localised areas and re-dispersing them in the whole world in such a form and to such an extent that cause adverse effects on the environment. A classical example of this is the mining of the locally abundant but environmentally rare element, lead (Pb) and dispersing it throughout the world via heavy industry and as an anti-knocking additive in gasoline (as Tetraethyl lead) in internal combustion engines. This "tertiary dispersion" of trace elements by the anthropogenic activities is causing concern among scientists due to the potential environmental hazards.

1.5.2 Essential and Non-Essential Trace Elements

A trace element is considered to be "essential" if it satisfies the following criteria:

- If it is present in all healthy tissues in all living things or within a botanical or a zoological family.
- Its concentration is fairly constant among various species.
- Its deficiency, depletion or withdrawal from the body induces reproducible structural and physiological abnormalities irrespective of the species studied.
- The deficiency symptoms or abnormalities induced by the deficiency disappear or reverse on replenishment of the element under consideration.
- The abnormalities induced by the deficiency of the elements are always accompanied by pertinent, specific biochemical changes, and
- These biochemical changes can be prevented or cured when the deficiency is prevented or cured.

Out of about 40 naturally occurring elements detected in living organisms, about 25 of them seem to be highly essential for the higher animals and humans. These include the following metals and non-metals:

- **Metals:** Na, K, Ca, Mg, V, Cr, Mn, Fe, Co, Cu, Mo, Zn and Sn.
- **Non-metals:** H, C, N, O, Si, P, S, Se, F, Cl, Br and I.

Some trace metals such as Pb, Cd and Hg and metalloids like As, Sb and Se are considered to be toxic. However, some of the metals listed as environmental hazards also seem to play some useful role in the development and growth of animals and humans. Elements like nickel, fluorine, bromine, arsenic, vanadium, cadmium, barium and strontium are considered to be possibly essential on the basis of suggestive but not completely convincing evidence.

About 25 trace elements which do not meet the above six exacting criteria described above occur more or less constantly in highly variable concentrations in living tissues. These include Al, Sb, Hg, Cd, Ge, V, Si, Rb, Ag, Au, Pb, Bi, Ti etc. These elements are believed to be acquired by the animal body as environmental contaminants due to contact of the organism with its environment. 'Skewed' (*i.e.* log-normal) distribution patterns have been reported for the concentrations of these elements in human organs, whereas the essential elements have a normal distribution pattern. In fact, the shape of the distribution curve for a trace element in tissue has been proposed as a method to determine whether an element is essential or not. Elements with "normal distribution" in plants and animals are considered to be essential, whereas those elements which tend to be distributed "abnormally" are considered as non-essential elements.

The term "normal distribution" implies that if a histogram is plotted of the frequency of occurrence of each elemental abundance value, the plot will be a perfectly symmetrical Gaussian curve. In the case of "log-normal distribution" the data plot will be asymmetric with a positive or negative "skew". If the logarithm of the concentration data is taken, the resultant histogram will again follow a symmetrical Gaussian curve. This has been observed both for plants as well as humans. The reason for the "normal distribution" of essential elements is that the concentrations of these elements in organisms are "internally" controlled and tend to be constant irrespective of the amount present in the environment. On the contrary, non-essential elements tend to be "externally" controlled, and hence the organisms accumulate the element to an extent proportional to its concentration in the environment.

The tendency of organisms to accumulate non-essential elements to an unlimited extent is particularly serious where pollution is involved, because toxic levels can soon be attained. For this reason, excesses of the non-essential elements tend to be more serious than excesses of essential elements. However, even if the essential elements are supplied to the organism in too great an excess, the regulatory mechanism can break down and toxicity symptoms or even death can result.

The trace elements are further classified into a sub-group known as "toxic" elements. This term may be justified for a small number of elements such as As, Pb, Cd and Hg, the biological significance of which is at present largely confined to their toxic properties at relatively low concentrations. However, this classification has little general application because all the trace elements are toxic if ingested at sufficiently high levels and for a long enough period. In fact, every element has a whole spectrum of actions, depending upon the dose and the nutritional state of the animal or system in respect to the element in question. The dose response curve for each of these elements shows two maxima. The first part of the curve, which shows an increasing effect with increasing concentration until a plateau is reached, expresses the biological action of the element. The plateau expresses optimal supplementation and normal function. The width of the plateau is determined by the homeostatic capacity of the animal or system. With further increase in the dose, the element enters a phase of irritation and stimulation of some function, expressing what may be called its pharmacological action. In this phase, the element acts as a drug independent of a deficiency state. If the dose is still further increased, the signs of toxicity appear and even death may result, thus expressing the toxic action of the element. The margin between the phases of biological and toxic actions differs widely among different trace elements.

Check Your Progress

11. What do you mean by trace elements?
12. State any three criteria for a trace element to be considered an essential?

NOTES

1.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Environmental chemistry deals with the study of the various chemical phenomena taking place in the environment.
2. The built environment is shaped by:
    a. Climate and Geology
    b. Economy
    c. Government
    d. Culture and Fashion
    e. Technology
    f. Customers
3. The features of the atmosphere layer Tropopause are:
    a. Top most layer of troposphere.
    b. It acts as a boundary between troposphere and stratosphere.
    c. This layer is marked by constant temperatures.
4. The thickness of Stratosphere layer is about 50 km above the earth surface and it consists of a rich layer of ozone.
5. The dominant chemical species found in Mesosphere are O2 and NO.
6. The heat budget of the Earth is the balance of incoming and outgoing heat. To maintain constant conditions, the budget must be balanced so that the incoming heat equals the departing heat, just like any other budget.
7. Vertical motion is more difficult to achieve in a stable atmosphere than in an unstable one. The atmosphere is said to be neutrally stable when it neither resists nor facilitates vertical motion.
8. Nitrogen cycle is important because:
    a. Plants and animals could not live without Nitrogen.
    b. The Nitrogen cycle helps to bring the Inert Nitrogen from the air into the biochemical process in plants and then to animals.
    c. Nitrogen cycle is absolutely essential for them because plants need Nitrogen to synthesise chlorophyll, which plants use in photosynthesis to make their food and energy.
9. The main sources of sulphur in atmosphere are combustion of fossil fuels, volcanic eruptions, surface of ocean and gaseous release.

10. Prochlorococcus, a microscopic marine cyanobacterium identified in 1986, is responsible for up to half of the open ocean's photosynthesis.
11. About more than 90 elements are found in the earth's crust out of which a mere 9 elements (*viz*., Al, Fe, Ca, Mg, O, Si, Na, K and Ti) only account for over 99% by weight. The remaining 81 elements together, which account for hardly 0.14% by weight, constitute the so called "trace elements".
12. A trace element is considered to be essential if it satisfies the following criteria:
    a. If it is present in all healthy tissues in all living things or within a botanical or a zoological family.
    b. Its concentration is fairly constant among various species.
    c. Its deficiency, depletion or withdrawal from the body induces reproducible structural and physiological abnormalities irrespective of the species studied.

1.7 SUMMARY

- The environmental chemistry may be considered as a multi-disciplinary study, involving physical and life-sciences, meteorology, agriculture, public health, engineering, etc.
- Environment mainly consist of Atmosphere, Hydrosphere, Lithosphere and Biosphere. Which can be roughly divided as (a) Micro Environment, (b) Macro Environment, (c) Physical Environment and (d) Biotic Environment.
- The built environment includes places and spaces created or modified by people including buildings, parks or green spaces and supporting infrastructures, such as water supply or energy networks, transportation systems, etc.
- Physical environmentPhysical Environment includes landforms, water bodies, climate, soil, rocks and minerals. Physical environment refers to geographical climate and weather or physical conditions wherein individual lives.
- Lithosphere refers to all the rocks of the Earth. It includes the planet's mantle and crust (outermost layer). The actual thickness of the lithosphere ranges from roughly 40 km to 280 km. It includes mountains, soil, land, and minerals.
- Soil is the thin layer of material covering the Earth's surface. It is any part of Earth's crust in which plants grow. For example, muddy bottoms of ponds, porous rock surfaces, bottoms of lakes, etc.
- All the water in its various forms, present in all the components of Earth's environment together constitutes the hydrosphere. It includes all liquid and frozen surface waters, groundwater held in soil and rock and atmospheric water vapour.
- Atmospheric environment is the envelope of air surrounding the Earth, including its interfaces and interactions with the Earth's solid or liquid surface.

NOTES

- Biotic environment is the environment comprising of living organisms which interact with each other and their Abiotic environment.
- The atmosphere is divided into five distinct layers characterized by the slope of its temperature profile.
- The uppermost region of the troposphere is almost transparent to the sun's rays. The sun's rays are mostly absorbed by the earth's surface due to various materials present in it.
- The layer above the tropopause is called the stratosphere. Its thickness is about 50 km above the earth surface and it consists of a rich layer of ozone.
- Mesosphere is the region above the stratosphere and extends up to a height of 85 km above the earth's surface. Concentration of ozone is very low in this region and decreases rapidly with increase in height.
- Thermosphere/Ionosphere is the region immediately above the mesopause, where the temperature rises very rapidly with increasing altitude is known as the thermosphere.
- There's not much information regarding Magnetosphere/Exosphere. It exists above the ionosphere and extends approximately up to 2000 km above the earth. This layer is almost airless and empty.
- The vertical temperature profile of the coupled surface-atmospheric system indicates a balance between radiation, convective and dynamical heating/ cooling.
- The average vertical temperature profile is calculated by averaging atmospheric temperatures across all latitudes and over the course of a year. This plot is referred to as a standard atmosphere.
- The heat budget of the atmosphere is made up of 48% solar radiation, with 14% originating from shortwave entering solar radiation and 34% coming from outgoing long-wave terrestrial radiation.
- Turbulence and cloud formation are mostly caused by vertical motion in the atmosphere. The strength of vertical motion is largely influenced by the atmosphere's vertical stability.
- The mineral cycling is also termed as biogeochemical cycle or nutrient cycle as it describes about the occurrence and regulation of the biogeochemical or nutrients Carbon, Nitrogen and Phosphorus in the ecosystem.
- Carbon is a fundamental part of the Earth system. Through Carbon Cycle, the Carbon is exchanged among the biosphere, lithosphere, hydrosphere and the atmosphere of the Earth.
- Nitrogen circulates among atmosphere, terrestrial, and marine ecosystems and get converted into multiple chemical forms and the conversion of Nitrogen can be carried out through both biological and physical processes.
- Movement of Phosphorus through the Lithosphere, Hydrosphere, and Biosphere is called Phosphorus cycle. Phosphorus cycle is faster through plants and animals than it does through rocks and sediments.

- Sulphur exists in gaseous (as oxides) and solid (compounds) both forms. It is an important constituent of proteins and amino acids. Because it exists in both gas & sold its cycle may be gaseous/sedimentary both.
- The flow of oxygen through the atmosphere (air), Biosphere (plants and animals), and Lithosphere (the earth's crust) is referred to as the oxygen cycle.
- Trace elements, notwithstanding their low abundance in nature, play a vital role in plant and animal nutrition. These elements occur in living tissues in such minute amounts that their precise concentration could not be measured by the early workers with the analytical techniques then available.
- In order to clearly understand and appreciate the role played by the trace elements in the environment, it is necessary to study the mechanism by which these elements attained the present level of distribution within the earth.
- Some trace metals such as Pb, Cd and Hg and metalloids like As, Sb and Se are considered to be toxic. However, some of the metals listed as environmental hazards also seem to play some useful role in the development and growth of animals and humans.
- The tendency of organisms to accumulate non-essential elements to an unlimited extent is particularly serious where pollution is involved, because toxic levels can soon be attained.

1.8 KEY TERMS

- **Chlorophyll:** It is any of several related green pigments found in the mesosomes of cyanobacteria and in the chloroplasts of algae and plants.
- **Methanogens:** These are microorganisms that produce methane as a metabolic by-product in hypoxic conditions.
- **Producers:** Producers are the green plants in the ecosystem which in the presence of sunlight, chlorophyll, inorganic nutrients and water produce their own food by the process of photosynthesis, hence are also called autotrophs.
- **Consumers:** Consumers includes herbivores that lives on producers (plants), carnivores that eat other organisms (animals) and omnivores that eat both plants and animals for their food.

1.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. What constitutes the natural environment?
2. What are the different components of Troposphere?
3. Write a short note on the vertical temperature of atmosphere.

4. State the steps in the Nitrogen Cycle.
5. What are the mechanisms which mobilize the trace elements?

Long Answer Questions

1. Discuss the composition and different concepts of soil.
2. Describe the three main types of organisms in the biological environment.
3. Explain the heat budget of the Earth atmospheric system in detail.
4. Discuss the various components of atmosphere.
5. Evaluate the significance and process of Carbon Cycle.

1.10 FURTHER READING

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UNIT 2 HYDROSPHERE

NOTES

Structure

2.0 INTRODUCTION

The hydrosphere (from Greek *hydōr*, 'water', and *sphaira*, 'sphere') is the aggregate mass of water found on, under, and above the surface of a planet, minor planet, or natural satellite. Despite the fact that the Earth's hydrosphere has been around for roughly 4 billion years, it is still changing shape. The land and ocean are rearranged as a result of seafloor spreading and continental drift. The amount of water on Earth is believed to be 1.36 billion cubic kilometres (332 million cubic miles). Groundwater, oceans, lakes, and streams all include liquid and frozen water. Fresh water accounts for only 2.5 percent of this total, whereas saltwater accounts for 97.5 percent. Only 0.3 percent of the fresh water on Earth is in easily accessible lakes, reservoirs, and river systems; 68.9% is in the form of ice and permanent snow cover in the Arctic, Antarctica, and mountain glaciers; and finally 30.8 percent is in the form of fresh groundwater. In this unit, we will discuss the chemical composition of different water bodies and hydrological cycle, along with the different sources of aquatic pollution. It will also focus on the water quality parameters and standards, along with the purification and treatment methods of water.

2.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe the chemical composition of different water bodies and hydrological cycle
- Explain the different sources of aquatic pollution
- Discuss the water quality parameters and standards
- Evaluate the purification and treatment methods of water

2.2 CHEMICAL COMPOSITION OF WATER BODIES

Water is a one-of-a-kind liquid; without it, life on Earth would be impossible. The composition of water bodies is complicated, containing a variety of gases, minerals, and organic molecules. Different types of chemical reactions, like as oxidation-reduction, complexation, and others, occur in water due to the presence of metal ions, dissolved gases, and other organic compounds. Atmospheric precipitation is the primary source of the water that fills the world’s lakes and rivers. The water is not pure; it contains dissolved and suspended mineral matter, as well as atmospheric gases.

Dissolved gases

The presence of dissolved gases in water bodies is due to the fact that the atmosphere and water bodies are in touch with each other, and gases are exchanged between the surface of the water body and the atmosphere. Oxygen and carbon dioxide are the most common gases found in water bodies, with methane and hydrogen sulphide appearing in lesser levels. The concentration of these gases in water is measured in parts per million (ppm) or milligrams per litre (mg/L). Photosynthesis allows aquatic plants (algae) to release O_2 (oxygen) into the water. This oxygen is known as dissolved oxygen because it dissolves in water (DO). DO is utilised during the degradation of organic waste (pollutant) in the water. The decrease of DO makes it harder for aquatic organisms to survive.

CO_2 (carbon dioxide) is the second most common gas found in aquatic bodies. The main sources of CO_2 in water are organic waste breakdown and the presence of CO_2 in the atmosphere. Carbonic acid, a loosely linked form of CO_2, is present in dissolved CO_2. When rain falls, it gently erodes calcareous rocks, resulting in calcium slats being deposited in nearby water bodies during drainage. During rainstorms, soluble atmospheric gases infiltrate water bodies. During rains, any atmospheric gases that are soluble in water will enter into water bodies.

Metal ions

Many chemical compounds are water soluble. Minerals and rocks in contact with water are the main sources of solutes. Metal ions (M^{n+}) in water come in a variety of shapes and sizes (ions, hydrated metal ions, undissociated compounds and colloids). Some ions (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, Cl^{-}, SO_4^{-2}, HCO_3^{-1}, CO_3^{-2}, etc.) are present in enormous amounts and are referred to as macro components since their concentration exceeds mg/L. Other elements, such as borate and fluoride, are considered micro components since they are present in small amounts (g/L).

2.2.1 Lakes

Lakes are inland depressions containing standing water. They vary in size and depth (few feet to 5000 feet). Some lakes wave outlet streams. In lake there are three to five well recognized horizontal strata namely.

- **Littoral zone:** Shallow water near the shore forms this zone. It contains upper warm and oxygen rich circulating water layer, which is called epilimnion. It include rooted vegetation.
- **Sublittoral zone:** It extends from rooted vegetation to the non-circulating cold water with poor oxygen zone i.e. hypolimnion.
- **Limnetic zone:** It is the open water zone away from the shore. It is up to the depth of effective light penetration where rate of photosynthesis is equal to the rate of respiration.
- **Profundal zone:** it is the deep water area beneath limnetic zone and beyond the depth of effective light penetration.
- **Abyssal zone:** It is found only in deep lakes since it begins at about 2000 meter from the surface.

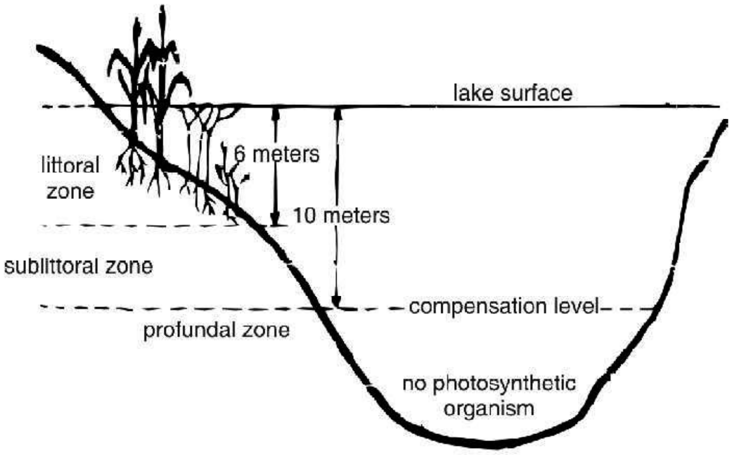


Fig. 2.1 Different Zones of a Deep Freshwater Lake

Stratification in lakes

Complex chemical and biological activities in water bodies alter the chemical composition of lakes. Because there is a lack of water circulation in such a large reservoir, chemical reactions on the surface of the water differ from those at the bottom. In still water, separate layers occur due to the temperature – density relationship of water. This is referred to as thermal stratification. The typical sessional cycle illustrated in Figure 2.2.

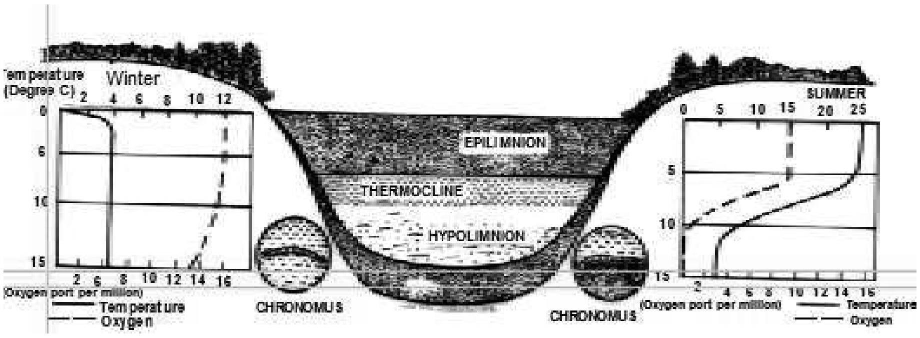


Fig. 2.2 Thermal Stratification in a North Temperate Lake

In the figure above, summer conditions are shown on the right, winter conditions on the left. Note that in summer a warm oxygen-rich circulating layer of water, the epilimnion, is separated from the cold oxygen-poor hypolimnion waters by a broad zone, called the thermocline, which is characterized by a rapid change in temperature and oxygen with increasing depth. Two typical hypolimnion organisms are shown.

During the summer the top water become warmer than the bottom waters, as a result only the warm top layer circulates and it does not mix with the more viscous colder water, called thermocline. The upper water layer is epilimnion. Colder non-circulating water is the hypolimnion. Subtropical lakes having surface temperatures that never fall below 4°C. In terms of water circulation patterns most of the lakes of the world can be conveniently assigned to one of the following categories (Hutchinson, 1957):

- **Dimictic (Mictic = Mixed):** Two sessional periods of free circulation.
- **Cold monomictic:** Water never above 4°C (Polar Regions), seasonal overturn in summer.
- **Warm monomictic:** Water never below 4°C. One period of circulation in winter.
- **Polymictic:** More or less continually circulating with only short, if any, stagnation period.
- **Oligomictic:** Rarely mixed.
- **Micromictic:** Permanently stratified.

The epilimnion is amply supplied with oxygen while the hypolimnion is devoid of oxygen due to thermal stratification and inadequate mixing between the levels (due to a lack of water circulation). When the temperature difference between the surface layer (epilimnion) and the bottom layer (hypolimnion) is considerable, the chemical and biological properties of these layers diverge. The epilimnion has a higher concentration of dissolved oxygen and is aerobic, whereas the hypolimnion has a lower concentration of dissolved oxygen and has more carbon dioxide. When the epilimnion cools in the autumn and spring, the temperature of both levels may equalize, and the lake will operate as a single hydrologic unit. This is called overturn.

Because of the chemistry of erosion products in different lake basins, the chemical composition of lake water varies, but the main ingredients are same. The total concentration of ions present, which include sodium, potassium, magnesium, calcium, carbonate, silicate, and chloride, is used to calculate salinity. The following is the order of abundance for cations and anions:

$$Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$$

$$CO_3^{2-} > SO_4^{2-} > Cl^{-}$$

Nitrate and phosphate (both plant nutrients), metals such as mercury, manganese, copper, lead, and organic matter are examples of inorganic ions. Hydrogen sulphide is also prevalent in anaerobic environments. When aquatic plants absorb carbon dioxide and hydrogen carbonate, the pH of lake water rises, resulting in calcium carbonate and dolomite deposition. A lake has a wide range of molecules and ions from weathering of soils in the watershed, the atmosphere, and the lake bottom in the absence of any living thing. As a result, a lake's chemical composition is largely determined by its climate. Each lake has a three-major anion and four-major cation ions balance.

2.2.2 Streams and Rivers

A river is a naturally flowing watercourse that flows towards an ocean, sea, lake, or another river, and is usually freshwater. A river may flow into the ground and become dry at the end of its course before reaching another source of water in some instances. Streams, creeks, brooks, rivulets, and rills are all terms used to describe small rivers. Because the chemical composition of surface water changes over time, sampling must be done at various locations throughout the stream and river course on a regular basis. During the dry season, groundwater supplies more water to rivers, whereas runoff contributes the most water during the rainy season. Pollution alters the composition of river and stream water.

The rivers are dominated with the presence of calcium, silica, and hydrogen carbonate, which are mostly derived from silicate rocks and carbonates. Potassium levels are low due to clays' retention. There are two types of dissolved inorganic components: macro components and micro components. Calcium, sodium, magnesium, potassium, chloride, sulphate, hydrogen carbonate, and carbonate are macro components that make up 90–95 percent of all components in fresh water. Lithium, rubidium, caesium, bromide, iodide, fluoride, copper, zinc, nickel, silver, lead, and other heavy metals are among the micro components with concentrations up to 1ppm. There are also dissolved gases including nitrogen, oxygen, argon, and carbon dioxide. The nutrients in surface water are limiting factors for aquatic plant growth. Nitrogen (in the form of ammonium, nitrite, nitrate, and organic molecules) and phosphorus are two of them (in inorganic and organic forms).

The majority of dissolved organic molecules enter the environment as pollutants. They may increase heavy metal mobility and have an impact on dissolved oxygen level and water flavour. River water has a low salinity-about 120 ppm by weight. Carbon as hydrogen carbonate and carbonate (also known as dissolved inorganic carbon, or DIC) accounts for 48% of said salt content, while silicon as silicic acid accounts for 33%. The remaining 19 percent is made up primarily of chloride, sodium, and magnesium, in that order. Several factors influence the composition of river and stream water, including water-rock interaction (weathering), temperature, and human activities.

2.2.3 Wetlands

Wetlands get their name from the fact that they are wetlands. They are areas of land that are regularly saturated by water. This comprises marshes, bogs, estuaries, and small ponds, as well as swamps and swampy parts of prairies and woods. Lakes are excluded because they are more or less permanent bodies of water that are dominated by aquatic life and the chemistry that goes with it. The wetlands are positioned below the water table and are saturated with water. Wetlands serve as filters, removing sediment and a variety of contaminants. Water progressively seeps out of the wetlands and into permanent bodies of water such as rivers, lakes, and the ocean.

Organic stuff, such as peat moss, is abundant in wetlands. In these conditions, nitrogen is usually a limiting factor for microorganisms. When agricultural effluent passes through a marsh or wetland, microorganisms in the area use the nitrate fertilisers to oxidise some of the carbon. The excess nitrate concentration in the water that goes into the ocean or lake is not as high as it would be otherwise. Many additional organic and inorganic contaminants in the water are also broken down or sequestered by the microbes. In most cases, iron sulphides are insoluble and end up sequestered in wetlands. In this environment, they don't react with oxygen. This inhibits the acidification that would occur if iron sulphides react with oxygen.

Estuarine and marine wetlands chemistry

Estuarine shrub wetlands account for 13% of total wetlands in the United States, whereas non-vegetated saltwater wetlands account for 14%. Salt concentrations are particularly significant for estuaries and marine wetlands from a chemical standpoint. NaCl and other salt concentrations can be higher or lower than in seawater. Freshwater is routinely added to dilute the water, however the salt concentration can reach dangerously high levels due to evaporation.

Freshwater wetlands chemistry

Forested wetlands make up 51 percent of the total area of the freshwater system and are the single largest freshwater category. Freshwater emergents (areas that are swampy for a portion of the year) accounted for 25.5 percent of the total area, shrub wetlands for 17%, and freshwater ponds for 6.5 percent.

2.2.4 Hydrological Cycle

The hydrosphere includes all types of water resources like oceans (~97.24 per cent), polar ice and glaciers (~2.0 per cent), underground water (~0.60 per cent), fresh water lakes (~0.01 per cent), saline lakes (~0.005 per cent), inland seas (~0.003 per cent), soil moisture (~0.006 per cent), rivers (~0.0001 per cent), streams (~0.00001 per cent) and water vapour in the air (~0.001 per cent). The major uses of water are for irrigation, in thermal power plants and other industries and for domestic purposes such as drinking, cooking, bathing, cleaning, etc.

The biggest source of surface water are oceans and seas that have saline water and thus, is not drinkable and can be used for less practical purposes, such as cooling of thermal power plants and sink for pollution. Rain water and water resulting from melting of ice on high mountains usually has no dissolved salts. Water of ponds, most of the rivers and lakes contains very little amount of salt. The underground water contains salts within tolerable limits. These waters are sweet water. Spring and well water is known as mineral water. This water contains many soluble salts and gaseous minerals.

The ground water is usually of good quality and thus, can be used for drinking and for day-to-day use. The other sweet or mineral water often contains suspended matters, undesirable dissolved salts as well as microorganisms harmful for health. This water is not drinkable (non-potable). In the rainy season, the surface water sources become muddy while bathing of men or other animals, washing of clothes, household utensils throughout the year contaminate the surface water and makes it unsafe for drinking and other practical purposes. However, the surface water can be purified by filtration and killing of harmful microorganisms using chemicals and then can be reused.

The components of hydrologic cycle are:

1. Evaporation
2. Transpiration
3. Cloud formation
4. Condensation
5. Precipitation
6. Runoff

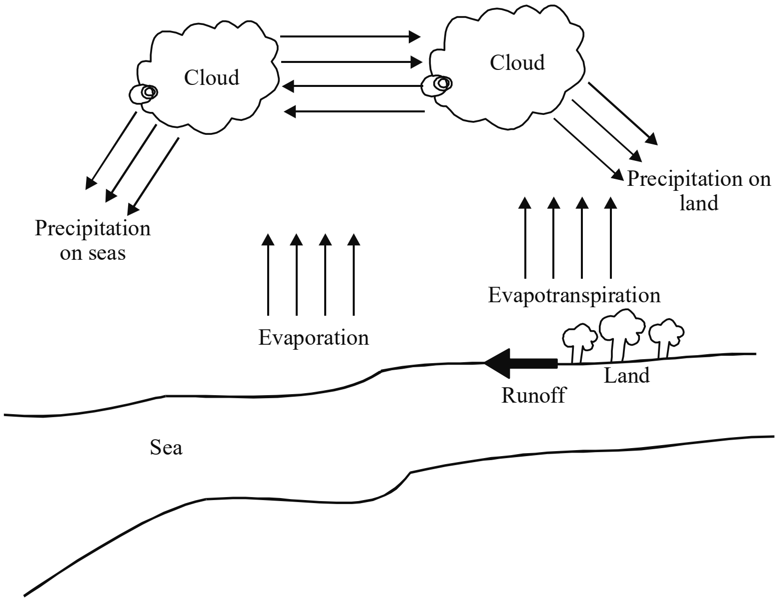


Fig. 2.3 Hydrologic or Water Cycle

Solar energy removes water from the oceans, seas, rivers, lakes, ponds, etc., by evaporation and from the leaves of plants by transpiration.

NOTES

The resulting water vapours in the atmosphere form clouds and are transported by moving air masses. The clouds meet the cold air in mountainous regions, above forests, etc., condense and fall as precipitation (mainly rain) due to the gravitational pull. A part of the precipitation reaches through the soil to the impervious layer of rock or clay and is collected as ground water. Some part runs down the drains and ultimately reaches the ponds, rivers, lakes and oceans. The cycle is repeated again and again. However, the rapid rate of deforestation and other activities contributing to global climate change has detrimental effect on the hydrologic cycle, *i.e.*, the balances have been altered.

Check Your Progress

1. What is the percentage of fresh water on Earth?
2. What is the source of DO?
3. Which of the micro and macro components constitute rivers and streams?
4. List the components of hydrologic cycle.

2.3 AQUATIC POLLUTION

Water the most abundant and wonderful of all natural resources, is extremely essential for the survival of all living organisms. Water that is found in nature is called natural water. The natural water (sea water, rivers, lakes, polar ice and glaciers) contains numerous organisms like phytoplankton, zooplankton, fish and many other things. Water contains dissolved gases like oxygen, essential for aerobic aquatic organisms, carbon dioxide for small plants to bloom so as to be utilized by aquatic animals. Pure water on the other hand, means water free from living organisms, especially microbes, all sort of toxic substances, having salts in the tolerable limits. The pure water is absolutely necessary for drinking and cooking, besides for industry, agriculture and various other activities. But today, pure water has become a precious commodity and its quality is threatened due to pollution. The water pollution thus, can be defined as the deterioration of physical, chemical and biological characteristics of water through natural as well as anthropogenic activities, to such an extent that it has become harmful for all living organisms including man. Water pollution has now become a global problem affecting both the developed and developing countries. The following are the signs of water pollution:

(*a*) Bad taste and offensive odour
(*b*) Unchecked growth of aquatic weeds
(*c*) Decreased number of fish
(*d*) Floating of oil and grease on water surfaces

There are large number of water pollutants. For our convenience, they have been classified into five different categories:

(*i*) Organic pollutants (*ii*) Inorganic pollutants (*iii*) Suspended solids and sediments (*iv*) Radioactive pollutants and (*v*) Thermal pollutants

2.3.1 Organic Pollutants: Pesticides, Microorganisms, Agricultural and Industrial Waste (Detergents, Oil Spills, and Oil Pollutants), Sewage, and Metals (Content of Chloride, Sulphate, Phosphate, and Nitrate)

Organic pollution is a type of chemical pollution caused by carbon pollutants, such as organic matter (liquid manure, sewage treatment sludge, etc.), Organochlorides (DDT) or even Polychlorinated Biphenyls (PCB). Organic pollutants found in wastewaters include dye, humic substances, phenolic compounds, petroleum, surfactants, pesticides, and pharmaceuticals. Organic pollutants in water can cause harmful compounds to be produced during disinfection. Humic compounds such as humic acid, fulvic acid, or humin, which are formed when organic matter decays, and medications such as antibiotics are the most abundant contaminants in farm wastewaters. The organic pollutants present in water may be classified into five different categories such as: Oxygen demanding waste; disease causing waste; synthetic organic compounds; oil; and sewage and agricultural runoff.

Microorganisms

Pathogens are disease causing microorganisms which grow and multiply within the host. The resulting growth of microorganisms in a host is known as infection. Water is the carrier of such pathogenic micro-organisms, causing immense harm to public health. The pathogenic micro-organisms enter water mainly from domestic sewage and other wastes. Generally, these microorganisms occur in the faeces or urine of the infected person and finally discharge into the water body. The discharge of an infected individual may contain billions of these pathogens and if they enter the water body, epidemics might occur. Epidemics of infectious diseases generally occur in a crowded population and under poor sanitary conditions. The infectious diseases associated with water can be classified into four groups according to the mechanism of transmission.

1. **Waterborne diseases:** They spread through ingestion of contaminated water. For example: cholera, typhoid, paratyphoid, bacillary dysentery.
2. **Water-wastes diseases:** They spread through unclean water. For example: trachoma and scabia.
3. **Water based diseases:** They spread through water contact, where the larva of the parasitic worm get attached to the human skin, penetrate it and ultimately enter the blood stream. They get mature in liver and lay eggs in the intestine. The intestinal discharge contaminates the water and large number of parasitic worms spread causing epidemics. For example: schistosomiasis and dracunculiasis.
4. **Water-related diseases:** In such diseases, human contact with water is not needed. It is the host which depends on water for its habitat. For example: (mosquitoes) → malaria, filaria, dengue, etc.

Different diseases are caused by different pathogens. For example, virus is responsible for hepatitis, meningitis, myocarditis, etc. Bacteria are responsible for cholera, typhoid, paratyphoid, etc. Protozoa are responsible for diarrhoea, dysentery, etc. Parasitic worms such as helminthes are responsible for diseases like ascariasis, trichuriasis, etc.

Nutrients

Nutrients are chemicals essential for the growth of living things. For plants there are sixteen elements required for their healthier growth. They are carbon, hydrogen, oxygen, (obtained mainly through CO_2 and water from the soil), nitrogen, phosphorus, potassium, calcium, magnesium, sulphur and micronutrients such as iron, cobalt, manganese, boron, molybdenum and copper.

The nutrients can become a pollutant when their enrichment allows thick growth or blooms of aquatic weeds, especially algae that cover up water. This prevents the entry of sunlight into water bodies. Aquatic plants, along with algae, thus die, the bacteria present in water now decompose all these dead plants and ultimately reduce the dissolved oxygen (DO) in water. The decayed organic matter adds unwanted color, odour, taste and turbidity to the water and acceptability for domestic purpose is reduced. The depletion of dissolved oxygen leads to the death of fishes, other aquatic animals and plants. The process of nutrient enrichment is known as eutrophication.

Among the sixteen elements, carbon, nitrogen and phosphorus are the most important nutrients which control the growth of algae blooms. Carbon is available from the atmosphere as CO_2 and decaying of other organic matter cannot be controlled. It is nitrogen and phosphorus which can be controlled to check algae growth rates.

The major sources of nitrogen and phosphorus polluting water bodies are soaps and detergents, chemical fertilizers like urea, ammonium sulphate or nitrate, super phosphate, etc. Besides eutrophication problems, if water contains enough nitrates (NO_3^-) and is consumed by children, certain bacteria in the intestinal tract of infants can convert nitrates to highly toxic nitrites (NO_2^-). Haemoglobin has higher affinity for nitrites compared to oxygen, therefore it leads to replacement of oxygen by nitrites causing a bluish discoloration of the infant and is commonly referred to as 'blue baby' syndrome.

The phosphorus from chemical fertilizers as well as detergents helps algae growth, resulting in enormous blooms. In detergents, the phosphates are in the form of tripolyphosphate. This tripolyphosphate slowly reacts with water forming orthophosphate and is used by plants for their growth.

$$\underset{\text{Tripolyphosphate}}{P_3O_{10}^{5-} + 2H_2O} \rightarrow \underset{\text{Orthophosphate}}{3PO_4^{3-} + 4H^+}$$

Salts

Water accumulates a variety of dissolved solids or salts while passing through soils and rocks and on its way to the sea. Generally, the cations in the salt are sodium, potassium, calcium and magnesium and the anions are chloride, sulphate and bicarbonate. The measure of salinity of water is usually the measure of concentration of total dissolved solids (TDS). Water having less than 1500 mg/l of TDS is considered to be fresh water, and above 5000 mg/l saline water.

NOTES

Drinking water has the recommended maximum TDS concentration of 500 mg/l. With concentration of TDS exceeding 2100 mg/l, irrigation becomes difficult. Again, if the sulphate and chloride salts of calcium and magnesium are present in excess amount, it is very expensive to wash clothes as it consumes excess soap. Again, if such water is used in the steam boilers, it will cause scaling due to precipitation of salts resulting in reduced lifetime of the boilers due to corrosion.

Thermal pollution

Heat cannot be completely converted into work. Hence, waste heat will always be produced where heat is converted into mechanical work. In thermal power plants, nuclear power plant, etc., where water from the nearby river or lakes is used as a coolant, the waste hot water is returned to the original water body and on an average the temperature is raised by 10°C. The rise in temperature decreases the amount of dissolved oxygen (DO) in water, adversely affecting the aquatic life. With rise in temperature the metabolic rate increases, whereas supply of DO decreases (with rise in temperature, solubility of O_2 decreases and the dissolved O_2 escapes, further bacterial decomposition of organic wastes goes on a rapid rate).

Furthermore, the fish and other aquatic animals may be sucked into the intake pipe killing them in large numbers. In case of nuclear power plants, there always remains the possibility of release of radioactive elements into the water body and with prolonged time it may build up to a dangerous level.

Pesticides

Chemicals which prevent, destroy or mitigate any pest (insects, fungus, bacteria, viruses, etc.) are called pesticides. Pesticides are classified on the basis of (*i*) chemical structure (*ii*) biological action (*iii*) class of pests they combat. Some chemicals, however, fall into more than one category. For example, parathion, while being an insecticide, is also a nematicide and acaricide.

The main groups of pesticides of our concern are insecticides. With increase in population growth man had to increase agricultural productivity. Use of insecticides, like DDT has not only improved the productivity of agricultural goods by protecting crops from pests but has also contributed in curbing diseases, like malaria which once was an epidemic. However, the extensive use of insecticides has proved that its use is not entirely in the interest of man due to its harmful side effects. There are three main groups of pesticides namely organochlorines, organophosphates and carbamates.

A great variety of insecticides, under different technical and trade names are used. Although the targets of pesticides are insects, fungus, nematodes and rodents which damage crops, they also target non-target beneficial organisms like earth worms, fish, birds, mammals and man. The killing of such species disturbs the balance of natural cycle and also the evolution of new species, necessitating more severe environmental control measures. The harmful effects of insecticides thus, have been a great cause of concern and persistence of insecticides in the environment after application is not at all desirable from environmental considerations.

The most widely used organochlorine pesticide is DDT (dichloro diphenyl trichloroethane), which has controlled insects carrying diseases like malaria (mosquitoes), plague (fleas) and typhus (body lice). The organochlorine insecticides are highly toxic to insects, but acute human toxicity is low. It is the bio-accumulation of organochlorine pesticides such as DDT in the food chain which creates toxicity. Such type of insecticides persist longer in the environment before under going degradation to other substances and are quite soluble in hydrocarbons and, easily accumulate in the fatty tissues. And so, because of their build up in the food chain, they get magnified to higher trophic level. Birds are high on the food chain and thus, more accumulation of DDT has adverse effects, interfering with enzyme regulating distribution of calcium, resulting in thinning of egg shell that supports its weight. The resulting difficulty to reproduce due to high levels of DDT, has brought the hunting birds like bald eagle, ospreys and brown pelicans on the verge of extinction.

The accumulation of DDT in human body is through food chains, *i.e.*, vegetables (foliar spray of DDT is absorbed on the leaf), fish $\left(\begin{array}{l}\text{Plankton} \rightarrow \text{fish} \\ \;\hookrightarrow \text{clam} \;\lrcorner\!\uparrow\end{array}\right)$, milk (animals like cows, buffaloes eating DDT accumulated vegetables and so the milk also gets contaminated, humans consume milk, thus get severely affected and breast fed babies ultimately get affected).

The other organochlorines widely used are chlordane, aldrin, endrin, dieldrine, kepone, etc.

Some of these types of insecticides show birth defects in mice, hamster and some cause liver cancer. Kepone, a class of plant insecticide, finds its application in controlling tobacco wire worm, ants and cockroaches. Exposures to this insecticide can cause severe neurological damage and when they undergo de-composition and are discharged into water, they can ultimately be incor-porated into the food chain.

As far as the effect of organochlorines is concerned, they pose a serious threat to the eco-system, human health and moreover the long term use of such chemicals is no longer found to be effective in controlling the pests due to the biological assistance development in these pests against the pesticides. Thus, another class of insecticides which are not persistent have been developed and are being replaced. Some examples of this class are Malathion, Phosdrin, Guthion, Diorom, etc. Although these insecticides are not accumulated in the food chain, they pose direct threat. They get absorbed rapidly through skin, lungs and gastro-intestinal tract and become acutely toxic than the organo chlorines that they have replaced. Excessive amount of such types of insecticides cause chest discomfort, vomiting, headache, nervous disorder, etc.

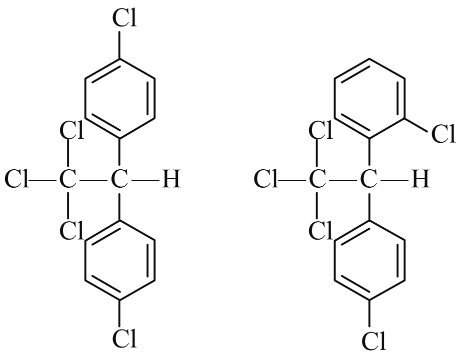
The third category of insecticides, carbamates, is derived from carbamic acid (NH_2COOH). These insecticides are not persistent like organo chlorines, but they get absorbed as organo phosphate insecticides, causing acute toxicity. Some of the carbamate insecticides are aldicarb, carbaryl, etc. Exposures to such chemicals cause blurred vision, nausea, vomiting. The accumulation of DDT in the body tissue of an average Indian is much greater than anyone in the world.

Some other pesticides commonly used to kill pests are:

- **Fumigants:** The insects die inhaling poisonous gaseous or fumigants like HCN vapour, CH_3Br, PH_3, para dichlorobenzene, nicotine, chloropicrin, etc.
- **Fungicides:** Fungus on plants and crops are killed by quinones, organomercury and its compounds and phenols.
- **Bactericides or antibiotic:** Bacterial growth in plants is checked or removed completely by streptomycin spray.
- **Rodenticides:** Rats like animals are killed by thallium sulphate, zinc phosphide, etc.

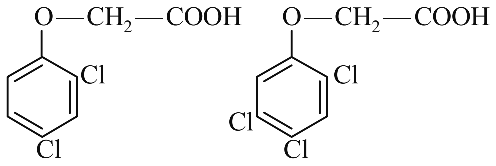
Pesticide poisoning

The indiscriminate use of pesticides in agriculture has posed a serious threat to human and animal life. Non-biodegradable pests accumulating in the food chain and biodegradable pests leaving behind more toxic side products, have produced health hazards with concentration exceeding the safe tolerance level.



p-p′-DDT *o-p′*-DDT

Two isomers of dichlorodiphenyltrichloroethane (DDT)



2, 4-D 2, 4, 5-T

2, 4-dichlorophenoxyacetic acid (2,4-D) and
2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T)

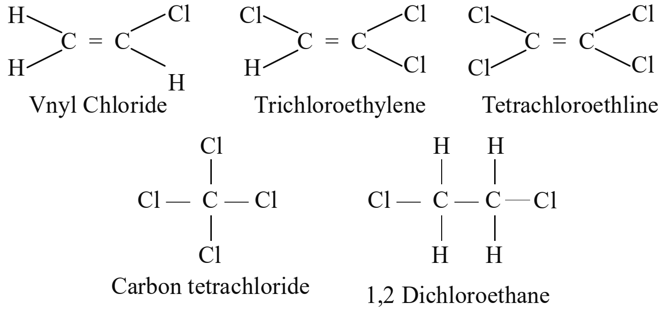
Fig. 2.4 *Some Different Types of Pesticides*

Thus, a new technology must be introduced to safeguard the ecology. New types of chemicals having no side effects or minimum side effect should come. Neem-based insecticides could be a good alternative. If proper research is carried out it could be utilized as eco-friendly substitute of other commonly used pesticides.

Volatile Organic Compounds (VOC)

As the name implies these organic compounds have low boiling point and evaporate quickly into the atmosphere. These chemicals are either synthesized directly or may be obtained as side product. From the atmosphere it comes down to the surface along with rain or from the industry it can go directly into the near by river or sea or other water resources. From the surface it can get evaporated into the atmosphere causing air pollution and if it seeps underground, its evaporation process will slower down resulting in high degree of ground water pollution. Chlorinated hydrocarbons can also be used as herbicides. For example, 2, 4, 5-trichlorophenoxy acids or 2, 4-dichlorophenoxy acid. They are used for killing weeds and undesirable vegetation. However, such types of chemicals are banned or need to be banned as the side-products obtained during their synthesis are highly toxic dioxin. Herbicide like paraquat used to destroy marijuana.

The volatile organic compounds are found to be either carcinogens or mutagens. Five such compounds are generally found to be highly toxic.


Vnyl Chloride Trichloroethylene Tetrachloroethline

Carbon tetrachloride 1,2 Dichloroethane

Fig. 2.5 *Toxic Volatile Organic Compounds*

- **Vinyl chloride:** It is used to produce polyvinyl chloride resins and is most toxic as it is a suspected carcinogen.
- **Trichloroethylene:** A commonly used cleaning agent and is a suspected carcinogen and ground water contaminant.
- **Tetrachloroethylene:** Major component in the production of chlorofluorocarbons and causes tumors in animals.
- **Carbon tetrachloride:** Finds application in fire extinguisher, synthesis of various chemicals, fumigants. Insoluble in water and trace amount found in water and is toxic when ingested.
- **1, 2-Dichloroethylene:** Used to produce various products including vinyl chloride, tetraethyl lead and soap compounds. It can effect central nervous system, liver and kidney if it exceeds tolerance level.

Eutrophication

The word eutrophication is originated from Greek words *eu* = 'well' and *trophes* = 'food'. Thus, it means 'well fed' or 'nutrient rich'. So, we can define eutrophication as excessive nutrient load in a water body or enrichment of water body by nutrients.

Nutrients may become pollutants if their concentration is sufficient to allow excessive growth of aquatic plants, especially algae. An aquatic system may be categorized into three classes in accordance with the nutrient status, *i.e.*, concentration of nutrients and productivity of aquatic plants.

(*i*) Oligotrophic: Water with poor nutrient status and very low productivity of aquatic plants.

(*ii*) **Mesotrophic:** Water with moderate (not low not high) nutrient status and moderate productivity of aquatic plants.

(*iii*) **Eutrophic:** Water with rich (sufficient concentrations) nutrient status and high productivity of aquatic plants.

A young lake or a newly formed lake has low nutrient content and thus, low plant productivity. Such types of lakes (oligotrophic lakes) with time acquire nutrients from surface runoff, drainage basins, excreta and exudates of animals using the water source, which ultimately increase aquatic growth. In this way, the oligotrophic water bodies turn gradually into mesotrophic water bodies.

With time, the nutrient status of the water bodies gradually increases. The biological productivity thus enhanced, leads water to become murky with phytoplankton, *i.e.*, algae blooms to occur. The lake thus, becomes eutrophic (well-fed).

Eutrophication is a natural process and may take thousand of years. However, this is greatly enhanced through human activities and is termed as accelerated or cultural eutrophication. The industrial wastes, municipal waste water, run-off from agricultural lands, provide plenty of phosphates, nitrates and various minerals stimulating algal growth. Due to which, the water body becomes green. In due course of time, the algal blooms may die abruptly. The decaying organic matter causes depletion of oxygen level, destroying fish habit and other aquatic species. Bad taste, bad odour, turbidity, thereby, greatly reduce its acceptability as a domestic water source. Again, because of the silt and organic debris the lake slowly becomes shallower and shallower, more plants spread roots along the shallow edges and the lake slowly transforms into a marsh and finally converts into a dry land. Thus, a water body so useful for us becomes totally useless within a short span of time, due to anthropogenic activities.

Controlling eutrophication

The main causes for the production of algae are the available nutrients. The three main nutrients are carbon, nitrogen and phosphorus. If the supplies of such nutrients are restricted, growth will be reduced. Carbon is usually available from natural sources and can be less restricted, so is nitrogen, as certain bacteria and blue-green algae fix atmospheric nitrogen. However, it is phosphorus which has least available natural sources and can be restricted. Anthropogenic activities provide enough phosphorous for algae bloom. The main anthropogenic sources of phosphorous are agricultural run off and domestic sewage. In domestic sewage, the source of phosphorus is the human faeces and detergents. Human faeces cannot, however, be restricted but the use of phosphorus in detergents can be limited.

Waste water containing detergents, reacts with water to form ortho-phosphate ion (PO_4^{-3}) and is directly used by plants for their growth.

$$P_3O_{10}^{-5}\ (\text{from detergents}) + 2H_2O \rightarrow \underset{\text{Orthophosphate}}{3PO_4^{-3}} + 4H^+$$

The other steps used in controlling eutrophication are recycling of nutrients through harvest, removal of algal blooms by drudging, applying algaecides like copper sulphate, chlorine, etc. on water bodies.

It is observed that phosphorus in excess of 0.015 mg/l and nitrogen in excess of 0.3 mg/l are sufficient to cause algal bloom.

Oil pollution

NOTES

Oil pollution generally takes place due to oil spills from cargo tankers, which carry petrol, diesel and their derivatives on the high seas, oil spill due to off-shore exploration of petrol, accidental fires in ships and oil tankers and leakage from oil pipe lines crossing waterways. The oil spill covers the water surface preventing light to pass, thereby the process of photosynthesis carried on by marine plants is hampered. The oxygen cannot pass through, thereby reducing dissolved oxygen and endangering water birds, fishes and other aquatic organisms. On the whole, the marine life and sea food are endangered.

2.3.2 Inorganic Pollutants

Heavy metals, which are harmful or deadly even at low concentrations, make up the majority of inorganic pollutants. Arsenic, mercury, lead, and chromium are examples of heavy metals. They can enter the body through water, food, or air, causing health problems. Commonly found inorganic contaminants of water include arsenic, fluoride, iron, nitrate, heavy metals, etc., and their presence at more than permissible levels degrades water potability for living organisms.

Heavy metals are referred to as metals with specific gravity greater than about 4 to 5. The most important heavy metal pollutants are mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As). ^{48}Cd and ^{80}Hg are non-typical transition elements. They belong to Gr. 12 (IIB), with electronic configuration,

$^{48}\text{Cd} \rightarrow [\text{Kr}]\ 4d^{10}5s^2$

$^{80}\text{Hg} \rightarrow [\text{Xe}]\ 4f^{14}5d^{10}5s^2$

^{82}Pb is group 14 element (IVA) with electronic configuration, $^{82}\text{Pb} \rightarrow [\text{Xe}]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$.

^{33}As is group 15 element (VA) with electronic configuration $^{33}\text{As} \rightarrow [\text{Ar}]\ 3d^{10}4s^24p^3$.

Biochemical effects of heavy metals

In this section, we will discuss the biochemical effects of different heavy metals.

A. Cadmium (Cd): The sources include:

1. Industrial effluent
2. Cadmium nickel batteries
3. Nuclear fission plants
4. Water pipes

Cadmium occurs in nature in association with zinc minerals. Plants take up zinc (Zn^{2+}) and along with trace amounts of associated Cd (Cd^{2+}) are also acquired. The Cd^{2+} thus absorbed, replace Zn^{2+} as they have same charge and almost similar size and get attached to the active sites of enzymes which leads to cadmium toxicity inhibiting its essential enzymes function. Cd^{2+} ion has greater affinity for sulphur containing ligands, e.g., SH in cysteine amino acids and SCH_3 in methionine.

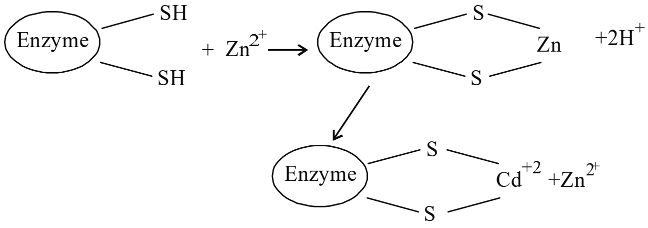


Fig. 2.6 *Enzyme-Cadmium Interaction*

The enzymes inhibited by Cd^{2+} include: (1) adenosine triphosphate (2) alkaline phosphate (3) carbonic anhydrase, etc.

The effects of Cadmium include:

1. Kidney damage
2. Disorder of liver and brain
3. Bone marrow disorder
4. Gastric and intestinal disorder

The outbreak of Cd poisoning occurred in Japan in the form of 'Itai-Itai' or 'Ouch-Ouch' disease. Many people got affected by this disease which rendered their bones fragile.

B. Mercury (Hg): Sources of Mercury are:

1. Mining and refining of Hg
2. Agricultural industry producing organic mercury as pesticides and fungicides
3. Paper industry using Hg as cathode
4. Chlorine and sodium hydroxide producing industry using Hg electrode
5. Laboratories using Hg

Importance of mercury as toxic metal came into limelight after the incidence of Minamata disease in Japan (1953-1960). At Minamata Bay in Japan many people lost their lives, many were permanently crippled and babies born to mothers consuming the mercury contaminated fish were genetically defective. The source of mercury was the effluent discharged into the bay from a vinyl chloride plant, Minamata Chemical Company. The fish in the bay were found to contain 25 to 100 ppm mercury in the form of methyl mercury.

The Minamata incidence was followed by a tragic incidence in Iraq, where many people died consuming wheat contaminated with organic mercury used as fungicides for seed dressings (methyl mercury nitrite, methyl mercury chloride, etc.).

It is to be noted that all the forms of Hg are not toxic. Elemental Hg is relatively inert and non-toxic. However, due to its high vapour pressure, when inhaled it causes severe damage to the central nervous system. Inorganic Hg is highly insoluble and also non-toxic. Mercurous ion (Hg_2^{2+}) is low toxic but not mercuric ion (Hg^{2+}). The toxicity of Hg^{2+} is due to its high affinity for sulphur atoms, by attaching itself to sulphur containing amino acids of protein, it forms

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bonds with hemoglobin and serum albumin containing sulphydryl groups.

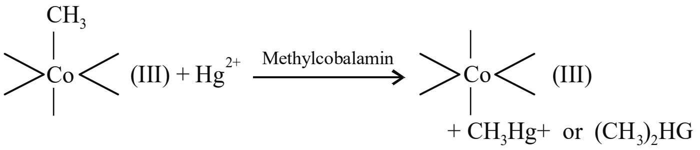
The most toxic species are, however, organic mercury, especially CH_3Hg^+ as it is soluble in fat, lipid of membranes and brain tissue. The covalent Hg-C bond cannot be disrupted easily and thus, remains for a long time in the cells. This, in turn, prohibits active transport of sugars, but allows passage of K to the membrane, resulting in energy deficiency in cells and disorder of central nervous system.

Mercury in food chain

It is very interesting to note that the mercury which was discharged from the vinyl chloride plant of Minamata Chemical Company was relatively non-toxic elemental HgO or inorganic salt, the fish however, contained highly toxic CH_3Hg^+. The prolonged research on this subject led to the revelation of how the conversion took place. The conversion stages are as given below:

(*i*) Hg and its salts convert to methyl mercury by anaerobic bacteria such as 'clostridium cochluarium' in water. The conversion is supposed to be facilitated by Co (III), containing vitamin B_{12} coenzyme.

(*ii*) The CH_3 group, bonded to Co (III) in coenzyme is transferred by methyl cobalamin to Hg^{2+}, forming CH_3Hg^+ or $(CH_3)_2Hg$.



$$\text{Co(III)}{-}CH_3 + Hg^{2+} \xrightarrow{\text{Methylcobalamin}} \text{Co (III)} + CH_3Hg+ \text{ or } (CH_3)_2HG$$

Fig. 2.7 Biological Methylation of Mercury

(*iii*) This CH_3Hg^+ undergoes translocation in plants and animals and finds its way into the food chain.

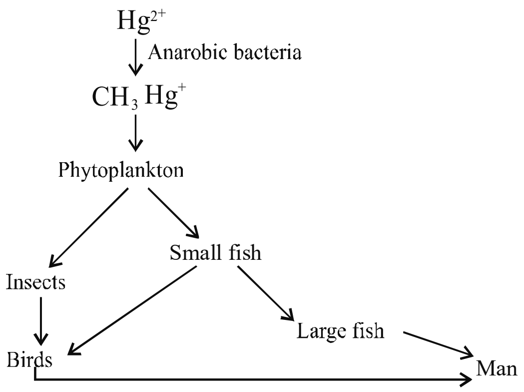


Fig. 2.8 Translocation of Mercury into Various Trophic Levels

The soluble methyl mercury through food chain (as shown above) gets magnified in every stage of consumption and finally gets deposited in fish tissue or insects, exceeding the permissible level. Man eating fish or bird thus, accumulate the mercury. Effects of Mercury are:

1. Numbness of limbs, tongue and lips
2. Blurred vision, deafness and mental disorder
3. Kidney damage

C. Lead (Pb): Sources of Lead are:

1. Mining and refining
2. Automobile emission (tetraethyl lead used as anti-knocking agent)
3. Electrical storage battery industry
4. Ceramic industry
5. Agricultural industry (preparation of insecticides, e.g., lead arsenate)
6. Paints, pigments, varnishes
7. Hair dyes, eye paints, canned foods, sea food, painted toys, etc.

Pb exerts its activity through sulphydryl inhibition. Pb has affinity for sulphur and it also reacts with carbonyl and phosphoryl groups. The main biochemical effect of lead is due to its interference with hemesynthesis, leading to hematological damage. It prohibits utilization of O_2 and glucose for the life sustaining energy production, *i.e.*, interferes with normal metabolic function. When the blood lead level reaches 0.8 ppm, symptoms of anemia occur with high degree kidney infection and brain damage.

One of the most harmful effects of Pb is that it can replace Ca in the bones, accumulate there and subsequently remobilize to soft tissue along with phosphates from the bones and cause severe toxic effects while transporting. Chronic exposure leads to weight loss, loss of teeth, etc.

Organic lead, like tetraethyl lead has been proved more poisonous than inorganic lead. Organic lead can penetrate the skin, can get absorbed in the body tissue faster as compared to the inorganic lead. Organic lead compounds being lipophilic, are selectively localized in central nervous system causing high degree of toxicity. Organic lead might cause genetic modification also. The tolerance limit of lead is 7 mg / kg body weight of an adult. Effects of Lead include:

1. Lever and kidney damage
2. Mental retardation
3. Genetic modification

It is now believed that the fall of Roman Empire (30 BC to AD 220), was due to lead poisoning. Lead was an expensive metal during the era of Roman Empire. Roman aristocracy used lead containers for storing wine and for cooking. The leaching of lead ultimately caused chronic lead poisoning and caused mental imbalance, degenerated behaviour and collapse of Empire.

D. Arsenic (As): The sources of Arsenic include:

1. Natural rocks and soils
2. Agricultural industry (chemicals like As_2O_3, lead arsenate, etc.)
3. Fungicides, pesticides and herbicides

4. Mining and extraction
5. Glass industry

In the earth's crust, the level of arsenic is 2 ppm (the main ore being sulphide). The main sources of arsenic pollution are agricultural chemicals. Arsenic can exist in two forms—trivalent and pentavalent. Trivalent arsenic is the most toxic one. The toxic action of arsenic is due to its affinity towards sulphur. It thus, attacks the sulphydryl (–SH) group of an enzyme, inhibiting its enzyme activity essential for the generation of cellular energy in the citric acid cycle.

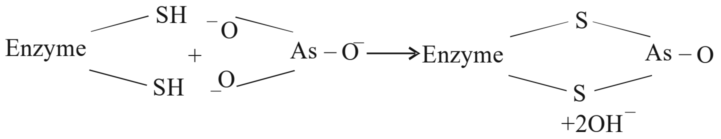


Fig. 2.9 *Complexation of Arsenic with Enzyme*

Thus, pyruvate-oxidase system becomes less effective in generation of main energy source, *i.e.*, adenosine triphosphate (ATP) due to its complexation with arsenic. Some biochemical processes involving phosphorous are also hampered due to the interference of arsenic because of its chemical similarity to phosphorous, preventing ATP generation. Arsenic (III) compounds coagulate protein at higher concentration levels.

One of the major contributions of arsenic pollution is contamination of ground water. Contamination of ground water has become a global phenomenon. If arsenic polluted water is used for drinking and cooking purposes for a prolonged time, a person may suffer from anaemia, melanosis, keratosis and conjunctivitis. Major effects of Arsenic are:

1. Affects liver
2. Causes central necrosis and cirrhosis
3. Damages bone marrow and cellular elements of the blood
4. May lead to skin cancer

Check Your Progress

5. Mention any three signs of water pollution.
6. What are the commonly found inorganic contaminants of water?
7. What are the categories of infectious diseases associated with water?

2.4 WATER QUALITY PARAMETERS

The five parameters that are essential for aquatic life are: Dissolved Oxygen, Temperature, Electrical Conductivity/Salinity, pH, and Turbidity. Impacts on the flora and fauna of a certain water body can be seen as a result of these impairments. Other concerns include Nitrogen (NO3-N), which is a nutrient found in both fresh and salt water naturally. In an aquatic ecology, it is necessary for plant growth.

When substantial volumes of nitrogen are introduced into the stream ecology, problems arise. As a result, excessive algal growth may occur, reducing the oxygen available in the stream, which fish and other aquatic species rely on. Also, Total coliform bacteria, faecal coliform bacteria, and E. coli are all markers of water that has been contaminated with faeces. Other pathogens (microorganisms that cause illness) may be present in contaminated water that are more difficult to detect. As a result, these indicator microorganisms are valuable in determining pollution levels. In this section, we will discuss some of the parameters.

2.4.1 Dissolved Oxygen (DO): Analytical Methods for Measuring Do

Amount of dissolved oxygen (DO) present in the water body is one of the important measures of water quality. The DO depends on the physical, chemical and biological activity of the water body. The measurement of DO gives an idea about the purity level of water, maintaining aerobic conditions in water bodies and aerobic treatment of sewage and industrial waste water. The DO contents of a water sample can be determined iodometrically by Winkler method as well as by polarographic method.

Effect of Oxygen Demanding Wastes on Rivers

One of the most important criteria for a river's health is dissolved oxygen (DO). With decrease in DO, survival of life becomes difficult. In extreme cases under anaerobic conditions, the right forms of life can get extinguished. Under such conditions, fungal growth and floating sludge can create noxious conditions.

There are many factors which attribute to the deficiency of DO:

1. With the increase in temperature, especially in summer, the solubility of oxygen decreases. With decrease in temperature, especially in winter, the floating ice prevents penetration of atmospheric oxygen.
2. Presence of oxygen demanding wastes reduces DO and with increasing temperature rate of aerobic biodegradation increases and DO drops drastically.
3. Respiration of organisms living in water as well as in sediments removes oxygen resulting in DO drop.
4. The green plants in the water body although add DO during day through photosynthesis, they reduce DO at night causing harm to the living organisms.

In a simplified model, the two most important parameters considered to assess DO are: (*i*) Deoxygenation, the removal of DO by microorganisms due to biodegradation (*ii*) Re-aeration, replenishment of oxygen at the interface between the river and the earth's atmosphere.

In order to explain the effect of the above two processes, it is assumed that the water and the wastes flowing down the river are uniformly mixed at any given cross section of the river (point source) and there is no dispersion of wastes in the direction of the flow (plug flow).

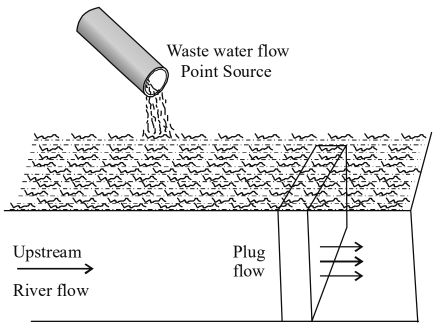


Fig. 2.10 ***Plug Flow Model for Dissolved Oxygen***

(*i*) Deoxygenation

The rate of deoxygenation at any point is proportional to BOD remaining at that point. Mathematically, we can express this as

Rate of deoxygenation $\propto C_t$

or $R = k_d C_t$

where k_d is the deoxygenation rate constant (time^{-1}) and C_t is the BOD (mg/l) remains after t days. For deep, slowly moving rivers, the rate at a specified temperature is approximately same to that obtained for laboratory test and under that condition $R = k_d C_0 e^{-k_d t}$. But for shallow rivers the flow is turbulent and under that condition the rate will be much different.

(*ii*) Re-aeration

The rate of replenishment of oxygen at any given location is proportional to the difference (D) between the saturated dissolved oxygen concentration and actual dissolved oxygen at any point, at a given time.

Thus, rate of re-aeration = $k_r D$

where, k_r = re-aeration constant (time^{-t})

D = deficit in dissolved oxygen ($DO_s - DO$)

DO_s = saturated value of dissolved oxygen

DO = dissolved oxygen at a given point at a given time

The aeration rate constant k_r, varies with the condition of the river at a time. A fast moving white water river will have higher re-aeration constant compared to a sluggish river.

Saturated value of dissolved oxygen depends on key parameters like temperature, atmospheric pressure and salinity.

At the point of disposal of wastes, decomposition of the higher amount of organic material leads to a greater drop in oxygen level and the rate of removal of oxygen is greater than the rate of re-aeration to bring other oxygen to the same level. With distance, the oxygen drop decreases but continues and a point arrives, the critical point, where the rate of removal of oxygen equals the rate of addition of oxygen by aeration. And beyond this critical point, the re-aeration rate supersedes deoxygenation caused by microorganisms and dissolved oxygen reaches to the previous saturation value and the river recovers.

When the rate of deoxygenation exceeds rate of re-aeration, DO drops. At critical points, both are equal. Beyond the critical point, re-aeration exceeds decomposition, DO curve goes upward and DO reaches saturation value. (Fig. 2.11)

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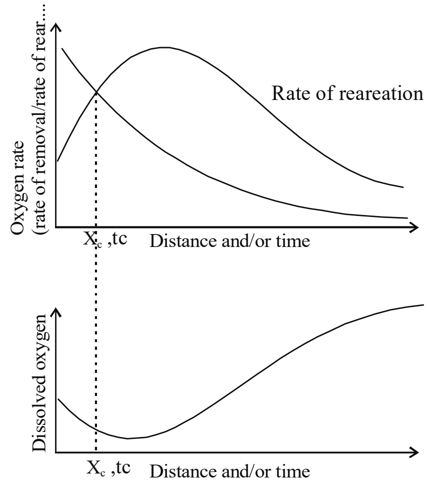

Fig. 2.11 *Plug Flow Model for Dissolved Oxygen*

The lowest value of DO is found to be 6.0 mg/l, an amount sufficient for the most aquatic life. If BOD is added in excess, DO drops below this lowest value creating unhealthy conditions, killing fishes and other animals might also diminish. From water quality view point, there are thick mats of fungi, sludge, blood worms and many kinds of bacteria growing, leading to further drop in DO and an anaerobic condition might occur resulting in the formation of toxic gases like ammonia, hydrogen sulphide, etc. Due to anaerobic decomposition by microbes, which in long run creates completely lifeless condition, the DO level falls to zero.

Even if the pollutant load is constant the drop in DO might also vary with seasons, temperature and time of the day.

With increase in temperature, solubility of oxygen decreases, aerobic decomposition of wastes becomes faster and re-aeration slower. Thus, a particular river which has sufficient DO in winter will have unacceptable deficit in summer.

Photosynthesis also affects DO. Algae and other aquatic plants which add DO in day time due to photosynthesis, use oxygen for respiration at night due to which DO drops. Thus, for a river which is already loaded with excess BOD and choked with algae, at night it becomes unfavourable for sustaining life.

The idea regarding deoxygenation, re-aeration and the effect of BOD on the condition of the health of a river will be helpful in taking decisions on the extent of on-site-waste treatment and the maximum amount of BOD which can be allowed to a river or generally to water resources.

A simple chemical analysis method (titration method), an electrochemical analysis method (diaphragm electrode method), and a photochemical analysis method can all be used to detect dissolved oxygen levels (fluorescence method). The most extensively utilised method is the diaphragm electrode method. This technology uses electrodes to monitor the amount of oxygen passing via a diaphragm that is particularly oxygen permeable. The galvanic electrode method and the polarographic electrode method are two ways for determining dissolved oxygen levels using electrodes. These strategies each have their own set of benefits and drawbacks, thus the method that best suits the situation is chosen.

2.4.2 Biochemical Oxygen Demand or Biological Oxygen Demand (BOD): Analytical Methods of Measuring BOD

The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called biochemical or biological oxygen demand. It is expressed in milligrams of oxygen required per liter of waste water (mg/l). The BOD can be categorized into two parts (1) Carbonaceous Biochemical Oxygen Demand (CBOD) (2) Nitrogenous Biochemical Oxygen Demand (NBOD).

BOD test is important as far as the analysis of waste water is concerned. The aerobic decomposition of organic matter by dissolved oxygen can be represented as below

$$\text{Organic matter} + O_2 \xrightarrow{\text{Microorganism}} CO_2 + H_2O + \text{Stable products}$$
$$(NO^{-}_{3}, PO_4^{3-}, SO_4^{2-} \ldots) \quad + \text{new cells.}$$

The aerobic decomposition produces non-objectionable products.

The results of such oxidation is the rapid depletion of dissolved oxygen from the water body affecting the aquatic life as well as addition of undesirable odour, taste and colour, ultimately reducing the acceptability of water for domestic purpose. Thus, oxygen demanding wastes are severe pollutants and require special attention and care. BOD test is thus, very important for analysis of waste water for assessing organic pollution. BOD test provides information regarding purification capacity, especially of streams and serves as a guideline for the regulatory authorities to check the quality of effluents discharged into these water systems.

Five-day BOD Test

A BOD test can take several weeks for completion, making it impractical for routine purposes. As a result, five day BOD test is introduced, realizing that the ultimate demand is quite high.

Five-day BOD, or BOD implies the total amount of oxygen utilized by microorganisms in the first five days of biodegradation. In this test, a sample of waste water is kept in the stoppered bottle and concentration of dissolved oxygen (DO) is measured at the beginning of the experiment and again after five days. The difference in DO divided by the volume of the sample water gives the result of the five-day BOD test.

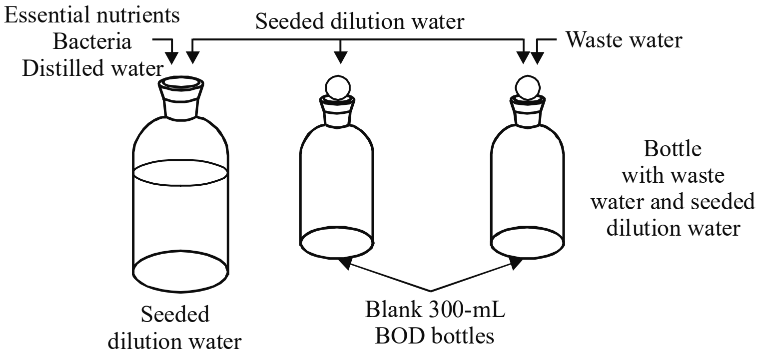

Fig. 2.12 *Five-Day BOD Test*

The following precautions must be taken while performing the experiment:

1. The stopper of the bottle must be fixed properly so that the replenished DO by biodegradation is not filled up by oxygen from air again.

2. The bottle must be kept away from the sunlight otherwise the algae will produce oxygen by photosynthesis by absorption of this sunlight.

3. The process must be carried out at 20°C for its standardization.

4. As saturated value of DO at 20°C is 9.0 mg/l, the sample must be diluted to keep final DO above zero otherwise the experiment will be invalid since more oxygen would have been removed had more been available.

The BOD of diluted solution can be given as:

$$\text{BOD}_5 = \frac{\text{DO}_i - \text{DO}_5}{f}$$

where,

DO_i = initial DO of the diluted waste water

DO_5 = DO after five days,

$$f = \text{dilution fraction} = \frac{\text{Volume of waste water}}{\underset{\text{(volume of waste water + volume of dilution water)}}{\text{Total volume of water}}}$$

A standard BOD bottle holds 300 ml, thus

$$f = \frac{\text{Volume of waste water}}{300\text{ ml}}$$

In our calculation for BOD_5 we have assumed that the water used for dilution has no BOD of its own. It is only possible if we use the boiled distilled water and keep it air tight prior to addition. If it is not so, then we must seed the water for dilution with microorganisms so that there is sufficient bacterial population to carry out the biodegradation. So, in such cases, the actual BOD of the waste water will be

= (BOD of the mixed sample-BOD of the water for dilution).

To carry out such an experiment two BOD bottles will be taken. In one, there will be seeded dilution water and in the other the mixture of waste water and seeded dilution water. The change in DO of the bottle containing seeded dilution water (called the 'blank') and that the change of DO in the mixture is noted. The BOD of the waste then will be given by

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$$\text{BOD}_w = \frac{(\text{DO}_i - \text{DO}_5) - (\text{B}_i - \text{B}_5)(1-f)}{f}$$

B_i = initial DO in the seeded dilution water

B_5 = DO in the seeded dilution water after five days.

If the experiment is not carried out just in five days, the generalized term instead of BOD_5 or DO_5 or B_5 can be BOD_f, DO_f or B_f.

There are other methods for measuring BOD as well such as Dilution methods manometric methods, and alternative methods such as Biosensors Fluorescent, polargraphic methods, software methods, and real-time BOD monitoring.

BOD Reaction Rate

The simplified representation of aerobic decomposition of organic matter can be given as

$$\text{Organic matter} + \text{O}_2 \xrightarrow{\text{Microorganism}} \text{Products}$$

Assuming first order reaction

$$\frac{-dc}{dt} \propto c$$

or $$\frac{-dc}{dt} = kc$$

where, $\frac{-dc}{dt}$ is the rate of change of concentration of oxygen, c is concentration of oxygen at anytime t, and k is a constant, called the velocity constant or BOD reaction rate constant (time $^{-1}$), if the initial concentration of oxygen is c_0, then at time $t = 0$, $c = c_0$

From the equation,

$$\frac{-dc}{dt} = kc$$

or $$\frac{-dc}{c} = kdt$$

Now after integrating we get,

$$-\ln c = kt + z$$

Now at time $t = 0$, $c = c_0$ and hence,

$$-\ln c = +z$$

or $$z = -\ln c_0$$

or $$-\ln c = kt - \ln c_0$$

or $$ln\frac{c_0}{c} = kt$$

or $$c = c_0e^{-kt}$$

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Also, we can write, $c_0 - c = c_0(1 - e^{-kt})$

where, c_0 is the total amount of oxygen required by the microorganisms to oxidize the organic wastes and c is the amount of oxygen consumed after time t.

$(c_0 - c)$ is the biological oxygen demand after time t.

Thus, $c_0 - c = \text{BOD}_t = c_0(1 - e^{-kt})$

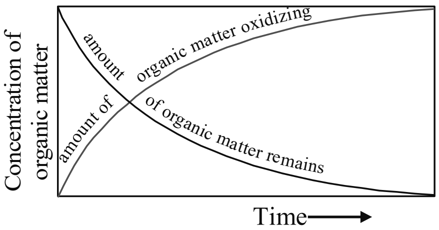

Fig. 2.13 *Kinetics of Biological Degradation*

For simplifying calculation, we can use logarithm to the base 10 in stead of e.

$\text{BOD}_t = c_0(1 - e^{-kt})$

Under this condition, k is the reaction rate co-efficient to the base 10. It can be shown that

$k = \text{K}\ ln10 = 2.303\ \text{K}.$

The BOD reaction rate constant K depends on number of factors,

1. Nature of the waste (*i.e.*, simple sugars degrade easily, where as cellulose takes longer time)
2. Nature of microorganisms
3. Temperature

The rate of biodegradation of wastes increases with increase in temperature. Under this circumstance, the modified equation for reaction rate constant is

$\text{K}_T = \text{K}_{20}\ \theta^{(T-20)}$

where, K_{20} is the reaction rate constant at standard 20°C laboratory reference temperature and K_T is the reaction rate constant at temperature T°C. The value of θ is generally taken as 1.047, although it is somewhat temperature dependant.

It is to be noted that our discussion and mathematical formulation regarding (BOD) is solely due to carbonaceous biochemical oxygen demand and not nitrogenous biochemical oxygen demand (NBOD), *i.e.*, oxygen needed to convert biochemical ammonia to nitrate.

$$2NH_3 + 3O_2 \xrightarrow{\text{nitrite bacteria (nitrosomonas)}} 2NO_2^- + 2H^+ + 2H_2O$$

$$2NO_2^- + O_2 \xrightarrow{\text{nitrite bacteria (nitrobacter)}} 2NO_3^-$$

The reason being, NBOD does not normally begin for the initial five to eight days.

2.4.3 Chemical Oxygen Demand (COD): Analytical Methods for Measuring COD

There are substances which are biodegradable as well as substances which are not biodegradable. Non-biodegradable substances may be cellulose, phenols and pesticides, etc. and are toxic to microorganisms. In BOD test, only biodegradable substances are taken into account. In COD, both biodegradable and non-biodegradable substances can be taken into account. Thus, COD does not depend on the ability of micro-organisms to degrade the waste or on the knowledge of the particular substance in question. In a COD test, a strong oxidizing agent, such as dichromate is used to oxidize the waste, it is not left to the microorganism to oxidize the matter.

American Society of Testing and Materials (ASTM), defines COD as the amount of oxygen (mg/l), required to oxidize the organic and oxidizable inorganic matter, under specified conditions, corrected for the influence of chlorides.

In COD determination, the waste water sample is refluxed with sufficient amount of $K_2Cr_2O_7$ in 50 per cent H_2SO_4 solution in the presence of Ag_2SO_4 catalyst and $HgSO_4$ (to eliminate interference due to chloride). The excess dichromate (untreated) is now titrated with a standard Mohr’s salt solution. The COD, thus is

$$\text{COD in mg/l} = \frac{(V_1 - V_2) \times N \times 8 \times 1000}{S}$$

where, V_1 is the initial volume of Mohr’s salt solution on normality N, required for the blank and V_2 for remaining untreated dichromate. S is the volume of the solution taken for testing.

The COD test obviously, is much quicker than a BOD test. However, COD because of the nature of the test cannot differentiate the actual oxygen demand felt in a natural environment due to biodegradation and chemical oxidation of inert organic matter. Whereas, BOD provides the rate of biodegradation, COD cannot. Since in the COD test, both biologically oxidizable and biologically non-oxidizable matter are oxidized, the COD value will be greater than BOD value, though for easily biodegradable substances the value will almost be same.

2.4.4 Acidification of Water (Effect of ph)

The dissolved carbon dioxide in water forms a solution of weak carbonic acid (H_2CO_3) with a pH of about 5.6. But due to acid rain which contributes nitric acid, sulphuric acid as well as hydrochloric acid, the pH of water resources falls to around 5.0 to 4.0 and in extreme cases to less than 3.0. The source for acid rain is of course, anthropogenic emission of SO_2, NO_2 and Cl_2.

Aquatic organisms are pH sensitive. Very few aquatic organisms are able to survive below pH 5.0. Secondly, when pH drops, *i.e.*, under acidified conditions toxic elements like Pb, Hg, As, Cd, etc., which are insoluble and therefore harmless, enter the solution and become lethal to aquatic organisms. However, it is the gift of nature that the bicarbonate, which is formed in the solution, can act as a buffer. Buffers, as is known, are substances capable of resisting the pH of a solution, *i.e.*, prevent alteration of pH due to added acid or base. The buffer action can be explained from the following chemical equilibrium

$$H_2CO_3 \text{ (carbonic acid)} \rightleftharpoons H^+ \underset{\text{Bicarbonate anion}}{HCO_3^-}$$

If an acid is received by water from any source, the concentration of H^+ increases and to maintain the equilibrium H^+ and HCO_3^- react to form less ionized H_2CO_3, resisting pH.

H_2CO_3 has limiting buffer capacity. With increased concentration of acid, there will be more and more removal of HCO_3^- and a point will reach when such small amount of HCO_3^- which remains, can resist the change in pH and the solution becomes acidic. So to maintain buffer action, new source of HCO_3^- has to be generated. This can be done by adding lime to water resources.

$$H^+ + CaCO_3 \text{ (lime stone)} \rightarrow Ca^{2+} + HCO_3^- \text{ (bicarbonate anion)}$$

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

The lime stone reacts with the incoming acid solution to form bicarbonate anion which helps buffer action to sustain the calcareous lakes which have an abundance of calcium carbonate and so they are invulnerable to acidification. Thus, to nullify the effects of acidification, water resources can be treated with limestone. This is to be remembered that bicarbonate buffer is effective for pH values above 6.

For lower pH (pH < 5), components of soil kaolinite, can be an effective buffer reagent.

$$\underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4} + 6H^+ \rightarrow 2Al^{3+} + 2Si(OH)_4 + H_2O$$

But in the process, it releases toxic Al^{3+} which is harmful to aquatic organisms.

2.4.5 Analytical Methods for Measuring Fluoride (F) in Water

Fluorides in overabundance, as well as a lack of fluorides in water, are both problematic. Those who drink water with a fluoride content greater than 1.0 mg/L develop mottled enamel, often known as dental fluorosis, on their teeth. Fluoride levels of 0.8-1.0 mg/L in drinking water have been scientifically proven to be necessary. As a result, dental cavities in consumers may be caused by a lack of fluoride or a low fluoride content.

Colorimetric methods are used to measure fluorides. If interfering chemicals are present, fluorides are separated by distillation. Fluorides are measured using a process that requires the fluoride ion bleaching a performed colour. The colour produced is the consequence of the reaction of zirconium ion with alizarin dye. When the amount of zirconium present is reduced, the colour created is referred to as a lake, and the intensity of the colour produced is diminished. The intensity of the colour lake drops as the fluoride ion interacts with the zirconium ion to create the stable complex ion ZrF_6^-.

The use of an ion selective electrode for fluorides is the most used electro analytic approach for determining fluoride ions in water solutions. The fluoride selective electrode is extremely sensitive, with a temperature range of 0 to 50°C. In commercial application, electrodes with homogenic membranes manufactured from fluoride lantana (LaF_3), which were first suggested by Frant and Ross, are commonly used for potentiometric analysis of fluoride ions.

2.4.6 Analytical Methods for Measuring Oils in Water

Analysis of oil in water is a global problem that affects a wide range of sectors, analytical methodologies, and regulatory authorities. The amount of oil allowed in water is strictly regulated due to the detrimental effects of oil on the ecosystem. Failure to adhere to these guidelines might result in hefty fines. While any sector that discharges generated water must test for oil in the water, the needs of each industry are different. Total Oils and Grease (TOG) measurements in both upstream and downstream wastewater are of particular interest to the petroleum industry. Testing for Fats, Oils, and Grease (FOG) in effluent is critical for industrial pre-treatment of wastewater, public water treatment plants, and most other non-petroleum enterprises discharging produced water. FOG varies from TOG in that it has a higher proportion of animal and vegetable components. FOG is particularly dangerous in effluent streams because it can cause clogged sewer pipes, resulting in Sanitary Sewer Overflows (SSOs).

The most popular method for evaluating oil in water in the field is to utilise non-dispersive/fixed filter IR analyzers. The instrument is simple, affordable, and sturdy thanks to the use of a fixed filter. The technology necessitates an oil extraction in a water sample, with the solvent used varying according to the type of non-dispersive/fixed filter analyser used. The extract is then dried and quantified using an instrument with a filter centred in the 3.4-3.5 m range (figure 2). The filter's bandwidth will allow the instrument to detect the CH_3 absorption peak as well as any aliphatic hydrocarbons connected to aromatic compounds, despite the fact that it is centred above the CH_2 absorption peak. However, this means that if the sample contains a lot of aromatics, the results will be skewed. There are two types of non-dispersive/fixed filter IR analyzers that are currently in use.

Other methods of analysing oils include Gravimetric Analysis (EPA 1664), Gas Chromatography–Flame Ionization Detection (GC-FID), UV Fluorescence, and Quantum Cascade Laser Infrared (QCL-IR).

2.4.7 Analytical Methods for Measuring Metals (As, Cd, Cr, Hg, Pb, Se, etc.) in Water

A large portion of anthropogenic heavy metal emissions ends up in wastewater. Surface treatment operations with elements including Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe, and Ni, as well as industrial products that are released in wastes, are major industrial sources. The detection of trace and heavy metal contamination in wastewater is a critical step in protecting human and environmental health. Different countries control wastewater in different ways, but the goal is to reduce pollution in natural waterways. Inorganic techniques such as Flame Atomic Absorption Spectrometry (FAAS); Graphite Furnace (or Electrothermal) Atomic Absorption

Spectrometry (GFAAS or ETAAS); Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES); and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can be used to measure trace elements in waste water.

The most appropriate approach for business requirements can be chosen based on the number of elements to be determined, the predicted concentration range of analytes, and the number of samples to be run. Heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, and others may be present in industrial wastewater streams. Toxic metals must be adequately treated/removed from wastewaters, whether they are present in high or low quantities. Chemical precipitation has been the most widely used treatment method for removing heavy or trace metals among the many treatment methods. The traditional heavy metal removal procedure has several drawbacks, including the need for a considerable amount of land, a sludge dewatering facility, skilled operators, and multiple basin configuration. In recent years, innovative technologies for heavy metal removal from wastewater, such as biosorption, neutralization, precipitation, ion exchange, and adsorption, have been developed and widely used.

2.4.8 Analytical Methods for Residual Chlorine and Chlorine Demand in Water

Chlorine is a reasonably inexpensive and widely available chemical that, when dissolved in sufficient amounts in clean water, will kill most disease-causing organisms while posing little risk to humans. The chlorine, on the other hand, gets depleted as organisms are destroyed. After all the organisms have been eliminated, there will be some chlorine left in the water, which is known as free chlorine. Free chlorine will remain in the water until it is lost to the environment or used up, killing new contaminants. As a result, if we test water and find that some free chlorine remains, it means that the majority of harmful organisms have been removed and the water is safe to consume. This is referred to as testing the chlorine residual. Measuring the chlorine residual in a water supply is a simple but crucial way to ensure that the water delivered is safe to consume.

The dpd (diethyl paraphenylene diamine) indicator test with a comparator is the most common test. This is the quickest and most straightforward way of determining chlorine residual. A tablet reagent is used to colour a sample of water red in this test. To calculate the chlorine concentration, the colour strength is compared to standard colours on a chart. The more intense the colour, the higher the chlorine concentration in the water. Commercially available kits for determining the chlorine residual in water are available. The kits are compact and easy to transport.

Chlorine demand

The difference between the amount of chlorine applied to water or wastewater and the amount of residual chlorine left after a specific contact time is known as chlorine demand. The chlorine demand varies depending on the dosage, time, temperature, pH, and the nature and number of pollutants in the water.

Chlorine Demand = Applied Chlorine – Residual Chlorine

2.4.9 Water Quality Standards

Water which cannot form lather easily with soap is known as hard water and this characteristic is called hardness. On the other hand, water which forms lather with soap is called soft water. The hardness which can be removed easily just by boiling is temporary hardness, otherwise, it is called permanent hardness. Permanent hardness can be removed through some appropriate physical or chemical methods.

The principle ions responsible for hardness are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Smaller quantities of other ions which cause hardness of water are iron (Fe^{2+}), manganese (Mn^{2+}), strontium (Sr^{2+}) and aluminum (Al^{3+}).

Hardness of water causes many problems. The reaction between hard water with soap produces sticky, gummy deposit known as 'soap curd', a dirty ring around the bathtub. Hard water, thus consumes lot of soap unnecessarily. When hard water is heated, calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$] precipitate out of the solution, forming rock like scale. The scale, in turn clogs hot water pipes and the efficiency of water-heaters, boilers is reduced day by day, with increased amount of deposit. The cleaning of such equipment is also costly. Due to reduced efficiency, the heat transmission goes down increasing energy consumption and also the equipment cannot last long. The unnecessary consumption of such soap, along with formation of scaling, makes hard water unsuitable for washing of clothes at home and in laundry.

Groundwater generally is harder (~ 300 mg/l) compared to surface water (~ 200 mg/l) and is termed as 'soft' water. Hardness is measured in mg/l as $CaCO_3$. The total hardness is taken as the sum of Ca^{2+} and Mg^{2+} as they are the main components causing hardness.

Hardness can be classified into two groups:

(*i*) **Carbonate hardness:** In this case, the cations Ca^{2+} and Mg^{2+} are associated with two anions CO_3^{2-} and HCO_3^-.

(*ii*) **Non-Carbonate hardness:** The cations Ca^{2+} and Mg^{2+} are associated with Cl^- and SO_4^{2-}, PO_4^{3-}, etc.

The carbonate hardness is temporary hardness and it can be removed easily by just boiling the water and is very important in the sense that the boiling leads to formation of carbonate causing scaling.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$$

$$\underset{\text{Bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{Carbonate}}{MgCO_3} + CO_2 + H_2O$$

For the removal of hardness two processes can be adopted (1) Lime soda process (2) Ion exchange process.

Lime Soda Process

In this process, quick lime (CaO) or hydrated lime ($Ca[OH]_2$) is added to hard water. The soluble bicarbonate of (Ca^{2+}) is precipitated out as insoluble carbonate and that of Mg^{2+} as hydroxide.

$$Ca(HCO_3)_2 + CaO \rightarrow 2\,CaCO_3 + H_2O$$

$$Mg(HCO_3)_2 + 2CaO \rightarrow 2\,CaCO_3 + Mg(OH)_2 + H_2O$$

To remove SO_4^{2-} and Cl^- ion containing calcium and magnesium salt, some soda ash is added in addition to CaO or $Ca(OH)_2$.

$$MgSO_4 + Ca(OH_2) + Na_2CO_3 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4$$

Ion Exchange Process

In this process, the hard water is passed through natural zeolites or synthetic resins. The Ca^{2+} and Mg^{2+} ions are exchanged by Na^+ ions, forming soluble salts.

$$CaCl_2 + Na_2R \rightarrow CaR + 2NaCl$$

'R' represents negatively charged ion resin. The sodium ion thus produced, may cause problem to heart patients. With continuous removal of Na^+ from the resin ion exchange the activity decreases and ions are regenerated by treating with concentrated sodium chloride.

$$CaR + 2NaCl \rightarrow Na_2R + CaCl_2$$

Ion exchange process can be used in treatment of waste water as well as surface water treatment.

Table 2.1 *The WHO Standard of Permissible Limits for Drinking Water*

Parameter	*Maximum permissible limits for drinking water (ppm)*
pH	6.5-9.2
BOD	6.0
COD	10.0
Total Hardness ($CaCO_3$ equivalent)	500
E.Coli	100/100ml
Total Dissolved Solids (TDS)	500
Calcium	100
Magnesium	150
Copper	1.5
Iron	1.0
Manganese	0.5
Boron	—
Arsenic	0.05
Lead	0.10
Mercury	0.001
Cadmium	0.01
Chromium	0.05
Ammonium	0.50
Chloride	500
Cyanide	0.05
Nitrate and Nitrite	45
PAH	0.2
Pesticides	—

NOTES

Check Your Progress

8. What parameters are essential for aquatic life?
9. What is the most extensively utilised method to analyze DO?
10. Define COD according to ASTM.
11. What is the source for acid rain?
12. Name some of the inorganic techniques that are used to measure trace elements in waste water.
13. What is Chlorine demand?
14. What is the difference between hard and soft water?

2.5 PURIFICATION AND TREATMENT OF WATER

'Water, water everywhere, not a drop to drink.' We are very familiar with this term. So far, we have discussed how the anthropogenic activities degrade our environment. Contamination of water now has reached to such a height that it is very unsafe to drink as well as cook food with such water and even water meant for washing purpose should also be taken care of. The waste water collected from various sources should be treated so as to remove contaminants in order to be released again into their origin. The treatment must remove pathogens, BOD materials, excessive nutrients and toxic chemicals. The drinking water standards can be categorized into:

- Primary standard, specifies maximum allowed contaminant, like organic and inorganic chemicals, radio nuclides like radon gas and micro biological contaminants levels relating to health.
- Secondary standard is related to taste, odour and colour, corrosivity and hardness and is less related to health. The type of contaminants are, excessive sulphate for laxative effect, excessive fluoride resulting in brownish discoloring of teeth, excessive iron and manganese for bad taste and odour, due to gases like CH_4, H_2S, SO_2, etc.

The water, therefore, must be treated so that raw water becomes drinkable. The two sources of drinking water are both ground water and surface water. The main characteristics of these two sources are:

Ground Water

The features are:

1. Little suspended materials
2. Less chances of contamination
3. Less hardness
4. Chances of greater concentration of objectionable dissolved gases

Surface Water

The features are:

1. High concentration of suspended materials
2. Greater chances of pollution
3. Greater chances of hardness
4. Objectionable dissolved gas, depending on the type of water resources

NOTES

2.5.1 Surface Water Treatment

Surface water has turbidity, large floating and suspended materials, lot of harmful pathogens and metal ions causing hardness of water. Following sequence of steps should thus, be followed to make surface water potable:

(*i*) Screening

Parallel steel bars followed by wire mesh screen with small openings, are generally used to remove relatively large floating and suspended materials.

(*ii*) Coagulation

The screened waste water might contain suspended particles, including bacteria which are too small to be screened and to settle in a reasonable time period and if the particles are of colloidal dimensions they will never settle down. Under these circumstances, the water is mixed with chemicals which help small suspended materials to coagulate into larger particles, thereby facilitating precipitation. Colloidal particles carry the same charge and thus repel each other. The repulsion of the similar charged particles does not allow them to come closer. The particles hence, remain suspended or scattered throughout the solution. If by any means the charges are removed the particles will come together to form bigger aggregates and will settle down under the influence of gravity. The intended action of coagulant is to neutralize the charges so that the particles can come together to form bigger aggregates to settle down.

The coagulation is thus, defined as the process by which colloidal particles come closer resulting into precipitation. Coagulation can be brought about in many different ways such as:

(*a*) Adding electrolytes
(*b*) Mixing oppositely charged sols
(*c*) Through boiling
(*d*) Through electrophoresis, etc.

In water treatment process, usually the electrolytes are added for coagulation. The electrolytes used for coagulation are called flocculating agent as they make the bigger particles to flocculate. The coagulating capacity depends upon the valency of the added ion, *i.e.*, the more the valency of the ion the more is the capacity and nature of colloid. Lyophobic colloids are much easily coagulated compared to lyophilic colloid.

The usual coagulant is alum ($Al_2(SO_4)_3.18H_2O$).

The use of such coagulant is based on the strong power of Al^{3t} ions to coagulate negatively charged colloidal impurities present in natural water. When alum is added, the positively charged Al^{3t} ions are taken upon the surface of the colloidal particles, as a result the charge of colloidal particles is neutralized and thus the particles get coagulated.

The coagulating power of trivalent ion is much higher than monovalent ion and is comparable to that of bivalent ion but still higher. The other electrolytes which can be used are $FeCl_3$, $FeSO_4$, etc.

The coagulating or flocculating agent is added to the raw water into a rapid mix chamber having rapidly rotating paddles, with a detention time of approximately 90 seconds. In this chamber the raw water and the flocculating agent are mixed well. After proper mixing, the mixture is allowed to pass through another chamber for gentle agitation for about 30 minutes. In this time period, the surface charge neutralization of colloidal particles takes place and they form bigger flocculent. The time of agitation must not be so high that the flow particles break apart.

(*iii*) Sedimentation

After flocculation, the water is allowed to flow through a sedimentation basin or clarifier. Sedimentation basin is a concrete tank and is circular or rectangular in shape. The concrete tank can hold water for a longer time without any damage. The usual detention time for water varies from one to ten hours. Obviously, with greater detention time settlement of suspended materials is much efficient. The solids settled at the bottom of the tank can be removed manually or mechanically by a scrapper.

(*iv*) Filtration

The filtration unit is sand filter. It consists of multiple layers of graded gravel. The gravels at the uppermost layer are bigger in size and those at the lowest layer are finer. The pore openings between the sand grains are smaller in size compared to the size of flow particles, so that they cannot pass out, allowing water to be filtered.

(*v*) Disinfection

The surface water is now free from suspended solids and small amount of bacteria but contains a lot of pathogenic organisms. To make water of drinkable quality, these pathogens should be disinfected as well as fluoridation has to be done for preventing dental caries.

The most commonly used chemicals for disinfection are either chlorine gas (Cl_2), sodium hypochlorite (NaOCl) or may be calcium hypochlorite [$Ca(OCl)_2$] and the method is known as chlorination.

Chlorine reacts with water to form hypochlorous acid and is known to be responsible for disinfection.

$$\underset{\text{Hypochlorous acid}}{Cl_2 + H_2O \rightarrow HOCl} + H^+ + Cl^-$$

$$HOCl \rightarrow HCl + \underset{\text{Nascent oxygen}}{(O)}$$

The strong oxidizing power, present due to liberation of nascent oxygen, destroys enzymatic processes in the pathogenic cell and thus kills them.

The advantage of chlorine as disinfectant is mainly due to its slow reaction with water and thus it can remain in water for a longer time and pathogenic microorganism cannot grow. Though chlorine is very effective against bacteria but it is very negligible against viruses and protozoan like giardia, lamblia and cryptosporidium.

The greatest disadvantage of chlorine is formation of trihalomethanes (THM), for example chloroform ($CHCl_3$) which is a carcinogen. The formation of THM is due to the reaction of chlorine with organic matters present in the surface water or due to the decaying of vegetation, dead animals, insects, etc. Concentration of THM can be greatly reduced if the organic wastes are removed first, followed by chlorination.

Chlorine dioxide (ClO_2) can be used to disinfect both bacteria and virus but it produces toxic chlorate and chlorite substances and involves a very costly process.

Disinfection can be carried out using ozone (O_3). It is both effective against bacteria and viruses. It does not produce toxic products and causes no problems in tastes and odours. It is, however, very expensive and is mainly used in European water treatment. (See Fig. 2.14).

2.5.2 Ways of Waste Water Treatment

Waste water contains a lot of chemical pollutants as well as dissolved solids and suspended solids. The major contributor of pollutants is industrial waste water. Waste water treatment can be classified as:

1. Primary treatment
2. Secondary treatment

A sample flow diagram for a waste water treatment plant that provides primary and secondary treatment is illustrated in Fig. 2.15.

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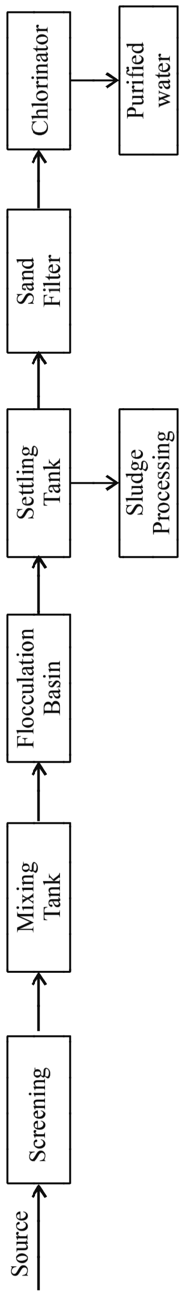

Fig. 2.14 Flow Diagram of Surface Water Treatment

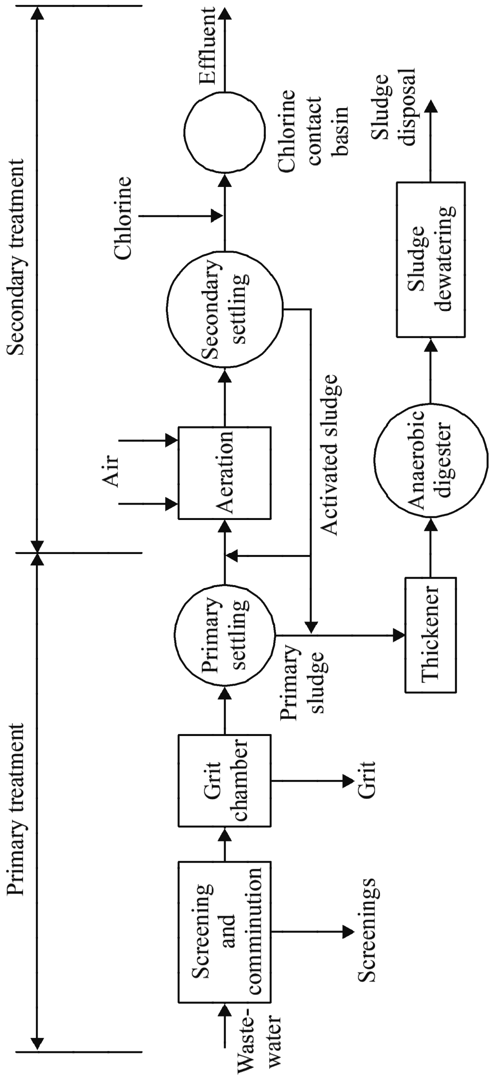

Fig. 2.15 Flow Diagram of Waste Water Treatment

1. Primary Treatment

The purpose of primary treatment is to remove pollutants like large, floating and suspended solid materials, grit, oil and grease, etc.

The large floating rubbish like sticks, rags, cans, cloth and various other objects are removed by screening. The screens are generally made up of steel bars spaced very few centimeters apart, followed by a wire mesh screen with smaller openings compared to the opening of steel bar assemblage. The collected materials are now disposed off. However, if a comminutor is used, it will cut the large materials into very small pieces and at a later stage can be settled in the grit chamber.

After screening, the waste water is passed into a grit chamber and time just sufficient for the heavy materials, like sand, grit, etc., to settle down is allowed. The settled materials can be disposed off in the land fill.

From the grit chamber, the waste water is now allowed to pass through primary settling tank or 'primary clarifier'. The flow rate is now reduced with a detention time of about two to three hours and most of the lighter suspended solids settle down because of gravity. The settled solids are generally circular in shape and the waste water flows horizontally. The settled suspended materials can then be removed by mechanical scrapping into hoppers and are pumped out subsequently. In the overall process, about 60 per cent of suspended solids and 40 per cent BOD can be removed.

However, finely divided suspended solids and colloidal particles cannot be removed by this process. Under this condition, mechanical flocculation and chemical coagulation can be employed. In mechanical flocculation, the finely divided suspended solids are allowed to coalesce by rotating paddles with sufficient detention time. Later on, they get separated with settlement due to gravity.

In coagulation process, chemical coagulate like alum or hydrated lime is added and for making the process more efficient, coagulant aids like activated silica or polyelectrolyte can be used and colloidal suspension can easily be removed.

2. Secondary Treatment

The purpose of the secondary treatment is to remove the finely suspended solid, dissolved solid and BOD which still remain after the primary treatment. The BOD is removed by biological processes using bacteria and other microorganisms. The processes may be aerobic or anaerobic.

Organic Matter

$$(\text{BOD}) + O_2 \xrightarrow[\text{(Aerobic decomposition)}]{\text{Bacteria/microorganism}} \underset{\text{(Stable product)}}{CO_2 + H_2O + NO_3, PO_4, SO_4}$$

$$\ldots + \text{New cells of microorganism}$$

$$(\text{BOD}) \xrightarrow[\text{(Anaerobic decomposition)}]{\text{Bacteria/micro-organism}} \underset{\text{(Unstable product)}}{CO_2 + H_2O + H_2S, NH_3, CH_3\ldots}$$

$$+ \text{New cells of microorganism}$$

Thus, in the secondary treatment, oil, grease and organic matter (BOD) are removed to the largest extent. The complex cell tissues thus, formed can be removed by agglomerating them and finally settling out.

The effluent from the primary sedimentation tank is first subjected to aerobic oxidation in systems like trickling filters, rotating biological contractor, active sludge units and oxidation ponds. The sludge obtained in the primary sedimentation tank, is allowed to undergo anaerobic oxidation in the sludge digesters.

Anaerobic decomposition is generally employed for digestion of sludge. However, organic wastes from dairies, slaughter houses, etc., can also be treated by this method. The efficiency of both aerobic and anaerobic decomposition depends on many factors such as:

1. temperature 2. pH 3. concentration of wastes 4. nature of waste

In the secondary treatment, the decomposition is done under controlled conditions in the treatment plant itself and about 85 per cent BOD and suspended solids can be removed efficiently.

However, neither the primary nor the secondary treatments are effective in removal of nutrients, dissolved materials and biologically resistant materials. Under such circumstances, tertiary treatment is required.

(a) Trickling Filters

The trickling filter consists of circular filter beds usually about 1.5 m deep and is surrounded by circular brick wall. The beds are made up of materials like rocks or plastic materials.

The diameter of the material varies from 3 to 10 cm. The spaces between the rocks or plastic materials are sufficient to allow air to circulate and aerobic conditions are thus maintained. The incoming waste water after the primary treatment now can be sprayed over these circular filter beds by a rotating distributor. The rotating distributor is a metallic pipe with holes along its length and the waste water emerges in horizontal jets. The bottom of the filter is provided with a floor of perforated tiles through which incoming air passes.

The individual rocks in the bed are covered with a gelatinous film consisting of bacteria, algae, fungi, protozoa, worms, insects, etc. The BOD in the incoming waste water is absorbed in the bed surface and undergoes aerobic decomposition by these bacteria or microorganism. With increase in the thickness of the film, a part of it gets attached and carried away along with the treated waste water to a secondary settling tank and is removed finally. The sludge so obtained is now pumped to the sludge digestion unit.

The efficiency of trickling filter depends on temperature, pH, nature of the waste, uniformity of loading of the waste matter and air supply.

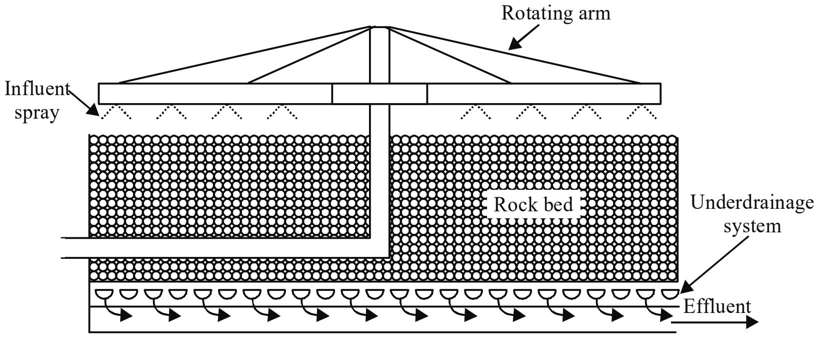

Fig. 2.16 *Trickling Filter*

If there is lack of oxygen in the trickling filter, then wrong type of organisms will develop and many toxic materials will be included in the final effluent. Thus, the bed should provide a home for a wide variety of organisms including bacteria, protozoa, fungi, worms and insects. The upper surface will also be colonized by algae.

Trickling filters are very simple to operate and BOD can be removed to the extent of 65 to 85 per cent. However, it is costlier and efficiency decreases if effluent of high BOD is passed continuously. Such problem can, however, be overcome if high BOD is replaced by low BOD occasionally.

(b) Rotating Biological Contractor (RBC)

An RBC consists of a series of closely spaced circular plastic disks (diameter, 3.6m) and is attached to a rotating horizontal shaft. The arrangement is so designed that about 40 per cent of each of the circular plastic disk is submerged in the tank containing waste water which needs treatment. The circular disks are covered with gelatinous film consisting of bacteria, fungi, algae, worm and insects. As the RBC rotates, the submerged portion adsorbs organics (BOD) and when they come out they are exposed to atmospheric oxygen. Under such condition, there is no scarcity of oxygen and the process becomes very efficient. The device is easy to handle and can be operated under high load conditions not possible by trickling filter. Compared to trickling filters, higher rate of BOD removal is achieved in RBC.

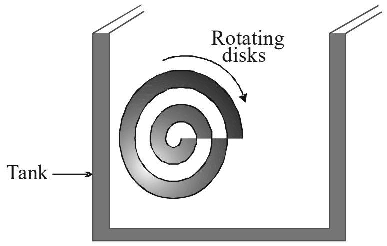

Fig. 2.17 *Rotating Biological Contactor*

(c) Activated Sludge Process

In the activated sludge process, the effluents from the primary sedimentation tank and recycled bacteria and other microorganisms (bio-organisms) from the secondary settling tank (the activated sludge), are collected in a tank called aeration tank.

The object of the process is to provide sufficient amount of oxygen for complete aerobic decomposition of the wastes. To do so, air with oxygen is pumped into the mixture and thoroughly agitated by mechanical stirrers. The water is kept in constant turbulent motion in the aerated tank (concrete tank). After about 3 to 6 hours of aeration (for sewage) and 6 to 24 hours of aeration (for industrial waste), the agitated effluent water again flows to the secondary tank and the effluent is separated from the sludge by settling and is discharged. Some part of the sludge is recycled again to the aeration tank, so as to maintain effective microbial population for fresh treatment, the remaining sludge can be processed and disposed of. The BOD removal from the waste water can be as high as 95 per cent.

In the activated sludge process, the BOD and suspended and dissolved solids are removed to a greater extend from the waste water and then that water is released to be used as a good water source. The remaining matter to be disposed off is only sludge (mixture of solids and water). The sludge can be dried up and used as fertilizer or it can be dumped into the sea. Whatever be the way of disposal, it must be environment friendly.

Another effective measure of sludge disposal is the digestion of the sludge under anaerobic condition at 35°C. Under anaerobic condition, the microorganisms convert the organics into simpler carbon dioxide, methane gas and many other stable products. The methane gas has fuel value and can be utilized to warm digestion tank. It is to be noted that methane forming bacteria are extremely sensitive to temperature, pH and oxygen and thus, proper condition should be maintained for sludge treatment.

The digested sludge still contains lot of water. The water can be removed by pumping sludge into drying beds or by the process of incinerators. The digested and dewatered sludge is inoffensive. It can be used as soil conditioner or disposed of in a land fill.

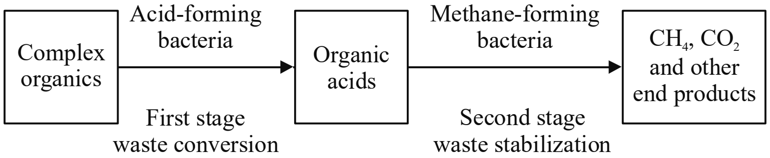

Fig. 2.18 *Sludge Treatment (Anaerobic Digestion)*

3. Tertiary Treatment

The main purpose of the tertiary treatment is to remove dissolved nutrients, especially nitrogen and phosphorus which have survived the primary and secondary treatment. The most important nutrient causing eutrophication is phosphorus. Phosphorus can be removed by precipitation with coagulant, like alum or lime or ferric chloride.

$$Al_2(SO_4)_3 + 2PO_4^{3-} \rightarrow 2AlPO_4 \downarrow + 3SO_4^{2-}$$

$$3Ca(OH)_2 + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \downarrow$$

$$FeCl_3 + PO_4^{3-} \rightarrow FePO_4 \downarrow + 3Cl^-$$

Nitrogen is difficult to remove. If nitrogen is present in the form of NH_4^+, aerobic bacteria convert it to nitrate (NO_3^-) and anaerobic bacteria under anaerobic condition convert nitrate (NO_3^-) to nitrogen gas.

$$NH_4^+ + 2O_2 \xrightarrow{\text{aerobic bacteria}} NO_3^- + 2H^+ + H_2O$$

$$2\,NO_3^- + \text{organic matter} \xrightarrow{\text{anaerobic bacteria}} N_2 \uparrow + CO_2 \uparrow + H_2O$$

However, very less organic matter is left after the primary and secondary treatment and hence, some amount of organic matter not harmful, needs to be provided.

The purpose of the tertiary treatment is to provide suitable water for drinking. Therefore, besides nutrient removal, some amount of fine suspended solids, some amounts of bacteria, small amount of organic material should also be removed.

Thus, water can be passed through activated charcoal which removes fine suspended solids, some bacteria and small quantities of organic material still present in the water through absorption. Some absorbents (ALM series) can also be utilized to remove heavy metals, if present. Removal of toxic metals can also be done by ion-exchange process. Finally, the water obtained is disinfected through processes mentioned earlier.

NOTES

(a) Oxidation Ponds

An oxidation pond is a large, shallow pond (0.5 to 1.5 m depth), where the waste water, mainly the sewage water, is treated through its decomposition by microorganisms. The waste water enters the pond at one end and the treated water is removed at the opposite end.

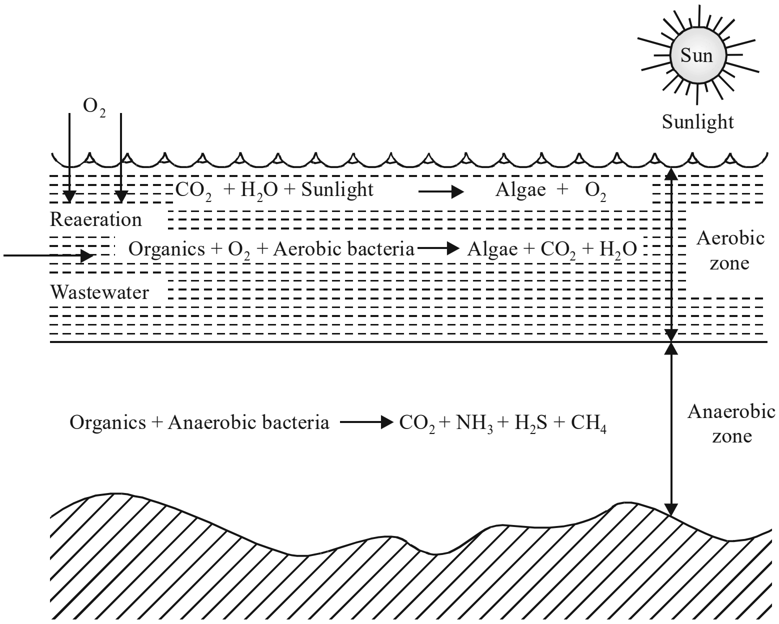

Fig. 2.19 Oxidation Pond

Although waste water treatment in oxidation pond is considered to be aerobic process, both aerobic and anaerobic processes operate together. The aerobic decomposition mainly takes place near the surface and anaerobic process, at the bottom. The oxygen required for the metabolism of bacteria is obtained from the surface through aeration as well as from the algae present in the pond and in turn the bacteria supplies CO_2 by decomposing the waste. For good supply of oxygen by algae, the ponds are made shallow so that sunlight can penetrate well, helping photosynthesis. The waste thus, present at the upper part of the pond, undergoes aerobic decomposition to form CO_2 and H_2O. The solids present in the waste get settled to the bottom and undergo anaerobic decomposition to form CH_4, CO_2 and NH_3. The oxidation pond, with both the aerobic and anaerobic conditions prevailing is called facultative pond. The bad odours due to anaerobic decomposition however, creates problem and thus, waste water before being released into the pond should be treated to remove the solid materials which may settle down and aeration should be provided throughout the pond by mechanical stirring. Secondly, in winters when photosynthesis gets retarded, oxygen supply is reduced creating an anaerobic condition and causes same problem with odours.

Water treatment in oxidation pond is cheap and the maintenance is simple. However, it requires larger space and causes odour problems.

Check Your Progress

15. What are the characteristics of ground water?
16. What is the purpose of primary treatment of water?
17. What is an oxidation pond?

2.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Fresh water accounts for only 2.5 percent of the total, whereas saltwater accounts for 97.5 percent.
2. Photosynthesis allows aquatic plants (algae) to release O_2 (oxygen) into the water. This oxygen is known as dissolved oxygen because it dissolves in water (DO).
3. Calcium, sodium, magnesium, potassium, chloride, sulphate, hydrogen carbonate, and carbonate are macro components that make up 90–95 percent of all components in fresh water. Lithium, rubidium, caesium, bromide, iodide, fluoride, copper, zinc, nickel, silver, lead, and other heavy metals are among the micro components with concentrations up to 1ppm.
4. The components of hydrologic cycle are: Evaporation, Transpiration, Cloud formation, Condensation, Precipitation, and Runoff.
5. The following are the signs of water pollution:
   a. Bad taste and offensive odour
   b. Unchecked growth of aquatic weeds
   c. Decreased number of fish
6. The commonly found inorganic contaminants of water include arsenic, fluoride, iron, nitrate, heavy metals, etc. and their presence at more than permissible levels degrades water potability for living organisms.
7. The infectious diseases associated with water can be classified into four groups according to the mechanism of transmission. Waterborne diseases; Water-wastes diseases; Water based diseases; and Water-related diseases.
8. The five parameters that are essential for aquatic life are: Dissolved Oxygen, Temperature, Electrical Conductivity/Salinity, pH, and Turbidity.
9. The most extensively utilized method to analyze DO is the diaphragm electrode method.
10. American Society of Testing and Materials (ASTM), defines COD as the amount of oxygen (mg/l), required to oxidize the organic and oxidizable inorganic matter, under specified conditions, corrected for the influence of chlorides.
11. The source for acid rain is anthropogenic emission of SO_2, NO_2 and Cl_2.

12. The inorganic techniques that are used to measure trace elements in waste water are: Flame Atomic Absorption Spectrometry (FAAS); Graphite Furnace (or Electrothermal) Atomic Absorption Spectrometry (GFAAS or ETAAS); Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES); and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
13. The difference between the amount of chlorine applied to water or wastewater and the amount of residual chlorine left after a specific contact time is known as chlorine demand.
14. Water which cannot form lather easily with soap is known as hard water and this characteristic is called hardness. On the other hand, water which forms lather with soap is called soft water.
15. The characteristics of ground water are:
    a. Little suspended materials
    b. Less chances of contamination
    c. Less hardness
    d. Chances of greater concentration of objectionable dissolved gases
16. The purpose of primary treatment is to remove pollutants like large, floating and suspended solid materials, grit, oil and grease, etc.
17. An oxidation pond is a large, shallow pond (0.5 to 1.5 m depth), where the waste water, mainly the sewage water, is treated through its decomposition by microorganisms. The waste water enters the pond at one end and the treated water is removed at the opposite end.

2.7 SUMMARY

- The hydrosphere (from Greek *hydōr*, ‘water’, and *sphaira*, ‘sphere’) is the aggregate mass of water found on, under, and above the surface of a planet, minor planet, or natural satellite.
- The composition of water bodies is complicated, containing a variety of gases, minerals, and organic molecules.
- The presence of dissolved gases in water bodies is due to the fact that the atmosphere and water bodies are in touch with each other, and gases are exchanged between the surface of the water body and the atmosphere.
- Many chemical compounds are water soluble. Minerals and rocks in contact with water are the main sources of solutes. Metal ions (M^{n+}) in water come in a variety of shapes and sizes.
- Lakes are inland depressions containing standing water. They vary in size and depth (few feet to 5000 feet). Some lakes wave outlet streams. In lake there are three to five well recognized horizontal strata
- During the summer the top water of lakes become warmer than the bottom waters, as a result only the warm top layer circulates and it does not mix with the more viscous colder water, called thermocline.

- A river may flow into the ground and become dry at the end of its course before reaching another source of water in some instances. Streams, creeks, brooks, rivulets, and rills are all terms used to describe small rivers.
- The rivers are dominated with the presence of calcium, silica, and hydrogen carbonate, which are mostly derived from silicate rocks and carbonates. Potassium levels are low due to clays' retention.
- Wetlands get their name from the fact that they are wetlands. They are areas of land that are regularly saturated by water. This comprises marshes, bogs, estuaries, and small ponds, as well as swamps and swampy parts of prairies and woods.
- The water pollution can be defined as the deterioration of physical, chemical and biological characteristics of water through natural as well as anthropogenic activities, to such an extent that it has become harmful for all living organisms including man.
- Organic pollution is a type of chemical pollution caused by carbon pollutants, such as organic matter (liquid manure, sewage treatment sludge, etc.), Organochlorides (DDT) or even Polychlorinated Biphenyls (PCB).
- The pathogenic micro-organisms enter water mainly from domestic sewage and other wastes.
- The nutrients can become a pollutant when their enrichment allows thick growth or blooms of aquatic weeds, especially algae that cover up water. This prevents the entry of sunlight into water bodies.
- The measure of salinity of water is usually the measure of concentration of total dissolved solids (TDS).
- In thermal power plants, nuclear power plant, etc., where water from the nearby river or lakes is used as a coolant, the waste hot water is returned to the original water body and on an average the temperature is raised by 10°C.
- Chemicals which prevent, destroy or mitigate any pest (insects, fungus, bacteria, viruses, etc.) are called pesticides.
- Non-biodegradable pests accumulating in the food chain and biodegradable pests leaving behind more toxic side products, have produced health hazards with concentration exceeding the safe tolerance level.
- We can define eutrophication as excessive nutrient load in a water body or enrichment of water body by nutrients.
- Heavy metals, which are harmful or deadly even at low concentrations, make up the majority of inorganic pollutants. Arsenic, mercury, lead, and chromium are examples of heavy metals.
- Heavy metals are referred to as metals with specific gravity greater than about 4 to 5. The most important heavy metal pollutants are mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As).
- Cadmium occurs in nature in association with zinc minerals. Plants take up zinc (Zn^{2+}) and along with trace amounts of associated Cd (Cd^{2+}) are also acquired.

- Pb or lead exerts its activity through sulphydryl inhibition. Pb has affinity for sulphur and it also reacts with carbonyl and phosphoryl groups.
- The main sources of arsenic pollution are agricultural chemicals. Arsenic can exist in two forms—trivalent and pentavalent.
- The five parameters that are essential for aquatic life are: Dissolved Oxygen, Temperature, Electrical Conductivity/Salinity, pH, and Turbidity. Impacts on the flora and fauna of a certain water body can be seen as a result of these impairments.
- Amount of dissolved oxygen (DO) present in the water body is one of the important measures of water quality. The DO depends on the physical, chemical and biological activity of the water body.
- In a simplified model, the two most important parameters considered to assess DO are: Deoxygenation and re-aeration.
- The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called biochemical or biological oxygen demand. It is expressed in milligrams of oxygen required per litre of waste water (mg/l).
- A BOD test can take several weeks for completion, making it impractical for routine purposes. As a result, five day BOD test is introduced, realizing that the ultimate demand is quite high.
- In a COD test, a strong oxidizing agent, such as dichromate is used to oxidize the waste, it is not left to the microorganism to oxidize the matter.
- Aquatic organisms are pH sensitive. Very few aquatic organisms are able to survive below pH 5.0.
- Colorimetric methods are used to measure fluorides. If interfering chemicals are present, fluorides are separated by distillation. Fluorides are measured using a process that requires the fluoride ion bleaching a performed colour.
- Analysis of oil in water is a global problem that affects a wide range of sectors, analytical methodologies, and regulatory authorities. The amount of oil allowed in water is strictly regulated due to the detrimental effects of oil on the ecosystem.
- The detection of trace and heavy metal contamination in wastewater is a critical step in protecting human and environmental health.
- Measuring the chlorine residual in a water supply is a simple but crucial way to ensure that the water delivered is safe to consume.
- Water which cannot form lather easily with soap is known as hard water and this characteristic is called hardness. On the other hand, water which forms lather with soap is called soft water.
- The waste water collected from various sources should be treated so as to remove contaminants in order to be released again into their origin. The treatment must remove pathogens, BOD materials, excessive nutrients and toxic chemicals.
- Surface water has turbidity, large floating and suspended materials, lot of harmful pathogens and metal ions causing hardness of water.

- Waste water contains a lot of chemical pollutants as well as dissolved solids and suspended solids. The major contributor of pollutants is industrial waste water.
- The purpose of primary treatment is to remove pollutants like large, floating and suspended solid materials, grit, oil and grease, etc.
- The purpose of the secondary treatment is to remove the finely suspended solid, dissolved solid and BOD which still remain after the primary treatment.
- In the activated sludge process, the BOD and suspended and dissolved solids are removed to a greater extend from the waste water and then that water is released to be used as a good water source.
- The main purpose of the tertiary treatment is to remove dissolved nutrients, especially nitrogen and phosphorus which have survived the primary and secondary treatment.
- Water treatment in oxidation pond is cheap and the maintenance is simple. However, it requires larger space and causes odour problems.

2.8 KEY TERMS

- **Complexation:** It is the combination of individual atom groups, ions or molecules to create one large ion or molecule. One atom or ion is the focal point of the complex.
- **Cation:** A cation has more protons than electrons, consequently giving it a net positive charge. For a cation to form, one or more electrons must be lost, typically pulled away by atoms with a stronger affinity for them.

2.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. What is the chemical composition of wetlands?
2. How are pesticides harmful to the aquatic envuironment?
3. How can eutrophication be controlled?
4. Write a short note on the effect of Oxygen Effect of Oxygen demanding wastes on rivers.
5. Briefly explain the processes that happen in secondary treatment of water. Demanding Wastes on Rivers

Long Answer Questions

1. Explain the chemical composition of water bodies with special emphasis on lakes.
2. Discuss the effects of heavy metals as pollutants.

3. Explain the concept of BOD and methods to analyze it.
4. Describe the analytical methods of measuring oils in water.
5. Discuss the process of making surface water potable.

2.10 FURTHER READING

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UNIT 3 SOILS

NOTES

Structure

3.0 INTRODUCTION

Soil is a biologically active, porous substance that has formed in the Earth's crust's uppermost layer. Soil is one of the most important substrata for life on Earth, acting as a reservoir of water and nutrients, a filtering and breakdown medium for harmful wastes, and a participant in carbon and other element cycling across the global ecosystem. It has evolved through weathering processes driven by biological, climatic, geologic, and topographic influences. In this unit, we will discuss the characteristics of soil, along with its composition including the micro and macro nutrients. It will also focus on the different types of soil pollutants and waste treatment for controlling the same.

3.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe the composition of soil including the micro and macro nutrients
- Explain the different types of soil pollutants
- Discuss the waste treatment for controlling soil pollution

3.2 SOILS: MEANING AND CHARACTERISTICS

NOTES

Soil is the upper most part of the earth's crust and is a mixture of both organic and inorganic materials. The term soil has been derived from Latin word 'Solumn', meaning earthy material necessary for the growth of plants. Soil is the storehouse of minerals, a reservoir of vegetable crops and the home of wild life and livestock. The science that deals with the study of soil is known as pedology (*pedos* means earth) or edaphology (meaning soil).

3.2.1 Formation of Soil (Pedogenesis)

The process involving the origin, development and formation of soil is known as pedogenesis. For millions of years there was continuous breaking of rocks into small particles due to heat, rain and wind. These small particles were carried away by wind and water and ultimately got deposited over other rocks. In this way, thick layer of clay, sand and small pieces of rocks are formed. This is known as soil.

The process of soil formation is known as weathering. Weathering is the process of disintegration of parent rocks into smaller particles (regolith). The weathering basis of agents can be classified as

(*a*) **Physical weathering:** The physical agents responsible for such weathering are temperature, wind, water, ice, gravity, etc. Temperature fluctuation leads to simultaneous expansion and contraction or vice versa and the enormous stress thus, generated leads to fragmentation of big rocks to smaller ones. The freezing of water inside the rock crevices generates pressure due to volume expansion and causes the rock to disintegrate. Fast-flowing rivers or streams exert enough external pressure on the parent rocks to disintegrate. High wind carrying small pieces of rocks lead to collision with big rocks forming smaller rocks. Earthquake can cause rock slippage from higher altitude to the plains, disintegrating rocks to smaller parts. Glaciers moving at a high speed from a high altitude cause rocks to break down into smaller pieces.

(*b*) **Chemical weathering:** When different chemical processes are involved in weathering it is known as chemical weathering. The important chemical weathering agents are moisture, water and air. The chemical weathering is temperature sensitive and rate of this weathering is enhanced with the increase in temperature. The physical weathering form smaller pieces of large number of rocks and thus, large surface area of rocks is now exposed and the rate of chemical weathering is enhanced. The chemical processes involved in chemical weathering are:

(1) Hydration
(2) Hydrolysis
(3) Oxidation
(4) Reduction
(5) Carbonation

Water soluble minerals are leached through hydration and hydrolysis by water. Some minerals are converted to oxides by oxygen and to carbonates or bicarbonates by carbonic acid formed through the reaction of water with dissolved carbon dioxide ($H_2O + CO_2 = H_2CO_3$). The oxides or carbonate or bicarbonates are either dissolved in water or washed away from the surface. These lead to further penetration of water molecule inside the rock matrix and the rock becomes more unstable.

(*c*) **Biological weathering:** Various types of microorganisms extract minerals from rocks as their energy source. This ultimately leads to change in the physical structures and mineral composition of the rocks. As a result these rocks become weak and break down into a number of pieces. This is known as weathering and since it is caused by biological means it is also known as biological weathering.

3.2.2 Soil Classification

The systematic categorization of soils based on differentiating properties as well as criteria that determine usage choices is known as soil classification. Following are the ways on the basis of which soil is classified.

(*i*) Classification based on the size of the particles:

Soil	*Particle size(diameter in mm)*
Stone and gravel	> 5
Coarse sand	0.2 – 2.0
Fine sand	0.02 – 0.20
Silt	0.002 – 0.02
Clay	< 0.002

(*ii*) Classification based on the texture:

(*a*) Sandy soil (mainly SiO_2)
(*b*) Clay sand (mainly clay and SiO_2)
(*c*) Loam soil (SiO_2 50 per cent, silt and clay 50 per cent)
(*d*) Sandy loam soil (SiO_2 and silt)
(*e*) Silt loam soil (mainly silt)
(*f*) Clay loam soil (mainly clay)

(*iii*) Classification based on the water holding capacity, air retention penetration and nutrient availability: The three different types of soil thus are:

- **Sand:** The particle size ranges from 0.02 mm to 2 mm in diameter and thus can be seen with naked eye. Due to large particle size, air can easily penetrate, however, water holding capacity is negligible, moreover, there is no nutrient for the plants to grow and survive. Hence, it is not fertile soil.
- **Silt:** The particle size ranges from 0.002 to 0.02 mm, intermediate between fine sand and clay. It contains sufficient amount of nutrients, water holding capacity is good and as well as air retention capacity, therefore, air can easily penetrate. So it is a very fertile soil.

- **Clay:** The particle size is in the colloidal dimension (10 – 1000Å). It has a high water holding capacity and has sufficient amount of nutrients. However, air retention capacity is less and it cannot penetrate easily. It is a fertile soil and could have been more fertile if it had the air retention or penetration capacity.

3.2.3 Soil Profile

The vertical section of matured soil is called soil profile. Soil profile consists of several layers called horizons lying one over the other. All the distinct layers have specific physical and chemical properties. These layers or horizons from top to bottom constitute soil profile. Each horizon has a specific thickness, colour, texture, structure, acidity, porosity and composition. The five horizons of soil profiles from top to bottom are named as follows: *O*-horizon, *A*-horizon, *B*-horizon, *C*-horizon and *R*-horizon. *A* and *B* horizons constitute the majority of the soil composition.

(*i*) *O*-Horizon: It is the surface layer of the soil and is also called topsoil. It contains inorganic materials mixed with organic materials in semi-decomposed and composed state. It can be sub-divided into O_1 and O_2 zones.

- **O_1 zones:** The uppermost part of surface layer, rich in freshly fallen leaves (litter) and twigs, the decomposition of which is yet to start.
- **O_2 zones:** This layer lies below O_1 zones. The upper portion of O_2 zones contains partially decomposed organic matter known as 'Detritus'. The lower portion of O_2 zones have completely decomposed organic matter known as 'Humus'.

(*ii*) *A*-Horizon: In this region, the materials of layer *O* come in contact with water and its downward movement takes place. It is divided into three sub-zones, A_1, A_2 and A_3 depending on physical, chemical and biological characteristics:

- **A_1 Layer:** In this layer, there is enough humus mixed with minerals. It is dark in colour and has soil bacteria and fungi.
- **A_2 Layer:** In this layer, the amount of humus is less compared to A_1 layer. It is a light coloured layer and is a zone of maximum leaching.
- **A_3 Layer:** It is a transitional layer, merging with horizon *B*.

(*iii*) *B*-Horizon: Materials leached out from *A*-Zone are precipitated in this zone. In this zone, the soil bacteria convert organic compounds to inorganic compounds and inorganic ions to the right kind of ions, which can be absorbed by plants. This zone is sub-divided into three zones B_1, B_2 and B_3 depending on the physical, chemical and biological characteristics:

- **B_1 Layer:** It is a transitional layer, merging with A_3 and is more like *B* than *A*.
- **B_2 Layer:** It is a deep coloured layer of maximum accumulation of clay minerals, as well as iron and organic matter.
- **B_3 Layer:** It is a transitional layer merging with layer *C* lying beneath it.

A-zone and *B*-zone together, form the true soil. Many kinds of insects, earthworms are found in the true soil and make the soil reach.

(*iv*) *C*–Horizon: It is a light coloured layer, composed of partially weathered material (various kinds of rocks) and negligible quantity of organic material.

(*v*) *R*–Horizon: This is the zone of unweathered rock bed called consolidated rock bed.

3.2.4 Soil Composition: Micro and Macro Nutrients

Soil comprises of a mixture of inorganic and organic matter with water and air in invariable proportions. The approximate weight percent composition is generally:

- Inorganic Matter – 45 per cent
- Organic Matter – 5 per cent
- Soil Water – 30 per cent
- Soil Air – 20 per cent

Inorganic Matter

Soil is a complex mixture of various inorganic compounds. The main elements are silicon, aluminum, magnesium, calcium, potassium, sodium and iron. Traces of elements like boron, manganese, copper, iodine are also present in the soil. The approximate weight percent composition of the elements is:

Oxygen – 46.6 per cent	Calcium – 3.6 per cent
Silicon – 27.7 per cent	Sodium – 2.8 per cent
Aluminium – 8.1 per cent	Potassium – 2.6 per cent
Iron – 5.0 per cent	Magnesium – 2.17 per cent

The compounds on the basis of anions are:

- Silicates of Na, K, Ca, Al and Fe, the soil is essentially silicate mineral. Approximately, 75 per cent of the inorganic materials are silicates. Finely divided SiO_2 (Quartz) is commonly found in soil.
- The most commonly available silicates in soil are orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$) and epidote ($4CaO_3$ $(AlFe)_2O_3$. $6SiO_2$. H_2O).
- Oxides of Fe, Mn such as magnetite Fe_3O_4, sulphates, chlorides and nitrates.
- Carbonates, sulphates, chlorides, nitrates of Ca, Mg, Na and K, etc. like $CaCO_3$, $MgCO_3$, $CaSO_4$, $CaCl_2$, $Ca(NO_3)_2$.

Clay is essentially a mixture of hydrated aluminum and iron silicates which bind cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+. Due to such binding, the cations are not leached easily and remain for a longer duration and are available as plant nutrient.

Organic Matter

The soil productivity is determined primarily by organic matter and usually it constitutes less than 5 per cent of the soil. The organic matter consists of biologically active compounds like polysaccharides, nucleotides, organophosphate, organosulphur compounds and humus. Partially decomposed organic matter in a soil is referred to as 'humus'. After the death of organisms, different substances like carbohydrate, proteins, fats, etc., are released into the environment and the rest is called 'humus'. There are billions of macro and microorganisms such as virus, bacteria, fungi (non-green plants), protozoa (amoeba, euglena, paramecium, entamoeba), etc., which live in the soil. The dead bodies and various parts of plants and animals (all considered as wastes) are decomposed by some of the above mentioned microorganisms known as decomposers and these living organisms that grow on dead or decaying organisms are known as 'saprotrophes'. These saprotrophes break down the complex organic matter, releasing minerals that get mixed up with soil and contribute to soil fertility. Some soil fungi yield citric acid and many other chelating organic acids which react with silicate minerals and liberate Na^+, K^+ or Ca^{2+} from the silicate matrix.

Soil Water

In soil, water is not only important as a solvent and a transporting agent, but it also maintains the soil texture, arrangement of soil particles and makes soil suitable for all living organisms.

Water in soil mainly comes through infiltration of precipitated water (dew, rain, snow, hail) and irrigation. Soil water exists both in combined and uncombined state. Chemically combined water is the water of crystallization of mineral grains and water of hydration of clay mineral particles. Uncombined water is not chemically bound to soil particles and is held in soil by adhesion (adhere to soil particles through short range interaction) and cohesion (attraction between the water molecules). Adhesion or cohesion occurs in four different forms:

(*a*) **Gravitational water:** The accumulated excess water in large soil spaces, through displacement of air in course of downwardly movement of water under the gravitational influence, is known as gravitational water. When gravitational water further percolates and reaches the level of parent rock, it is called ground water.

(*b*) **Capillary water:** Water which is held by capillary forces such as surface tension and cohesive forces of water molecules, which work when the gravitational and ground water is drained, is called capillary water.

(*c*) **Hygroscopic water:** Water molecules held tightly on the surface of soil particles is called hygroscopic water.

(*d*) **Water vapour:** Water present in the form of vapours or moisture in soil is known as water vapour.

The total waste in the soil is also called holard. The water that can be absorbed by plants from holard is called chresard and that cannot be absorbed is called echard. Thus,

$$\text{Holard} = \text{Chresard} + \text{Echard}$$

Soil air

The air present in the spaces between soil particles is called soil air. The composition is usually O_2, N_2, CO_2 and H_2O (vapour). The soil air provides aeration of the soil, which in turn helps in absorption of water by plant roots. Soil air is also very important for oxidation of organic material in the soil, the absence of which leads to anaerobic activity.

NOTES

Soil organism

There are billions of organisms present in soil. Some of these organisms contribute to soil fertility acting as decomposers of complex organic compounds into simple inorganic substances. The organisms can be classified according to their size and characteristics as following:

1. **Micro fauna:** Size of microorganism (20m – 200m). For example, protozoa, nematodes, etc.
2. **Meso fauna:** Size of organism (200μ – 1cm). For example, spiders, insect larvae, etc.
3. **Micro fauna:** Size of the organism is more than 4 cm. For example, earthworm, centipedes, millipedes, etc.
4. **Micro flora:** They are soil bacteria, soil algae and fungi, etc. They are the decomposers which breakdown complex organic molecules to simpler inorganic substances.

Micro and macro nutrients

Carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), sulphur (S), calcium (Ca), magnesium (Mg), boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) are the 17 key elements required for plant growth (Zn). These 17 important elements, often known as nutrients, are usually divided into three categories. Carbon (C), hydrogen (H), and oxygen (O) are the three macronutrients that plants can receive from water, air, or both (O). Because these nutrients are not required by the soil, they are not sold as fertilizers. The remaining 14 necessary elements are divided into two categories: macronutrients derived from soil and micronutrients derived from soil. This division is based on the actual nutrient amount required for proper plant growth.

The soil-derived macronutrients are nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg). The soil-derived micronutrients are boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn). The six soil-derived macronutrients are present in plants at relatively high concentrations—normally exceeding 0.1 percent of a plant's total dry weight.

Check Your Progress

1. From where the term soil has been derived?
2. What is the classification of soil based on the size of the particles?
3. What are the soil-derived macronutrients?

3.3 SOIL POLLUTION AND ITS SOURCES

Soil pollution differs from water pollution on air pollution, because the pollutants remain in direct contact with the soil for relatively longer periods and hence alter the chemical and biological properties of the soil. The hazardous chemical can also enter the human food chain from soil or water plants. The major sources of metallic contamination of soils include mining, smelting, sludge, fertilizers, pesticides, composted town refuse, etc. Metals such as Cd, Pb, Hg, Ni, Mo, Ni, Cr, etc. are toxic to plant and animal life. Indiscriminate dumping of industrial wastes and municipal wastes leads to the leaching and/or seepage of toxic substances into the soil and pollution of ground water. Further due to some modern agricultural practices, obnoxious pesticides, fungicides, insecticides, biocides, bacteriocides, etc. contaminate land. Direct pollution of soil by dangerous pathogenic organisms is also important.

Fly ash generated from thermal power plants, industrial waste discharged into streams of dumped into the surrounding land, mining wastes, non-biodegradable organic pollutants, industrial sludge such as flue gas desulphurization sludge, heavy metal sludges, etc. cause serious water and soil pollution problems. Commercial and domestic urban wastes consisting of dried sewage sludge as well as garbage and rubbish materials such as plastics metal cans, glasses, street sweepings, waste paper, fibres, rubber, etc. contribute to soil pollution. Human and animal excreta, farm wastes, soil conditioners, soil fumigants, radioactive wastes, etc. also cause soil pollution.

Effects of soil pollutants

Soil Pollution was originally defined as the contamination of the soil system by considerable quantities of chemical or other substances, resulting in the reduction of its fertility or productivity with respect to the qualitative and quantitative yield of the crops. However, if some of the contaminants are such that if they are taken up by the plants (with or without any detrimental effects on them), and enter into the food chain and impart detrimental or toxic effect on the consumers, then that also should be treated as soil pollution. Soil pollution is receiving greater and greater attention due to its direct impact on public health. The major effect of various types of pollutants are given in the following sections.

3.3.1 Synthetic Fertilizers

Synthetic fertilizers are employed to increase the soil fertility and crop productivity. These fertilizers concentrate the essential nutrients in layer of top soil. However, the soil enriched by chemical fertilizers cannot support the microbial flora which are so essential to enrich the humus that helps in plant growth. Excessive and indiscriminate use of chemical fertilizers may result in the following undesirable effects:

- Wheat, maize, corn, etc. grown on soils fertilized with NPK fertilizers may result in considerable reduction in protein content of the crops.
- Excessive use of nitrogenous fertilizers leads to the accumulation of nitrates in the soil which may contaminate the ground water. Nitrate concentrations exceeding 90 ppm in drinking water may lead to diarrhoea, blue Jaundice

(Cyanosis) in children, 'methemoglobinemia' (or blue baby syndrome) in infants. Further, the nitrates and nitrites entering the human body may be eventually converted nitroso amines and other nitroso-compounds which are suspected nitroso amines and other nitroso-compounds which are suspected to cause stomach cancer. Surveys in Rajasthan and other parts of the country indicated much higher nitrates levels than the permissible 45 ppm levels.

- Vegetation growth in nitrate-rich soils may exert toxic effects in cattle.
- Excessive use of chemical fertilizers may enter the water bodies and contribute to eutrophication (the excessive growth of algae and aquatic plants to undesirable levels).
- Excessive use of chemical fertilizers may reduce the ability of plants to fix nitrogen.
- Excessive quantities of potassium fertilizers in soils may reduce the quantities of valuable ascorbic acid (vitamin C) and carotene in fruits and vegetables grown in such soils.
- The large-sized fruits and vegetables grown in highly fertilized soils may be more vulnerable to attacks by pests and insects.

3.3.2 Pesticides

As per the reports of the World Health Organization (WHO), about 50,000 people in developing countries are poisoned and about 5,000 people die because of improper use of pesticides and other chemicals in modern agricultural practices. Pesticides pose potential hazard to animals, humans and aquatic life. They also cause deleterious effect on soil fertility and crop productivity. Pesticides applied to crops are retained in the soil in considerable quantities. They enter into cyclic environmental processes such as absorption by soil, leaching by water, etc. and contaminate both lithosphere and biosphere. Pesticides including herbicides, fungicides and rodenticides, are persistent pollutants. Owing to interactions between lithosphere and biosphere, pesticides may enter the food chain and pose serious health hazards.

Some of them undergo metabolic transformation and bio-degradation. The degradation products of some of the pesticides are more dangerous than their respective parent compounds. Some of the pesticides residues are carcinogenic while their metabolic products too are toxic. The rate of degradation of pesticides depend upon their properties and structural characteristics. The following types of pesticides are commonly used:

- Chlorinated hydrocarbons (eg. DDT, Aldrin, Dieldrin, Lindane, BHC etc.)
- Carbamate compounds (eg. Carboryl or Sevin, Zectrion etc.)
- Organo-Phosphorous compounds (eg. Methyl or ethyl parathion, melathion, guthion etc.)
- Inorganic compounds (eg. As_2O_3, PbO_2, $NiCl_2$, $CuSO_4$ etc.)
- Miscellaneous compounds (eg, Organic mercurials, 2, 4D; 2, 4, 5T etc.)

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Some of the adverse effects of pesticides are given below:

- Some arsenic pesticides may render the soil permanently infertilile.
- Pesticide residues in soil may be taken up by plants and cause phyto-toxicity. They may enter the aquatic environment and enter the food chain.
- Pesticides such as, endrin, dieldrin, DDT, hepachlor etc. may seep through the soil and contaminate groundwater and surface waters. They may eventually contaminate drinking water supplies.
- Fruit, vegetables, rice, wheat, barley, maize etc. are known to contain considerable quantities of toxic pesticide residue such as of DDT, BHC and other organochloro pesticides.
- Polychlorinated biphenyls (PCB) having half-life periods of about 25 years in soil are among the most hazardous soil pollutants. They may accumulate in soil and plants and when they eventually enter the animal or human body, they may severe health disorders, including eye damage, skin problems, nervous disorders, foetus deformities and liver or stomach cancer.
- Irrigated water from pesticide contaminated soils may evaporate and spread the toxic pesticide vapours in the atmosphere.
- DDT can enter the food chain and accumulate in human fats and may lead to disorders such as impotency.
- Persistent pesticides can damage human tissues and interfere with the normal metabolic activities by disturbing enzymatic functioning.
- Chlorinated pesticides and herbicides are hazardous soil pollutants which can affect the soil texture and damage the ecosystem.
- Herbicides such as dioxan may cause congential birth defects in offsprings.
- Hunting birds feeding on grains contaminated with DDT are threatened of extinction.
- Organophosphate pesticides may cause muscular disabilities, tremors and dizziness.
- Excessive use of synthetic pesticides may lead to defoliation of forests and adverse effect on fauna and flora.
- Farm animals drinking stagnant water in fields sprayed by pesticide developed toxic symptoms and some mortalities were reported.
- Farmers and farm workers are particularly prone to pesticide poisoning because of greater exposure while handling and spraying.
- Accidental spillages and leakages in pesticide manufacturing industries cause disastrous effects on the people residing in nearby areas due to pollution of air, water and soil. The Bhopal tragedy on 3rd December, 1994 is a lingering example.

- Contaminated soils may act as potential carriers of pathogenic bacteria and other dangerous organisms which may endanger human health.
- Volatile pesticides may cause pollution of air in the surrounding area.

3.3.3 Industrial Effluents: Plastics and Metals

Solid, liquid and gaseous chemicals from various industries such paper and pulp, iron and steel, fertilizers, dyes, automobiles, pesticides, tanneries, coal-based thermal power plants etc. contain a variety of pollutants such as toxic heavy metals, solvents, detergents, plastics, suspended particulates, and refractory/non-biodegradable/recalcitrant chemicals. If they are not properly treated at source, they give rise to water-, air- and soil pollution. Fly ash resulting from coal-based thermal power plants is one of the alarming and continuously increasing source of soil-pollution leading to degradation of soil, apart from water- and air-pollution in the nearby areas. Some trade wastes such as tannery wastes may contain pathogenic bacteria. Indiscriminate dumping of untreated or inadequately treated domestic, mining and industrial wastes on land is an important source of soil pollution. Fall-out of gaseous and particulate air-pollutants from mining and smelting operations, smoke-stacks, etc. is a major source of soil pollution in nearby areas.

3.3.4 Urban Wastes

Millions of tonnes of urban waste are produced every year from critically polluted cities. The inadequately treated or untreated sewage sludge not only pose serious health hazards but also pollute soil and decrease its fertility and productivity. Other waste materials such as rubbish, used plastic bags, garbage, sludge, dead animals, waste medicines, hospital wastes, skins, tyres, shoes, cans, etc. also cause land and soil pollution. Some solid wastes may cause clogging of ground water filters. Suspended matter present in sewage can act as a blanket on the soil and interfere with its productivity. Apart from the above major sources, radioactive waste dumped in the soil from natural and man-made sources, soil erosion due to deforestation, unplanned irrigation and unscientific agricultural practices also result in land and soil pollution.

3.3.5 Control of Soil Pollution

As discussed in earlier sections, the major sources of soil pollution are the domestic wastes, industrial wastes, and agricultural wastes including those toxic chemicals (eg. Pesticides) arising from modern agricultural practices. The various approaches to control soil pollution are as follows:

- Implementing stringent and pro-active population control programmes.
- Launching extensive afforestation and community forestry programmes.
- Implementing deterrent measures against deforestation.
- Formulation of stringent pollution control legislation and effective implementation with powerful administrative machinery.
- Imparting informal and formal public awareness programmes to educate people at large regarding the health hazards and undesirable effects due to

environmental pollution. Mass media, educational institutions and voluntary agencies should be involved to achieve these objectives.

- Banning the use of highly toxic and resistant synthetic chemical pesticides or atleast regulating/restricting their use only for special purposes under thorough monitoring.
- Encouraging the use of bio-pesticides in place of toxic chemical pesticides.
- Conservation of soil to prevent the loss of precious top soil from erosion and to maintain it in a fertile state for agricultural purposes.
- Transforming intensive agriculture into a sustainable system by measures such as:
    - o Maintaining a healthy soil community in order to regenerate soil fertility by providing organic manures, increasing fellow periods, avoiding excessive use of chemical fertilizers and pesticides.
    - o Infusing bio-diversity in agriculture by sowing mixed crops, crops rotation, etc.
- Effective treatment of domestic sewage by suitable biological and chemical methods and adopting modern methods of sludge disposal.
- Municipal wastes have to be properly collected by segregation, treated and disposed scientifically in landfills. Recycling and reuse of materials should be done wherever possible, such as recycling of glass, plastics, paper and production of bio-gas.
- Industrial wastes have to be properly treated at source, by segregation of wastes and/or adopting integrated waste treatment methods. Proper care should be taken in treating heavy metal wastes and other obnoxious waste materials.
- Security land-fills have to be constructed for permanent disposal of hazardous and recalcitrant industrial wastes.
- Sponsoring more intensive R & D efforts on bio-fertilizers, bio-pesticides, utilization of wastes by recovery, reuse and recycling processes, and safer treatment and disposal of hazardous waste.
- Enforcing environmental audit for industries and promoting eco-labelled products.
- Avoiding excessive use of chemical fertilizers and insecticides and providing more organic manures to the fields and thereby maintaining healthy biota. This in turn regenerates soil fertility. A soil rich in organic matter also helps in controlling soil erosion.

Check Your Progress

4. What are the major sources of metallic contamination of soils?
5. Mention any three types of pesticides that are commonly used.

3.4 WASTE TREATMENT

The quantity of solid wastes generation in big cities of India is almost 400-600 gm per person and is increasing day by day at an enhanced rate. Again, due to high illiteracy, indiscipline and carelessness in our basic character, we prefer to throw the waste in the street rather than collection and proper disposal. We never think about the consequences of such things at all. These wastes, either alone or under prevalent conditions, can combine with other secondary wastes creating high degree of health hazardous problem. As far as municipal solid waste is concerned, the vegetables, leaves and fish remnants are the major constituents.

The biological decomposition of vegetable wastes, fish remnants and the dead animals release hydrogen sulphide (H_2S) and many other organic-sulphur gases, creating objectionable odour. The garbage is an ideal place for flies, mosquitoes, insects, rats and other rodents to live in. They live, grow and reproduce in garbage. Mosquitoes bring diseases like malaria, filaria and enchephalities. The flies carry contaminated food from the garbage and finally to human beings, causing dysentery, diarrhea, etc. Rats cause plague, leptospirosis, tularemia, trichinosis, and many more diseases. The open burning or fire generation due to organic decomposition may lead fire to continue for a longer period and may cause high degree of water and air pollution due to the release of leachable toxic materials into water, exerting oxygen demand and other pathogen along with noxius gases, creating health hazard problem. Again the workers handling the garbage are directly affected with roundworm and whip-worm.

Generally, hazardous waste can be defined as: 'The wastes or combination of wastes which pose substantial threat to human health and environment.' United States Environmental Protection Agency (USEPA), treats 'hazardous wastes' separately from other classes of wastes. They define hazardous waste as: 'A waste or combination of wastes, which because of the quantity, concentration or physical, chemical or infectious characteristics may cause or significantly contribute to increase in mortality or is a potential hazard to human health or the environment when improperly treated, stored, transported or disposed of or otherwise managed.'

A waste will be called hazardous waste if it possesses any of the four following characteristics:

- **Reactivity:** Due to instability, the waste reacts vigorously with air or water, generates toxic gases, is unstable to shock or heat and thus explodes. For example, gun powder, nitroglycerine, sodium and potassium, metal, etc.
- **Ignitability:** Catches fire easily, *i.e.*, burns at relatively low temperature (< 60°C). For example: ether, acetone, gasoline, methanol, etc.
- **Corrosivity:** It destroys materials and living tissues by chemical reaction. These chemicals are generally liquids with $pH < 2$ and $pH > 12.5$, for example: H2SO4, HNO3, NaOH, battery acid and any product containing strong acid or base.

- **Toxicity:** Substances are poisonous even in very small amounts. They are harmful when ingested or absorbed. For example: benzene (petroleum based products), cadmium and lead (batteries), chromium, mercury (mercury batteries), rat poison, etc. Toxicity can be acute toxicity (immediate effect), causing death or violent illness or chronic toxicity (long exposure to small dose). Certain toxic wastes are known to be carcinogenic (causing cancer) and other may be mutagenic, causing biological changes in the children of exposed persons or animals.

3.4.1 Classification of Hazardous Wastes and their Effects

The hazardous waste thus includes: (*i*) Radioactive wastes, (*ii*) Bio-medical wastes (*iii*) Chemical wastes.

Radioactive wastes

Radioactive elements decay to produce alpha (a), beta (b) and gamma (g) rays and pose threat to human health. The sources of radioactive materials include:

- Mining and processing units generating radio isotope
- Refinery and full fabrication units
- Discharge from nuclear reactions
- Radio isotope used in industry, agriculture, medicine and research work

Fortunately, most of the radionuclides which emit radiations do not persist for a long time in our environment. However, Sr–90 and I–137 are slow decaying and produce hazardous effects on human life. Radiation has deleterious effects on living cells. These effects are classified as 'somatic' and 'genetic':

- **Somatic effect:** It is the damage to organism itself. The effect may appear in a short period of time if massive dose is taken. For smaller dose, it takes time and the effect may manifest in malignancies such as leukemia or cancer.
- **Genetic effect:** In this case, organism unexposed to radiation can get affected. The radiation might cause gene mutations and chromosome aberrations, as well as changes in number of chromosomes. Thus, the damage passes from one generation to other generation. The changes result in abnormalities in the offspring. The damage is the maximum in the reproductive organs, the digestive tract and developing embryos.

Biomedical wastes

Solid or liquid waste generated from hospitals, clinics, research, testing laboratories and drug companies forms the major component of biomedical waste. Biomedical waste includes:

- Human or animal anatomical waste and body fluids, consists of tissues, organs, waste body parts, body fluids, blood. For animals these are generated due to the experimental use in research.
- Microbiological wastes, consists of laboratory culture stocks or specimens of microorganisms, human and animal cell culture used in research.

- Waste sharps, consists of needle, blades, syringes or laboratory glass used for punctures or cuts.
- Discarded, expired medicines, glass equipment used for pathological activity, dressings and liquid wastes generated from washing during the use of equipment.

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Chemical wastes

A chemical hazardous waste is a solid, liquid, or gaseous item that has a hazardous characteristic or is listed as a hazardous waste by name. To be securely handled and managed, this form of hazardous waste must be classified according to its identity, contents, and dangers. Chemical waste is a broad word that refers to a variety of materials. A list of ingredients can be found on the Material Safety Data Sheet (MSDS), Product Data Sheet (PDS), or Label. These sources should specify whether the chemical waste is a hazardous waste that requires special treatment or not.

3.4.2 Methods of Treatment

Chemical, thermal, biological, and physical procedures can all be used to treat hazardous waste. Ion exchange, precipitation, oxidation and reduction, and neutralisation are all chemical techniques. High-temperature incineration is one of the thermal technologies that may not only cleanse but also destroy some organic wastes. Thermal equipment is used to burn trash that is solid, liquid, or sludge. Fluidized-bed incinerators, multiple-hearth furnaces, rotary kilns, and liquid-injection incinerators are among them. The possibility for air pollution is one issue that hazardous-waste incineration poses. Certain organic wastes, such as those from the petroleum sector, can also be biologically treated.

Landfarming is a biological treatment method for hazardous waste. This method involves properly mixing garbage with surface soil on a suitable piece of land. Microbes that can metabolise trash, as well as nutrients, may be added. In some circumstances, a bacteria strain that has been genetically modified is employed. Crops for food and forage are not produced on the same farm. Microbes can also be employed to stabilise hazardous material on previously contaminated areas, which is known as bioremediation. The waste material's molecular form is changed by the chemical, thermal, and biological treatment procedures described above. Physical treatment, on the other hand, concentrates, solidifies, or shrinks the waste volume. Evaporation, sedimentation, flotation, and filtering are examples of physical processes. Solidification is another method, which involves encasing the trash in concrete, asphalt, or plastic. Encapsulation creates a solid mass of material that is leach-resistant. Waste can also be combined with lime, fly ash, and water to create a solid, cement-like substance.

Check Your Progress

6. What is the quantity of solid wastes generation in big cities of India?
7. What happens in the solidification process?

3.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The term soil has been derived from Latin word 'Solumn', meaning earthy material necessary for the growth of plants.
2. Following is the classification of soil based on the size of the particles:

a. Stone and gravel	> 5mm
b. Coarse sand	0.2 – 2.0mm
c. Fine sand	0.02 – 0.20mm
d. Silt	0.002 – 0.02mm
e. Clay	< 0.002mm

3. The soil-derived macronutrients are nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg).
4. The major sources of metallic contamination of soils include mining, smelting, sludge, fertilizers, pesticides, composted town refuse etc. Metals such as Cd, Pb, Hg, Ni, Mo, Ni, Cr, etc. are toxic to plant and animal life.
5. The following types of pesticides are commonly used:
    a. Chlorinated hydrocarbons (eg. DDT, Aldrin, Dieldrin, Lindane, BHC etc.)
    b. Carbamate compounds (eg. Carboryl or Sevin, Zectrion etc.)
    c. Organo-Phosphorous compounds (eg. Methyl or ethyl parathion, melathion, guthion etc.)
6. The quantity of solid wastes generation in big cities of India is almost 400-600 gm per person and is increasing day by day at an enhanced rate.
7. Solidification is a waste treatment method, which involves encasing the trash in concrete, asphalt, or plastic. Encapsulation creates a solid mass of material that is leach-resistant.

3.6 SUMMARY

- Soil is the upper most part of the earth's crust and is a mixture of both organic and inorganic materials.
- The process involving the origin, development and formation of soil is known as pedogenesis.
- The process of soil formation is known as weathering. Weathering is the process of disintegration of parent rocks into smaller particles (regolith).
- The physical agents responsible for soil weathering are temperature, wind, water, ice, gravity, etc.
- When different chemical processes are involved in weathering it is known as chemical weathering. The important chemical weathering agents are moisture, water and air.

- Various types of microorganisms extract minerals from rocks as their energy source. This ultimately leads to change in the physical structures and mineral composition of the rocks.
- The vertical section of matured soil is called soil profile. Soil profile consists of several layers called horizons lying one over the other. All the distinct layers have specific physical and chemical properties.
- Good soil and a congenial climate for productivity are valuable assets for any nation. But due to human activities, soil is the receptor of many pollutants.
- Soil pollution differs from water pollution on air pollution, because the pollutants remain in direct contact with the soil for relatively longer periods and hence alter the chemical and biological properties of the soil.
- Soil pollution is receiving greater and greater attention due to its direct impact on public health.
- Synthetic fertilizers are employed to increase the soil fertility and crop productivity. These fertilizers concentrate the essential nutrients in layer of top soil. However, the soil enriched by chemical fertilizers cannot support the microbial flora which are so essential to enrich the humus that helps in plant growth.
- As per the reports of the World Health Organization (WHO), about 50,000 people in developing countries are poisoned and about 5,000 people die because of improper use of pesticides and other chemicals in modern agricultural practices.
- Solid, liquid and gaseous chemicals from various industries such paper and pulp, iron and steel, fertilizers, dyes, automobiles, pesticides, tanneries, coal-based thermal power plants etc. contain a variety of pollutants.
- The quantity of solid wastes generation in big cities of India is almost 400-600 gm per person and is increasing day by day at an enhanced rate.
- Generally, hazardous waste can be defined as: ‘The wastes or combination of wastes which pose substantial threat to human health and environment.’
- The hazardous waste includes: Radioactive wastes, bio-medical wastes, and chemical wastes.
- Chemical, thermal, biological, and physical procedures can all be used to treat hazardous waste. Ion exchange, precipitation, oxidation and reduction, and neutralisation are all chemical techniques.

3.7 KEY TERMS

- **Hydrolysis:** It means the chemical breakdown of a compound due to reaction with water.
- **Carbonation:** It is the chemical reaction of carbon dioxide to give carbonates, bicarbonates, and carbonic acid.

3.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

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Short Answer Questions

1. What are the different agents affecting weathering of soil?
2. Briefly explain the different horizons of soil profiles from top to bottom.
3. How are synthetic fertilizers bad for soil?
4. What are the characteristics of hazardous waste?

Long Answer Questions

1. Describe the composition of soil in detail.
2. Explain the various approaches to control soil pollution.
3. Discuss the categories of hazardous waste.

3.9 FURTHER READING

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UNIT 4 ATMOSPHERE

NOTES

Structure

4.0 INTRODUCTION

The environment may broadly be considered to comprise of the following four segments: lithosphere, hydrosphere, atmosphere and biosphere. The atmosphere surrounding the earth acts as a gaseous blanket, protecting the earth from dangerous cosmic radiations from outer space and helps in sustaining life on the earth. The various chemical and photochemical reactions taking place in the atmosphere, mostly depend upon the temperature, composition, humidity and intensity of sunlight. This unit will describe chemical composition of atmosphere, greenhouse effect and acid rain. It will also discuss chemical and photochemical reactions in atmosphere along with the process of smog formation. It will explain oxides of nitrogen, carbon, sulphur and oxygen and their effects. In addition, it will discuss air pollution controls and various analytical methods for measuring air pollutants with the help of monitoring instruments.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Evaluate the chemical composition of atmosphere
- Analyse chemical and photochemical reactions in atmosphere

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- Explain pollution caused by different sources
- Discuss the concepts of acid rain and greenhouse effect
- Describe different air pollution controls, preventive methods and monitoring instruments

4.2 CHEMICAL COMPOSITION OF ATMOSPHERE: PARTICLES, IONS AND RADICALS, AND THEIR FORMATION

The atmosphere screens the dangerous UV radiations from the sun (< 300 nm) and transmits only the radiations in the range 300 nm to 2500 nm, comprising of near ultra-violet, visible and near infra-red radiations and ratio-waves (0.01 to 4×10^5 nm). The atmosphere plays a vital role in maintaining the heat balance on the earth by absorbing the radiation received from the sun and re-emitted by the earth. In fact, it is this phenomenon, called "the greenhouse effect", which keeps the earth warm enough to sustain life on the earth. Apart from this, the important gaseous constituents of the earth, *viz*., O_2, N_2 and CO_2 plays important roles in sustaining life on earth. Oxygen supports life on earth, nitrogen is an essential macro-nutrient for plants (via nitrogen fixation and fertilizer manufacture) and carbon dioxide is essential for photosynthetic activity of plants. Moreover, atmosphere is a carrier of water from oceans to land, which is so vital for the hydrologic cycle. Any major disturbance in the atmospheric composition, either by extraordinary or anthropogenic activities, may lead to disastrous consequences or may even endanger the very survival of life on the earth. The composition of clean, dry air, near sea-level in given in Table 4.1.

Table 4.1 *Composition of Clean, Dry Air, Near Sea-Level*

	Components	Content per cent by volume	 ppm
(a)	**Major components**		
	Nitrogen (N_2)	78.09	7,80,900
	Oxygen (O_2)	20.94	2,09,400
	Water vapour (H_2O)	0.1-5	1,000-50,000
(b)	**Minor components**		
	Argon (Ar)	0.934	9,340
	Carbon dioxide (CO_2)	0.032	320
(c)	**Trace components**		
	Neon (Ne)	0.00182	18.2
	Helium (He)	0.000524	5.24
	Methane (CH_4)	0.00018	1.8
	Krypton (Kr)	0.00011	1.1

Nitrous oxide (N_2O)	0.000025	0.25
Hydrogen (H_2)	0.00005	0.5
Xenon (Xe)	0.0000087	0.087
Sulphur dioxide (SO_2)	0.0000002	0.002
Nitrogen dioxide (NO_2)	0.0000001	0.001
Ammonia (NH3)	0.000001	0.01
Carbon monoxide (CO)	0.000012	0.12
Ozone (O_3)	0.000002	0.02
Iodine (I_2)	Traces	Traces

The proportions of the various components of the atmosphere more or less remain constant up to a height of about 16 km from the earth's surface. Above this height, gravitational separation begins, although this becomes significant above 130 km. The weight of the atmosphere is about 4.5 to 5 × 10^{15} metric tonnes, which is about one millionth of the total weight of the earth.

Chemical species and particulates present in the atmosphere

The various chemical species present in atmosphere are as follows:

(i) Ions: The region of the atmosphere which is at an altitude of 50 km to 100 km, is called "Ionosphere" because appreciable levels of electrons and positive ions, such as $O2^+$, O^+, NO^+, etc. exist in this region with considerable residence times. The UV radiations from the sun are mostly responsible for the formation of the ionic species in ionosphere. During night times, when the UV radiations are not present, the positive ions tend to recombine with the free electrons, yielding the neutral species from which they are originated initially. This process occurs more rapidly in the lower regions of the ionosphere where the concentration of these species is relatively high.

(ii) Radicals: Apart from the ionic species, the atmosphere also consists of highly reactive free radicals, generated by photo-chemical reactions *e.g.*, HO•, CH3•, SO_2•, ROO•, NO_2•, and HCO•. The free radicals, which may be organic or inorganic, comprise of atoms or groups of atoms with impaired electrons having short half-lives. Owing to their high reactivity, they interact with other chemical species available, to propagate chain reactions until chain termination takes place due to destruction of one of the free radicals in the chain, by any of the various possible mechanisms. Free radicals play significant role in the formation of photo-chemical smog.

(iii) Particles: Several types of particles exist in the atmosphere in varying sizes from 0.1 μ to 10 μ. Even pure air may contain several hundreds of particles per c.c., whereas hightly polluted air may contain about a lakh of particles per c.c. whereas highly polluted air may contain about a lakh of particles per c.c. Particles of colloidal dimensions are called "aerosol>". The word "particulates" is generally used to describe the particles present in caerosols. Aerosols of natural origin having diameter <0.2 μ are called "Aitkin" particles. The various particles existing in nature include dust, smoke, fog, pollen grains, volcanic ash and bacteria. Dusts, mist, smoke, smog and fumes may also result from anthropogenic activities. Inorganic particulate, such as iron oxide, calcium oxide etc., may result from combustion of coal and metallurgical operations. Particulate lead results from automobile exhausts. Aerosol mists are generated from oxidations of SO_2 to SO_3 which in presence of water vapour forms droplets of H_2SO_4.

Organic particulate matter arises from automobile exhausts, combustion of fuels and evaporation of organic matter from vegetation. Certain organic particulates contain polycyclic aromatic hydrocarbons (PAH) which are carcinogenic. They are generated from the pyrolysis of higher paraffin present in fuels and in some vegetable matter. Atmospheric particulates may enter the respiratory tract and cause serious health hazards. Removal of obnoxious particulates from gaseous emissions is an important step in controlling air pollution.

The size and chemical characteristics of the particles in atmosphere are more significant than their concentration. The particles in the range of 0.1 μ to 1 μ manifest in several important effects in the atmosphere, such as:

- They play a vital role in maintaining the radiation balance and heat balance of the earth.
- They provide nuclei for condensation of water vapour.
- They are responsible for fog and cloud formation.
- They may bring about heterogeneous gas-phase reactions. The particles may absorb gases and catalyze some reactions. For example, the decomposition of ozone is catalyzed by a solid surface.
- They absorb and destroy free radicals, thereby reducing the rate of free radical chain reactions.
- The absorption of gases on some solid surfaces may change the absorption spectrum of the gas for sun light. For instance, oxygen absorbed on carbon particles might absorb sunlight more strongly than what free oxygen would do.
- They would help in several types of reactions in the atmosphere, such as,
  - o Catalysing the oxidation of SO_2 by O_2 or O_3 in aqueous droplets
  - o Neutralization reactions between sulphuric acid droplets and lime stone dust
  - o Reaction between O_3 or NO_2 with salt particles in water droplets
  - o Photochemical reactions involving dusts and aerosols

Atmospheric structure

The atmosphere, which extends up to about 500 km above the earth's surface, can be broadly divided into four major regions, with widely varying temperatures, even within each region. We have already discussed the different regions of atmosphere in the Unit 1, here we will discuss some important characteristics of the four major atmospheric region *viz*., troposphere, stratosphere, mesosphere and thermosphere, are summarised in Table 4.2.

Table 4.2 *Characteristics of the Major Regions of the Atmosphere*

Name of the Region	Height above the Earth's	Temperature Range Surface (km)	Major Chemical Species Present °C
Troposphere	0 – 11	15 to – 56	O_2, N_2, CO_2, H_2O
Stratosphere	11 – 50	– 56 to – 2	O_3
Mesosphere	50 – 85	– 2 to – 92	O^+_2, NO^+
Thermosphere	85 – 500	–92 to 1200	O^+_2, O+, NO^+

(1) **Troposphere:** This is the region nearest to the earth's surface and extends upto an altitude of 11 km. The upper limit may vary by a few kilometers, depending upon temperature, nature of the terrestrial surface and some other factors. The troposphere acounts for over 70% of the atmospheric mass. The composition of air in this region remains more or less constant in the absence of any significant air pollution. This is mostly due to the turbulence and constant circulation of air masses, as a result of convection currents arising from differential heating and cooling rates between the equator and the poles. The density of air, in this region, decreases exponentially with increasing altitude. The troposphere contains most of the water, cloud and particulate matter of the atmosphere. The temperature of air in the troposphere decreases fairly steadily with increasing altitude from the ground temperature to a temperature of about –56°C. It can be seen that the temperature-altitude curve then changes its slope (*i.e.*, the temperature starts increasing with increasing altitude) rather suddenly in a narrow transitional layer at the top of the troposphere, known as the "Tropopause", which is usually at an altitude of 10 km to 20 km. The temperature of the tropopause is the least at the equator. The change of temperature with height is called the "lapse rate". The decrease of temperature with increasing altitude in the troposphere is called positive lapse rate. The transition from positive lapse rate to negative lapse rate at the tropopause marks what is called the "temperature inversion".

(2) **Stratosphere:** The region above the tropopause is called the stratosphere. In this region, the temperature-altitude curve shows a warming trend with increasing altitude *i.e.*, it exhibits a negative lapse-rate. The temperature in this stratospheric region continues to increase with height, until 50 kms, where the temperature attains a maximum of–2°C. This warming up tendency in the stratosphere is due to the absorption of solar UV radiation by ozone, whose concentration in this region is in the range of 1 to 5 ppm by volume and this is responsible for the negative lapse-rate. The air in this region is very dry and the clouds and convection currents from the troposphere normally do not penetrate into it. The presence of ozone in the stratosphere serves as a shield to protect life on the earth from the harmful effects of the solar UV radiations. Moreover, it serves as a source of heat for separating the quiescent stratosphere from the turbulent troposphere. Because of the quiescent nature of the stratosphere, the molecules and particles in the region have long residence times. This is significant from the point of view of atmospheric pollution because any pollutant reaching this region may spell long term global hazard, as compared to their impact in the troposphere, which is much denser and more turbulent. The region immediately above the stratosphere (above 50 km height) is called "Stratopause" which is the second transitional layer that is relatively warm. This is not much coller than the earth's surface. It reflects sound waves from earth back to the surface.

(3) **Mesosphere:** This is the region above the "Stratopause" and extends upto 85 km height. In this region, the temperature again decreases with height *i.e*, it exhibits a positive lapse-rate. This is due to relatively low levels of ozone and other species that can absorb UV radiations from the sun. The temperature, at the top of the Mesosphere, reaches about –92°C. Immediately above the Mesophere is another transitional layer, called "Mesopause" which is the region of minimum or coldest temperature in the atmosphere (*i.e*, about –100°C)

(4) **Thermosphere:** This is the region immediately above the mesopause, where the temperature rises very rapidly with increasing altitude, exhibiting a negative lapse-rate. The maximum temperature that is attained in this region is about 1200°C. This region is characterised by low pressures and low densities. The atmospheric gases present in this region (e.g., oxygen and nitric oxide) absorb the solar radiations in the far ultra-violet region and undergo ionisation.

The region above the stratosphere, in the altitude range of 50 km to 100 km, is called "Ionosphere". In this region, positive ions e.g., O_2^+, O^+, NO^+ etc and electrons exists at significant levels. These charged species persist for long periods of time, without mutual neutralization, due to the rarefied conditions existing in the region. The troposphere, the stratosphere and the mesosphere are fairly uniform in composition. From air pollution point of view, troposphere is of particular significance.

Check Your Progress

1. What is the name of the phenomenon that keeps the earth warm?
2. Name the major components of the air.
3. Which radiations are responsible for the formation of the ionic species in ionosphere?
4. How are polycyclic aromatic hydrocarbons (PAH) produced?

4.3 CHEMICAL AND PHOTOCHEMICAL REACTIONS IN ATMOSPHERE

The various chemical and photochemical reactions taking place in the atmosphere, mostly depend upon the temperature, composition, humidity and intensity of sunlight. Thus the ultimate fate of a chemical species in the atmosphere depends upon these parameters. Photochemical reactions take place in the atmosphere by the absorption of solar radiations in the UV region. Absorption of photons by chemical species gives rise to electronically excited molecules, which can bring about certain reactions, which are not possible under normal laboratory conditions, excepting at higher temperatures and in presence of chemical catalysts. The electronically excited molecules produced by the absorption of a photon may undergo any of the following changes:

- Reaction with other molecules on collision
- Polymerisation
- Internal rearrangement
- Dissociation
- De-excitation by fluorescence or de-activation by return to the original state

Any of the first four changes stated above may serve as an initiating chemical step or a primary process. The three steps involved in an overall photochemical reaction are: (i) absorption of radiation, (ii) primary reactions, and (iii) secondary reactions. The various chemical species that can undergo photo-chemical reactions in the atmosphere include NO_2, SO_2, HNO_3, N_2, Ketones, H_2O_2, organic peroxides and several other organic compounds and aerosols such as metal oxides. Let us study major reactions in detail.

Oxidation of nitrogen

The oxides of nitrogen present in the atmosphere are N_2O, NO and NO_2. Nitrous oxide mainly originates from various microbiological processes whereas NO and NO_2 mainly originate from the combustion of fossil fuels and other anthropogenic activities. The NO and NO_2 together are referred to as NO_x, which is an important constituent of polluted air.

In the stratosphere, N_2O undergoes photochemical decomposition to NO, which in turn, depletes the protective ozone layer:

$$N_2O + hv \longrightarrow N_2 + O$$

$$N_2O + O \longrightarrow NO + NO$$

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

The most important primary photochemical reaction is the dissociation of NO_2.

$$N_2O + hv \longrightarrow NO + O$$

The NO so formed may be oxidised by O_3 or more slowly by O_2, thus leading to a cyclic chain reaction. The chain may be broken only when the NO_2 is completely converted into HNO_3 by hydration and catalytic oxidation in presence of aerosols, fog or photochemical smog. The reactions may take place in the following sequence:

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

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

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

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

$$N_2O_5 + H_2O \longrightarrow 2HNO_2$$

HNO_3 and HNO_3 may also undergo photochemical dissociation as follows:

$$HNO_2 + hv \longrightarrow NO_2 + H\bullet$$
$$HNO_2 + hv \longrightarrow NO + HO\bullet$$
$$HNO_3 + hv \longrightarrow NO_2 + HO\bullet$$

In the stratosphere, NO_2 may react with the HO• free radical, forming HNO_3:

$$NO_2 + HO\bullet \longrightarrow HNO_3$$

The HNO_3 so formed is removed as acid rain or is converted into particulate nitrates due to neutralisation by NH_3 or particulate lime.

Oxidation of sulphur dioxide

Sulphur dioxide, present in the atmosphere, absorbs solar radiation in the range of 300–400 nm and produces electronically excited states of SO_2. This undergoes oxidation to SO_3 and in presence of water vapour, this is converted to H_2SO_4.

$$SO_2 + hv \longrightarrow SO_2\bullet$$
$$SO_2\bullet + O_2 \longrightarrow SO_4\bullet S$$
$$SO_4\bullet + O_2 \longrightarrow SO_3 + O_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The overall reaction in presence of sunlight and relative humidity 30-90% may be represented as:

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

This photochemical oxidation of SO_2 leading to the formation of H_2SO_4 aerosol is greatly accelerated in the presence of olefinic hydrocarbons and oxides of nitrogen which are usually present in photochemical smog. Photochemical smog is initiated by the photochemical dissociation of NO_2 and the consequent secondary reactions involving unsaturated hydrocarbons, other organic compounds and free radicals, leading to the formation of organic peroxides and ozone. This phenomenon takes place during sunny days with low winds and low level inversion. The photochemical smog and the consequent formation of aerosols reduce the visibility, cause irritation to eyes and damage plants and rubber goods.

The oxidation of SO_2 can also take place by interaction with the free radical HO• present in photochemical smog.

$$SO_2 + HO? \longrightarrow HOSO_2\bullet$$
$$HOSO_2\bullet + O_2 \longrightarrow HOSO_2\ O_2\bullet$$
$$HOSO_2O_2 \longrightarrow \underset{\text{(sulphate)}}{HOSO_2O\bullet} + NO_3\bullet$$

Chemical oxidation of SO_2 may also take place in water droplets present in aerosols. This reaction is accelerated in presence of NH_3 and catalysts *e.g.*, oxides of Mn, Fe, Cu, Ni. Solid particles, such as soot, bring about catalytic oxidation of SO_2 by providing a heterogeneous phase for contact. Soot is formed during combustion of solid and liquid fuels in domestic and industrial operations and automobile emissions. Sulphur dioxide is a pollutant responsible for smog formation, acid rains, and corrosion of metals and alloys.

Oxidation of organic compounds

Organic compounds such as hydrocarbons, aldehydes and ketones absorb solar radiation and undergo various photochemical and chemical reactions involving free radicals. Some of these reactions are catalysed by particulate matter such as soot and metal oxides. Some of the intermediates and final products formed contribute to photochemical smog formation.

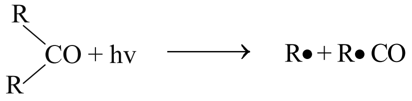
$$\underset{\text{Methane}}{CH_4 + O_2} \longrightarrow H_3C\bullet + HO\bullet$$

$$CH_4 + HO\bullet \longrightarrow H_3C\bullet + H_2O$$

$$H_3C + O_2 + M\ (\text{Third body}) \longrightarrow H_3\,COO\bullet + M$$

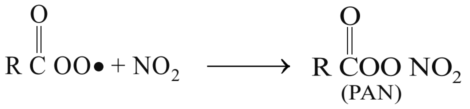
$$\underset{\text{Propylene}}{CH_3CH = CH_2} + HO\bullet \longrightarrow CH_3 - CH\bullet - CH_2OH$$

$$\underset{\text{Aldehyde}}{RCHO} + hv \longrightarrow R\bullet + HCO$$



$$\underset{\text{Ketone}}{R_2CO} + hv \longrightarrow R\bullet + R\bullet\,CO$$

Here R is an alkyl or aryl radical or even a hydrogen atom. The alkyl or aryl radicals may react with oxygen to form a peroxyl radical, which in turn may react with another oxygen atom to give O_3. The peroxyl radical may react with NO_2 to given peroxyacyl nitrate (PAN), formaldehyde (which is an irritant) and various polymeric compounds which reduce visibility.



$$R\overset{O}{\overset{\|}{C}}OO\bullet + NO_2 \longrightarrow \underset{(PAN)}{R\overset{O}{\overset{\|}{C}}OO\,NO_2}$$

4.3.1 Smog Formation

'Smog' is the combination of smoke and fog. The name was so given because the fog in the atmosphere condenses on the carbon particles of the smoke to form smog. However, it may not be so simple as the name implies. Smog can have a number of other compositions and methods of formation. The factors responsible for formation of smog are: (1) inversion of temperature (2) mixing of the polluted gases emitted from industries and motor vehicles with foggy air. Depending upon the compositions and the methods of formations, smog is of two types:

1. **London smog or sulphurous smog:** The smog formed from oxides of sulphur (SO_x), particulate matter coming from smoke and humidity or water is known as London smog or sulphurous smog. The smog affected London city badly in 1952, killing about 4000 people. The fuel introduced at that time was coal and was found to be main culprit. The mixture of smoke, SO_x and fog is, chemically a reducing mixture and is also known as reducing smog. Sulphurous smog occurs mainly in the early morning hours in winter, where there is a relatively high humidity. Air near the ground is cooled by

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conduction from cooled surface, especially on a clear night. Sulphurous smog causes bronchitis and acute respiratory problems. SO_2 in the atmosphere gets converted into SO_3 on oxidation by a number of chemicals present in the particulates. SO_3 so formed combines with water in the atmosphere forming a fog of sulphuric acid droplets. These droplets then condense on the carbon particles of soot (smoke) and smog known as sulphurous smog is formed.

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad\qquad SO_2 + H_2O \rightarrow H_2SO_3$$

Or,

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad\qquad H_2SO_3 + O_2 \xrightarrow[\text{salt}]{\text{metal}} H_2SO_4$$

2. **Photochemical smog:** Photochemical smog results from the photochemical reactions in atmosphere. It does not involve any smoke or fog and the word smog is a misnomer here. Photochemical smog is an atmospheric haze (yellowish brown haze), generally formed in large cities due to the action of sunlight on the hydrocarbons and nitrogen oxides. As the main component of this type of smog is oxides of nitrogen, it is also known as nitrogenous smog. The main unhealthy ingredient of this smog is ground level or tropospheric ozone as it initiates the photochemical reaction. This type of smog was first observed in Los Angeles in 1950 and hence, is named 'Los Angeles smog'. The following stages lead to the formation of photochemical smog:

   (*i*) Reactive hydro carbon (olefin having C = C type bond) from auto-exhaust, interact with troposheric O_3 to form free radical $RCH_2^\bullet$.

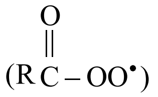
   (*ii*) $RCH_2^\bullet$ rapidly reacts with O_2 to form another free radical $RCH_2O_2^\bullet$.

   (*iii*) $RCH_2O_2^\bullet$ reacts with NO to produce NO_2 and free radical $RCH_2O^\bullet$.

   (*iv*) The new free radical then interacts with O_2 to yield a stable aldehyde (RCHO) and hydroperoxy radical $HO_2^\bullet$.

   (*v*) $HO_2^\bullet$ further reacts with another molecule of NO and gives NO_2 and $HO^\bullet$.

   (*vi*) $HO^\bullet$ is extremely reactive and rapidly reacts with the stable hydro carbon RCH_3 to yield H_2O and regenerate $RCH_2^\bullet$, thereby completing the cycle.

   (*vii*) The aldehyde may initiate another route by interaction with the $HO^\bullet$ radical, leading to the formation of peroxyacyl nitrate (PAN) through the intermediate steps of acyl radical ($RC^\bullet = O$) and  $(R\overset{\overset{O}{\|}}{C}-OO^\bullet)$ peroxyacyl radical formation.

The formation of PAN is discussed below:

   (i) Formation of tropospheric ozone (O_3): In the early morning, concentration of volatile organic compounds and NO increases in the atmosphere mainly from the automobile exhausts. As the morning progresses, there is a drop in the levels of NO and a rise in NO_2 levels as NO is oxidized by O_2 to NO_2. Now as the day progresses, sun's intensity increases, rate of photolysis of NO_2 is enhanced, and O_3 increases.

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + hn\ (\lambda < 390\ nm) \rightarrow NO + O$$

The freed atomic oxygen (O) can then combine with diatomic oxygen (O_2) to form ozone (O_3).

$$O + O_2 + M \rightarrow O_3 + M$$

M is the third body, a molecule, usually N_2, which is most abundant in air. M absorbs the excess energy formed in the reaction to stabilize O_3, otherwise, it would dissociate back to O and O_2.

(ii) Mechanism of formation of PAN (Peroxyacyl nitrate): The overall process is a photo initiated reaction of hydrocarbons (olefins) and NO to form NO_2, O_3 and PAN, which appears as a yellowish brown haze and is the photochemical smog. Reactive hydrocarbon (RCH_2, *i.e.,* olefin hydrocarbon with C = C linkage).

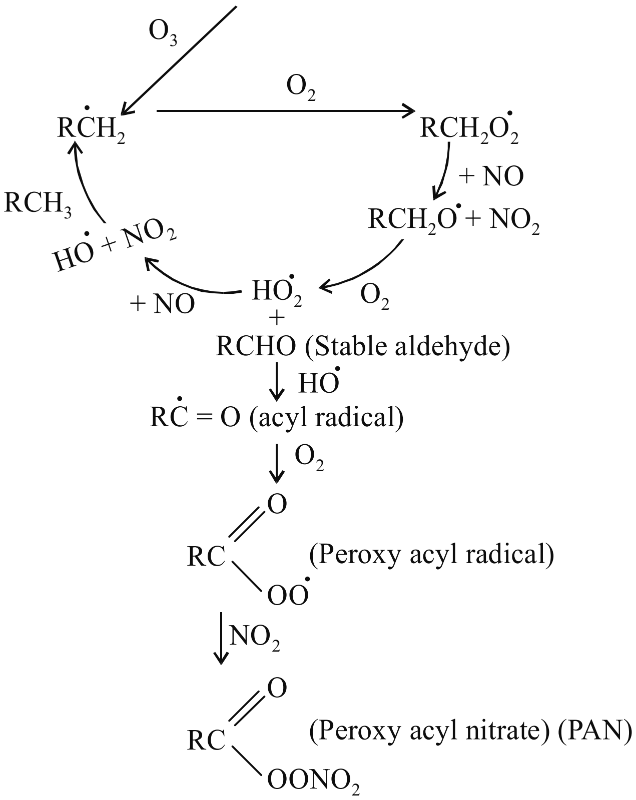


Fig. 4.1 *Mechanism of Formation of PAN*

Photochemical smog causes eye irritation, sore throat, respiratory irritation, headache, etc. The biochemical effects of PAN arise due to free radical generation of its formation. The free radical attacks –SH group of enzymes and inhibit its function. The O_3 damage tree foliage, thereby reducing growth rate and crop production.

4.3.2 Oxides of C, N, S and O and their Effects

There are six pollutants which have the main contribution in creating air pollution. They are primary pollutants like carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen dioxide (NO_2), lead (Pb), and particulate matters (PM), with secondary pollutants like ground level ozone (O_3). Let us study these pollutants in detail.

Carbon monoxide

It is a colourless, odourless, tasteless, poisonous gas. The structure is $(\overset{..}{C} \overset{\leftarrow}{=} \underset{..}{\overset{..}{O}})$. It combines with haemoglobin, the oxygen carrier of the blood in the body, to form carboxy haemoglobin, a stable compound. The oxygen transportation is thus, disturbed and in extreme cases it can be fatal. However, it is a blessing that soil fungi and higher plants absorb it and destroy it by converting it to CO_2.

$$O_2 + Hb \rightarrow \underset{\text{oxyhaemoglobin}}{O_2Hb}$$

In the presence of CO: $O_2Hb + CO \rightleftharpoons \underset{\substack{\text{carboxy-}\\\text{haemoglobin}}}{COHb} + O_2$

Some of the major sources of the pollutant are as follows:

- Incomplete combustion of coal, wood, petrol in steel plants, automobiles, thermal power plants, jet engines.
- Mid ocean surface water.
- Oxidation of CH_4 formed through anaerobic decomposition of organic matter.
- Tobacco smoking.

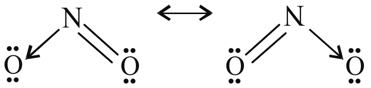
Oxides of Nitrogen

There are six oxides of nitrogen, viz., nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4) and nitrogen pentoxide (N_2O_5), which are known to occur. However, two oxides of nitrogen, which are important air pollutants are (NO) and (NO_2). Some of the major sources of these pollutant are as follows:

- Burning of fossil fuels
- Nitrogen based fertilizer plants
- Explosive industry
- Coal fired and gas fired furnaces
- Textile industry
- Manufacture of HNO_3
- Decomposition of organic waste
- Thunder showers
- Aerial oxidation of N_2 at high temp (~1000 K)
- Automobile exhaust

Nitrogen dioxide (NO_2)

It is a reddish brown gas and exists at room temperature. At low temperature it dimerises to N_2O_4. Nitrogen dioxide is paramagnetic. It has an angular structure ($<$ ONO = 132^o) and N – O distance is about 1.19 Å. It is a resonance hybrid of two structures.



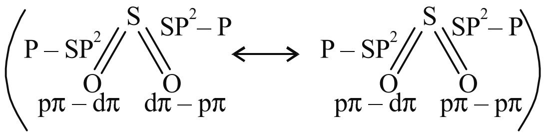
At a lower concentration of NO as found in atmosphere, there are no adverse effects on health and green plants also absorb it without damage. But NO, which is oxidized subsequently, to form NO_2 accumulating in a higher concentration, has much adverse effect on health. Some of the common effects of this pollutant are as follows:

- Respiratory irritation
- Impairment of lung defense
- Headache
- Bronchitis
- Loss of appetite
- Corrosion of teeth
- Leaf damage to sensitive plants

NO and NO_2 also react with volatile organic compounds in the presence of sunlight to produce photochemical oxidants, which have high adverse effect on health. Besides human health, NO_2 has other environmental consequences too. It reacts with the hydroxyl radical ($OH^{\cdot}$) in the atmosphere to form nitric acid, contributing to acid rain problems and corrosion of metal surfaces. It might cause significant damages to eutrophication and terrestrial plants. NO is also known to be responsible for ozone layer depletion in the stratosphere.

Sulphur dioxide (SO_2)

It is a colourless, poisonous gas, highly soluble in water. It has a pungent and suffocating odour. SO_2 has a planar triangular (V-shaped) structure with dipole moment 1.60D. It is a resonance hybrid of two structures and has two different types of p bonds – (*p*p – *p*p) and (*p*p – *d*p).



Some of the common sources of this pollutant are as follows:

- Burning of fossil fuels
- Thermal power plants
- Fertilizer plants

- Textile industry
- Steel plants
- Sulphuric acid plants
- Petroleum industry
- Oil refining
- Smelting of sulphide ores

On an average, about 25 million tons of sulphur dioxide is emitted into the atmosphere annually.

The main source of sulphur is fossil fuels like coal, that has the maximum content of sulphur, about 1 to 6 percent. When fossil fuels are burnt, the main gas released into the atmosphere is SO_2 along with trace amount of SO_3. SO_2 also can react with $OH^\bullet$ radical (obtained from photo dissociation of H_2O molecules), followed by series of reactions.

$$SO_2 + OH^\bullet \rightarrow HOSO^\bullet_2$$

$$HOSO^\bullet_2 + O_2 \rightarrow SO_3 + HO^\bullet_2$$

Thus, the SO_3 formed reacts very fast with H_2O to form sulphuric acid, the principle cause of acid rain.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The acid molecules then either deposit on particulates existing in the air, or merge with water vapours to form droplets. Thus, in the atmosphere we may obtain significant amount of sulphur (SO_4) aerosols. Most of the surface has effective sites in the range of 0.2 to 0.9 mm, comparable to the wavelength of visible light affecting visibility. Lesser size also allows deep penetration into the respiratory system. Some of the common effects of this pollutant are as follows:

- Increased breathing rate and feeling of air starvation
- Suffocation
- Respiratory irritation
- Asthma and chronic bronchitis
- Irritation of throat and eyes

The dangerous effect of this gas is that by combination with particulate matter it can act synergistically and the effect of both together being much more detrimental than either of them separately. SO_2 affects plants severely. SO_2 gas enters plants through the stomata and gets oxidized to SO_3 there. This SO_3 reacts with H_2O and forms H_2SO_4. The acid interferes in metabolic process and productivity falls. Acid rain causes soil pH to go down, dissolving aluminum compounds, which ultimately hampers the uptake of nutrients. SO_2 causes yellowing of paper and reduces its mechanical strength, affecting the storage of books. It discolours paint, causes organic fiber to weaken. Even metals get corroded easily by SO_2. Prolonged exposure to sulphate causes damage to buildings and marble monuments, as the carbonates like lime stone and $CaCO_3$ react with H_2SO_4 to produce gypsum ($CaSO_4$), which is washed away leaving behind the eroded surface. It is now believed that there is a severe acid rain threat on the Taj Mahal.

Particulate Matter

Small solid particles and liquid droplets are collectively known as particulates. In this case, the individual components aggregate to form molecular clusters (diameter 0.005 mm – 100 mm) like fumes, dust, ash, smoke, fog, oil, fly ash. Particulates are categorized on the basis of size and phase (liquid or solid). The most general term is aerosol, which is a suspension of tiny solid particles (1 mm to 50 mm) or liquid droplets, dispersed in the atmosphere. Examples of particulate matter can be listed as follows:

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- Dust – Solid particles dispersed in air.
- Fume – Solid or liquid particles formed when vapours condense.
- Fog – Liquid dispersed in gas medium.
- Smoke – Carbon resulting from incomplete combustion.
- Smog – Particulate matter originated from smoke and fog.

The chemical nature and size of the particles are very important from the pollution point of view. The particles possess large surface area and act as nuclei for many chemical reactions.

Some of the common sources of particulate matter are as follows:

- Volcanic eruptions, dust and soil blowing by the wind.
- Stone crushing, mineral crushing, combustion of fuels like woods, oil, coal, natural gas.
- Combustion of leaded gasoline, producing Pb particles.
- Polycyclic aromatic hydrocarbon (PAH).
- Biological materials like virus, bacteria, algae, etc.

Some of the common effects of particulate matter are as follows:

- Blocking of solar radiation causes the lowering of earth's temperature and affects the overall weather conditions.
- Deposition on plant leaves affect photosynthesis.
- Respiratory disease, neural disorders, cancer.

Lead

It is also known as plumbum (Pb). The important ores are galena (PbS), anglesite ($PbSO_4$), cerusite ($PbCO_3$) and lanarkite (PbO, $PbSO_4$). It is bluish grey metal (mp 327°C). It is very soft. Some of the common sources of lead are as follows:

- Mainly automobile emissions, due to the burning of gasoline containing the anti-knock additive tetraethyl lead $Pb(C_2H_5)_4$
- Burning of gas and oil
- Glass manufacturing
- Mining and plumbing
- Metal smelters and plants, manufacturing lead–acid batteries
- White paint containing $Pb_3(CO_3)_2(OH)_2$ and red paint containing Pb_3O_4.

- Lead is emitted into the atmosphere primarily in the form of inorganic particulates. The maximum portion of it however, settles down in the immediate vicinity of the source. The soil, water and food however get contaminated
- Water pipes made of lead can get leached, further causing lead pollution

Some of the common effects of lead are as follows:

- Liver and kidney damage
- Mental retardation in children
- Abnormalities in fertility and pregnancy

Ground Level Ozone (O_3)

We have discussed the role of (O_3) in the stratosphere. In the stratosphere, ozone acts as a policeman by protecting us from harmful ultraviolet radiations. In the troposphere, ozone is a secondary pollutant. The mechanism of formation can be given as:

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

where large concentration of NO_2, exposed to the atmosphere from various sources are photo dissociated by photons (l < 390nm) to form NO and atomic oxygen. The atomic oxygen thus, produced reacts with O_2 gas in the presence of a third body, especially N_2, which is abundant in air and forms ozone.

$$O + O_2 + N_2 \rightarrow O_3 + N_2$$

Without the third body, the so formed O_3 would not have been stable and would have reverted back to O and O_2. When we inhale air containing O_3, it poses a threat.

Check Your Progress

5. Which oxides of nitrogen are present in the atmosphere?
6. How is photochemical smog initiated?
7. What is formed in stratosphere when NO_2 reacts with the HO• reacts with HNO_3?
8. Define smog.
9. Write the two types of smog on the basis of its composition and methods of formation.
10. Give one example of a secondary pollutant.
11. Why is oxygen transportation considered fatal in some cases?
12. What is the colour of nitrogen dioxide?

4.4 POLLUTION BY DIFFERENT SOURCES

The following section discusses some of the harmful pollutants that contaminate our atmosphere.

4.4.1 Pollution by Chemicals

Chemicals and particles are released into the atmosphere. Carbon monoxide, sulphur dioxide, chlorofluorocarbons (CFCs), and nitrogen oxides are common gaseous pollutants created by industry and motor vehicles. When nitrogen oxides and hydrocarbons combine with sunlight, photochemical ozone and smog are produced. Carbon monoxide, nitrogen dioxide (no2), carbon dioxide, sulphur dioxide, and sulphur trioxide are all hazardous compounds found in air pollution.

4.4.2 Pollution by Petroleum

Petroleum is a type of naturally occurring liquid oil that is found in deposits under the earth's surface. It is a sort of oil made up of rock minerals, which distinguishes it from other types of oil. Emissions from the petroleum sector can be found throughout the entire supply chain. From extraction through consumption, the oil-producing process is described. Various by-products. Carbon monoxide and methanol are two examples. When oil or petroleum distillates are burned, the combustion is frequently incomplete, and the chemical reaction produces by-products other than water or carbon dioxide. Despite the vast numbers of pollutants, there are differences in the amount and concentration of some contaminants. Inhalation of petroleum hydrocarbons such as gasoline, diesel, or jet fuel invading into indoor spaces from underground storage tanks or brownfields poses a safety risk (e.g., explosive potential) and has negative health consequences.

4.4.3 Pollution by Minerals

Mining operations have a negative impact on air quality. When mineral resources are exposed on the surface by mining, unprocessed materials are liberated. Such materials go airborne as a result of wind erosion and neighbouring motor movement. Toxic elements such as lead, arsenic, cadmium, and others are frequently found in such particles. People who live near a mining site may be exposed to these toxins, which can be harmful to their health. Inhalation of such airborne particles has the potential to cause respiratory diseases and allergies.

4.4.4 Pollution by Chlorofluorohydrocarbons

CFCs and HCFCs are halogenated paraffin hydrocarbons that contain just carbon (C), hydrogen (H), chlorine (Cl), and fluorine (F), and are created as volatile derivatives of methane, ethane, and propane. The presence of CFCs in the atmosphere causes the ozone layer to be depleted. Refrigerators, aerosol sprays, coolers, and other devices use them as coolants. Air pollution is caused by an increase in the concentration of chlorofluorohydrcarbon molecules in the atmosphere.

CFCs have an impact on the atmosphere that goes beyond their position as ozone depleting compounds. Infrared absorption bands prevent heat from exiting the earth's atmosphere at that wavelength. Because of the relative transparency of the atmosphere within this region, CFCs exhibit their highest absorption bands from C-F and C-Cl bonds in the spectral region of 7.8–15.3 m, which is referred to as the "atmospheric window."

CFCs and other unreactive fluorine-containing gases such as perfluorocarbons, HFCs, HCFCs, bromofluorocarbons, SF6, and NF3 create a "super" greenhouse effect due to the strength of CFC absorption bands and the unique susceptibility of the atmosphere at wavelengths where CFCs (indeed all covalent fluorine compounds) absorb radiation.

4.5 GREENHOUSE EFFECT

The earth is heated by sunlight and some of the heat that is absorbed by the earth is radiated back into space. However, some of the gases in the lower atmosphere, acting like glass in a greenhouse, allow the solar radiations (in the range 300 to 2500 nm, i.e., near UV, visible and near I.R. region, while filtering the dangerous UV radiations i.e. < 300 nm) but do not allow the earth to re-radiate the heat into space. In order words, these gases in the atmosphere are transparent to the sunlight coming in but they strongly absorb the infra-red radiation, which the earth sends back as heat. A part of the heat so trapped in these atmospheric gases is reemitted to the earth's surface. The net result is the heating of the earth's surface by this phenomenon, called the "greenhouse effect". The gases that are responsible for this greenhouse effect are CO_2, water vapour, CH_4 and man-made chloroflourocarbons (CFCs). Water vapour strongly absorbs I.R. radiations in the range 4000 to 8000 nm and CO_2 in the range 12,000 to 16,300 nm. The radiations in the range 8000 to 12,000 nm escape unabsorbed and this is known as the region of atmospheric window.

Carbon dioxide is released by volcanoes, oceans, decaying plants as well as human activities, such as deforestation and combustion of fossil fuels. Automobile exhausts accounts for 30% of CO_2 emissions in developed countries. Methane is released from coal mines, decomposition of organic matter in swamps, rice paddy cultivation, guts of termites in forest debris and stomachs of ruminants.

Chloroflourocarbons (CFCs) are used as coolants in refrigerators, propellants in aerosol sprays, plastic foam materials like "thermocoles" or "styrofoam" and in automobile air-conditioners.

In fact, the "greenhouse gases" (particularly CO_2 and water vapour) are responsible for keeping our planet warm and thus sustaining life on the earth. If the Greenhouse gases are very less or totally absent in the earth's atmosphere, then the average temperature on the earth would have been at sub-zero levels. But, however, if the concentration of greenhouse gases is larger, they may trap too much of heat, which may threaten the very existence of life on the earth. For instance, the CO_2 present in the atmosphere of the planet Venus, is about 60,000 times more than that in the earth's atmosphere. Hence the average temperature of Venus is about 425°C, thus making the existence of life impossible there.

Oceans and bio-mass are the major sinks for the atmospheric CO_2. Oceans convert CO_2 into soluble bicarbonates. The photosynthetic activity in the green plants increases with increase in CO_2 level in the atmosphere. Forests are the places where lot of photo-synthetic activity occurs. They also act as vast reservoirs of fixed but readily oxidisable carbon in the form of vegetation, wood and humus. Hence, forests maintain a balance in the atmospheric CO_2 level. Therefore, deforestation definitely upsets this balance and increases the atmospheric CO_2 level.

It is estimated that the atmospheric CO_2 content has increased by 25% during the last two centuries. This is mostly attributed to the industrial revolution over these two centuries. This is one of the reasons for the slight increase in the global temperature (about 0.5°C). Since the concentrations of the Greenhouse gases have been continuously increasing because of deforestation, industrialization, increased burning of fossil fuels, mining, exhausts from increasing number of automobiles and other anthropogenic activities, there is an increasing concern about the possible "global warming". Some scientists fear that if proper precautions are not taken, the concentration of the green-house gases in the atmosphere may double within the next 50–100 years. If this happens, the average global temperature may increase by 4 to 5°C. This will increase the evaporation of surface waters, which may influence climatic changes depending upon the pattern of cloud formation. For instance, low-level dense clouds may exert cooling effect whereas high level thin cloud formation may exert heating effect due to increased greenhouse effect.

The projections from computer modelling regarding the climatic changes that could be triggered off due to "global warming" reveal alarming scenarios. Even 1.5°C raise in surface temperature can adversely affect the food production in the world. Thus, the wheat growing zones in the northern latitude may be shifted from the USSR and Canada to the polar regions, i.e., from fertile soils to poor soils near the north pole. The biological productivity of the ocean would also decrease due to warming of the earth's surface layer, which in turn, may reduce the transport of the nutrients from deeper layers to the surface by vertical circulation. The computer modelling also indicate the following effects due to "global warming": melting of the polar ice caps; dry areas becoming drier; humid areas like the Amazon suffering more intense tropical storms; drastic drop in food production, particularly in lands within 35 degrees north and south of the Equator; increased breeding of pests and diseases due to more humid conditions; shorter, wetter and warmer winters; and longer, hotter and drier summers, particularly in mid-continental areas. Global warming may also trigger increased thermal expansion of oceans and melting of glaciers, which results in lifting up of the sea-level by 20 cm to 1.5 meters by the later part of the 21st century. Thus, cities like Bombay, Miami, London, Venice, Bangkok and Leningrad may become extremely vulnerable. Defences against the raising sea-levels and expanding oceans are very difficult and expensive, which many nations of the world cannot afford. Further, a global temperature raise, even about 1.5°C, is likely to cause floods, hurricanes, tornadoes, apart from raising of the sea-level due to melting of the polar ice caps and inundating coastal cities like Madras, Sydney, New York and Boston.

There are differences of opinion among experts regarding the dynamics and effects of "global warming" due to the complexity of natural phenomena that might be operating simultaneously. More accurate future climatic projections will be possible with better super-computer models, based on greater understanding of the complex natural climatic forces involved. But until that time, the possible devastating effect due to "global warming" by the greenhouse effect cannot be underestimated. Some of the steps suggested to minimise the greenhouse effect include reduction in the use of fossil fuels, encouraging the use of alternative sources of energy (*e.g.* solar, geothermal, wind, bio-gas, etc.). Conservation of forests, extensive afforestation, encouraging community forestry, reduction in the use of automobiles, research in development of more efficient automobiles engines, ban on CFC's and nuclear explosions, development of environmentally compatible technologies with the help of intensive inter-disciplinary research, effective check on the growth of population and imparting of non-formal and formal environmental education.

Climate change

Though climate is an average weather of an area or environmental factors of an area. These include quantity of light, temperature, humidity, wind, gases, water, etc. which average for about 30 yrs. Thus the changes in environmental conditions of an area over long period of time is called climate change. These changes effect the agriculture, migration of animals, hydrological cycle, thermal gradient between the poles and equator, wind pattern, distribution of rainfall, etc.

The scientific and technological revolution has given multiple facilities to mankind, but at the same time man-made (anthropogenic) activities are responsible for depletion of resources and upsetting the delicate balance between the various components of the environment. They are, excessive use of fossils fuels, deforestation, and desertification, loss of fertility of soil, rapid industrialization, and increase of automobiles. Changes in the atmosphere conditions resulting in to serious problems like greenhouse effect, depletion of ozone layer and rise of world temperature, etc.

The global change in temperature will not be uniform everywhere and will fluctuate in different regions. The places at higher latitudes will be warmed up more during late autumn and winter than the places in tropics. Poles may experience 2 to 3 times more warming than the global average, while warming in tropics may be only 50 to 100° C on an average. The increased warming at poles will reduce the thermal gradient between the equator and high latitude regions, decreasing the energy available to the heat engine that drives the global weather machine. This will disturb the global pattern of winds and ocean currents as well as the timing and distribution of rainfall. Shifting of ocean currents may change the climate of iceland and Britain, it may result in cooling at a time when rest of the world warms.

4.5.1 Greenhouse Gases

The greenhouse gases present in the troposphere and resulting in an increase in the temperature of air and the earth are discussed here.

- **Carbon dioxide (CO_2):** The CO_2 is considered as the most dominant factor responsible for the greenhouse effect. The troposphere contains only 00.0375% CO_2 (by volume) and its amount is controlled by carbon cycle. The four major pools or reservoirs of carbon are fossil fuels, the atmosphere, the biosphere and the oceans. Its concentration in atmosphere has increased from 290 PPM (1860) to 350 PPM (1990) and is expected to be 700 PPM in 2010. It was studied that in 1976 the world consumption of about 5000 million tons of fossil fuels per year was contributing the equivalent of 2.3 PPM of CO_2 to the atmosphere. The net annual increase of CO_2 in the air is 0.77 ppm which indicates that 1.60 ppm of fuel generated CO_2 is being absorbed elsewhere. In last couple of decades the fossil fuels may to have contributed more CO_2 to the atmosphere than the terrestrial biosphere. Clearance of forests is another factor for the increase of CO_2.

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- **Chlorofluorocarbons (CFCs) :** The main source of CFCs include leaking air conditioners and refrigerators, evaporation of industrial solvents, production of plastic foams, aerosols, propellants (CFC-11), etc. The concentration of CFCs is rising nearly 5% per year. CFCs trap heat 20,000 times more efficiently than CO_2 and also destroy ozone layer, thus posing a serious twofold environmental problem. CFCs are responsible for 14 – 24% of global warming. It is said (Dickson and Cicerone 1986) that by the end of year 2050 they alone could contribute more than CO_2 to global warming.
- **Methane (CH_4)**: It is produced in a number of ways including the action of anaerobic bacteria on vegetation, decomposition of organic matter, incomplete combustion of vegetation, natural gas pipeline leaks, burning of biomass during production and uses of oil and natural gas and petroleum oil, etc. It is rising approx. 2% every year. It absorbs 20 – 25% times more heat than CO_2.
- **Nitrous oxide (N_2O)**: It is released from nylon products, from burning of biomass and fuels (especially coal). From breakdown of fertilizers in soil, livestock wastes and nitrated contaminated ground water, nylon products etc. It is responsible for about 6% of global warming. Besides trapping heat in the troposphere it also depletes ozone in the stratosphere. It absorbs about 250 times more heat than CO_2. The N_2O concentration in atmosphere is 0.3 ppm and is increasing 0.2% annually.
- **Ozone**: It comes mostly from hydrocarbons and nitrogen oxides. It causes irritation to eyes and respiratory organs. It decreases the resistance power to infections and aggravates illness.

4.5.2 Global Warming

The average global temperature is 15°C. The lower most layer of atmosphere i.e., troposphere, traps the heat by a natural process due to the presence of certain gases called greenhouse gases. They are carbon dioxide, ozone, methane nitrous oxide, chlorofluorocarbons (CFCs) and water vapours. In absence of these gases the temperature (15°C) would have been –18°C. Thus warming of the earth's climate owing to the increased concentration of greenhouse gases is called greenhouse effect. Therefore, this effect contributes a temperature rise to the tune of 33°C. These gases act like the glass in the botanical greenhouse trapping the reradiated heat near the earth's surface and warming the planet. These gases along with water vapour and clouds absorbs the infrared radiation, trapping heat near the earth's surface. The two predominant greenhouse gases— (i) the water vapours whose level in the troposphere has relatively remained constant is controlled by hydrological cycle while (ii) CO_2 whose level has increased is controlled by the global carbon cycle. Other gases whose levels have increased due to human activities are methane, NO and CFCs. Deforestation has also elevated levels of

CO_2. Change the temperature by more than 2°C is disastrous for various ecosystems on the earth including man. Some areas will become inhabitable because of drought or floods following a rise in average sea level.

Impact of global warming

Following are the impacts of global warming:

(i) **Climatic change (Increase in global temperature):** Increase the level of greenhouse gases causes the global warming have affected the global climate. This effect will increase in future. According to IPCC (1996) the world climate has warmed from 0.3 to 0.6°C during the last century. Over the next century GHGs will increase further by 1°C – 3.5°C December 03 report has predicted the global warming would be 5.5°C higher by 2100 AD. It seems likely that many species will be unable to adjust quickly to global warming and associated climatic change. As a result, biological communities may suffer profoundly. More than 10% of the plant species will not be able to survive. The climatic change also effects rainfall, species composition, plant reproduction cycles and biogeochemical cycles.

(ii) **Effect on sea levels**: Rising temperatures will cause glaciers to melt and the polar ice caps to shrink. As a result sea level may rise by 0.2 – 1.5 m over the next 50 – 100 yrs. It is proved that sea level have already risen by 10 – 25 cm. If it continues, many low lying areas may be submerged in near future, and it is possible to destroy 20% - 80% of the coastal wetland. Rising sea levels are detrimental to coral reef species, which grow at a precise depth with optimum temperature and water movement. Abnormally high water temperatures in the Pacific Ocean during 1982 – 83 caused the death of symbiotic algae that live inside the coral.

(iii) **Reduction of biodiversity:** As we have discussed, increased temperatures, inundation of some coastal biological communities and changes in the pattern of distribution of many species over a long period of time are likely to cause reduction in biodiversity in aquatic and terrestrial ecosystems.

(iv) **Effect on agriculture:** There are different views regarding the effect of global warming on agriculture. It may be positive or negative. However, the effects of this change will vary for C_3 (i.e. wheat, rice and beans) and C_4 (e.g. maize, millet and sugarcane) plants. As temperature increase with rising CO_2 level, some crops may no longer be grown in certain regions. With rise in temperature soil moisture will decrease and evapo-transpiration and pest growth will increase. This will effect certain crops. With increased CO_2 concentration some plants will show increased photosynthesis, greater root production, and increased nitrogen fixation in root nodules which may increase the growth of plants by 30%.

(v) **Effect on human health**: The global warming will lead to changes in the rainfall pattern in many areas, thereby effecting the distribution of vector borne diseases like malaria filariasis, elephantiasis, etc. Warmer temperature and more water stagnation would favour the breeding of mosquitoes, snails and some insects, which are vectors of such diseases. Higher temperature and humidity will increase respiratory and skin diseases. Keeping in view of ill effects of global warming UNEP (United Nations Environmental Programme) is celebrating 5th June as 'World Environmental Day' every year since 1989.

(vi) **Effect on Arctic ecosystems:** Global climate change will have profound effects on arctic ecosystems. Tundra is more sensitive to global climate change than most other ecosystems on earth. According to Shaver *et al.*, 1992 warmer temperature may increase primary production, thereby increasing Carbon input and soil respiration hence increasing carbon output.

(vii) **Ecological disturbance:** Global warming increases the desert. It increases temperature in North America, South Africa, Mexico, India and other countries. Changes of hurricanes, cyclones and floods will be more which will damage the lagoons, estuaries and coral reefs. Global warming may cause extinction of more than one million species of animals and plants by 2050 A.D.

Some of the measures to check global warming are as follows:

- Plant more trees (afforestation).
- Control population growth.
- Cut down the current rate of CFCs and fossil fuel.
- Use more non-conventional sources of energy.
- Use methane as a fuel.
- Reduce beef production.
- Remove CO_2 from smoke.
- Use photosynthetic algae to remove atmosphere CO_2.
- Adopt sustainable agriculture.
- Use energy more efficiently.

Check Your Progress

13. List the major sources of CFCs.
14. What is the concentration of N_2O concentration in atmosphere?
15. What is the average global temperature?

4.6 ACID RAIN

The concept of acid rain was first given by a British Alkali Inspector, Robert Angus Smith in 1872. Literally, it means the presence of excessive acids is rain water. The pH of acid rain generally varies from 3 to 6. Acid rain mainly contains H_2SO_4 and HNO_3 and HCl along with weak H_2CO_3. The oxides of sulphur, nitrogen and carbon interact with other components of the atmosphere and form corresponding acids.

Rain is valued by mankind as good crops and abundant water supplies depend fully on plentiful rainfall. Rain is always slightly acidic

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(pH $\simeq$ 5.7) due to the reaction of atmospheric carbon dioxide with water which produces carbonic acid. This amount of acidity is enough to dissolve minerals in the earth's crust and make them available to plants and at the same time not enough acidic to cause damage. The other natural calamities like volcanic eruptions, forest fires, although cause rain acidity, contribute very little to any damage. The greatest threat is the contribution of SO_x, NO_x, etc., due to anthropogenic activities which have disturbed the acid balance and converted the natural mild acidic rain into precipitation with far-reaching environmental consequences. Some of the common sources of oxides are as follows:

- Burning of fossil fuels
- Thermal power plants
- Textile industry
- Steel plants
- Oil refining
- Automobile exhausts
- Explosive industry
- Coal and gas fired furnaces
- Fertilizer industry
- Petroleum refineries

The formation of acid rain in the presence of catalyst such as metal oxide, soot and dust can be represented as,

$$S + O_2 = SO_2$$

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

$$SO_3 + H_2O = H_2SO_4$$

$$SO_2 + H_2O = H_2SO_3$$

(1200 – 1800°C)

$$N_2 + O_2 = 2NO$$

$$NO + \frac{1}{2} O_2 = NO_2$$

$$NO_2 + \frac{1}{2} O_2 = NO_3$$

$$NO + NO_2 = N_2O_3$$

$$NO_2 + NO_3 = N_2O_5$$

$$N_2O_3 + H_2O = 2HNO_2$$

$$N_2O_5 + H_2O = 2HNO_3$$

$$C + O_2 = CO_2$$

$$CO_2 + H_2O = H_2CO_3$$

The photochemical reaction also leads to acid formation. For example,

$$NO + O_3 \xrightarrow{h\nu} NO_2 + O_2$$

$$NO_2 + O_3 \xrightarrow{h\nu} NO_3 + O_2; \quad NO_2 + NO_3 \rightarrow N_2O_5;$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Sulphur dioxide present in the atmosphere absorbs the radiation ($\lambda \geq 300 - 400\ \mu m$) and excited state of SO_2^* is formed. This undergoes oxidation to SO_3 and in the presence of H_2O, forms H_2SO_4.

$$SO_2 + h\nu \rightarrow SO_2^* ;\quad SO_2^* + O_2 \rightarrow SO_4^*;$$

$$SO_4^* + O_2 \rightarrow SO_3 + O_3;\quad SO_3 + H_2O \rightarrow H_2SO_4$$

The formation of acid rain might also occur through free radical such as,

$$SO_2 + OH^{\lambda} \rightarrow HOSO_2^{\lambda};\quad HOSO_2^{\lambda} + O_2 \rightarrow SO_3 + HO_2^{\lambda}$$

HO_2^{λ} radical can react with NO to return as initiator OH^{λ} and SO_3 reacts with H_2O to form H_2SO_4, i.e., $SO_3 + H_2O = H_2SO_4$.

In the stratosphere, NO_2 may react with HO^{λ} free radical and form HNO_3.

$$NO_2 + HO^{\lambda} \rightarrow HNO_3$$

It is to be noted that the acid rain also contains hydrochloric acid. Hydrochloric acid gas exposed to the atmosphere may be from oxidation of organochlorine compounds and the polyvinyl chloride in plastics and also the chlorine gas exposed to the atmosphere from chemical plants, textile industry which are photodissociated by UV rays and reacts with methane in the atmosphere to form hydrochloric acid and becomes a component in acid rain. The contribution of the acids in the 'acid rain', are in the order of $H_2SO_4 > HNO_3 > HCl$. The acid so formed can be deposited in the following two ways:

- **(*i*) Dry deposition:** In this case, the oxides which escape into the atmosphere react with water vapours to form corresponding acids and rapidly become particles by condensing on particles that exist in the atmosphere and are removed continuously in a slow process without precipitation and fall back directly to the ground around the emission point.
- **(*ii*) Wet deposition:** In this case, the oxides which escape into the atmosphere react with water vapour to form corresponding acids and merge on water vapours to form $H_2O - H_2SO_4$ droplets and then fall back onto the ground.

Some of the adverse effects of acid rain are discussed below:

(i) On aquatic biota

- Many aquatic species disappear due to the acidification of lakes.
- Acid rain reduces the production of phytoplankton in the lake.
- Many bacteria and blue-green algae are killed due to acidification.
- Activity of bacteria and many other microscopic animals is reduced in acidic condition. The result being that the dead materials and many other accumulated materials lying at the bottom of the lakes are not decomposed rapidly. Many essential nutrients like nitrogen and phosphorus are locked up and less available for use.

(ii) On terrestrial eco-system

- Leaves of plants and trees are damaged and become yellow and brown, retarding photosynthesis.
- Acid rain weakens the structure of trees, thereby making it vulnerable to pathogens.

- The reduction in photosynthesis results in reduced agricultural productivity.
- Many essential nutrients like Ca, Mg, S, Fe, Mo and Co are leached out due to acid rain, hampering productivity. Due to solubilization of aluminum, nutrient imbalance in plants occurs.

(iii) On buildings

- Acid rain causes severe damage to buildings and structural materials of marble, limestone, etc. For example,

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

(lime stone)

- Acid rain attacks monuments, statues, bridges, etc. This is one of the reasons why the *Taj Mahal* is in danger.

(iv) On human beings

- Solubilization of heavy metals like Cd, Hg, and Cr due to acid water may reach human body via the plants and animal in the food chain or through drinking water supplies.
- Acid rain causes respiratory and skin diseases and may attack nervous system in the extreme case.

Measures for acid rain

Following are the measures to control acid rain:

- Short term control of acid deposition problem can be achieved by using lime (CaO).
- The major step that can be taken is to reduce acid forming gas like NO_x and SO_2 and if possible, to stop it. This can be achieved by introducing pollution controlling devices in the factories, industries, recovering pollutant gases and reusing them in other form such as NO_2 as HNO_3 and SO_2 as H_2SO_4.
- General public awareness should be created regarding the ill effects of environmental pollution and consequences of acid rain.

Check Your Progress

16. Who introduced the concept of acid rain?
17. Mention the ways in which acid deposition occur.

4.7 AIR POLLUTANTS CONTROLS AND THEIR CHEMISTRY

Pollution of air in the atmosphere cannot be fully abated but can be controlled if certain measures are taken.

- Develop people's awareness in all spheres including the governments.
- Free burning of wood, coal, wastes of forests, agricultural wastes and many other solid matters must be stopped at open places.

- Vehicular emissions must be checked periodically.
- Use of natural gas or low sulphur containing fuels should be encouraged in place of petrol and diesel.
- Industries must adopt waste gas treatment facility before releasing it to air.
- Lead free petrol should be introduced to control lead pollution.
- All sorts of waste materials must be disposed properly.
- Large importance should be given to utilize solar energy.
- Use of chlorofluorocarbons or other toxic materials must be reduced or substituted.

4.7.1 Analytical Methods for Measuring Air Pollutants

The determining factor of air quality at a given site is weather, the wind speed, its direction, temperature profile, solar radiation, humidity, atmospheric pressure, etc. The study of the dynamics of atmosphere, which ultimately govern the air quality at a given site, is known as meteorology.

Ambient Lapse Rate (ELR)

The rate of change in air temperature with altitude is called lapse rate. When a packet of air moves upward in the atmosphere, it experiences less pressure and hence it expands and cools down (expansion is done at the cost of internal energy of the air molecules and hence it cools down) and the surrounding air gains heat and becomes little hotter. On the other hand, when the packet moves down, more pressure will compress the air in the packet and its temperature will increase, consequently the surrounding air will be little cooler. This rate of change in air temperature with altitude or the lapse rate is known as Ambient Lapse Rate or Prevailing Lapse Rate and is also known as Environmental Lapse Rate. The Ambient Lapse Rate (ALR/PLR/ELR) differs from place to place, time to time even at the same place and depends on wind speed, geographical factors and sunlight. Experimentally, this can be measured by sending a balloon equipped with a thermometer and measuring temperature at different altitudes.

Adiabatic Lapse Rate (ALR)

When a packet of air moves upward in the atmosphere, it experiences less pressure and hence, expands and cools down and the surrounding air gains heat and becomes little hotter. Now, if we assume that as the packet moves, there is no heat transferred across its boundary, the process is adiabatic. Under this condition, the lapse rate is called adiabatic lapse rate (ALR).

The ease with which pollutants can disperse vertically into the atmosphere is largely determined by the rate of change in air temperature with altitude (Lapse rate). For some temperature profiles, the air is stable, *i.e.*, air remains stagnant at a given elevation and thus discourages dispersion and dilution of the pollutant. For some temperature profiles, the air is unstable and under such conditions there is rapid vertical mixing which encourages pollutant dispersal and increases air quality.

The relationship between atmospheric stability and temperature can easily be found out through a simple designed experiment. Let us imagine a packet of air with imaginary boundary that is moving up. This can be compared to a situation in which the air is enclosed in a cylinder and pressure is created by a piston or on the piston by the surrounding air.

Now assuming the air molecules to behave ideally, we can apply the first law of thermodynamics (the packet of air acting against the piston which is the surrounding air above it and heat is being drawn up from the surroundings while going up; the work is done by this packet of air).

$$dQ = dE + dW = dE + PdV$$

where,

dQ = heat added or drawn from the surrounding.

dE = change in the internal energy of the moving packet of air molecules.

dW = the work done by the packet of air to lift the surrounding air up.

P = constant atmospheric pressure against which the packet of air works.

dV = the change in the volume from initial to final.

Now we know, $dE = C_v\, dT$

where, C_v is the specific heat at constant volume, and dT is the change in the temperature of the air packet.

For ideal gas,

$$PV = RT \text{ (one mole of gas)}$$

or $$d(PV) = d\,(RT) = RdT$$

or $$PdV + VdP = RdT$$

or $$PdV = RdT - VdP$$

Hence,

$$\begin{aligned} dQ &= dE + PdV = C_v dT + PdV \\ &= C_v dT + RdT - VdP \\ &= (C_v + R)\, dT - VdP \\ &= C_p dT - VdP \end{aligned}$$

dP is the pressure change in the packet and C_p is the heat capacity at constant pressure.

Under adiabatic condition,

$$dQ = 0$$

Hence,

$$C_p dT - VdP = 0 \quad \text{or} \quad C_p dT = VdP$$

or $$\frac{dT}{dP} = \frac{V}{C_p}$$

The relationship shows how the atmospheric temperature would change with air pressure. Now, we would like to find out how atmospheric temperature changes with the altitude.

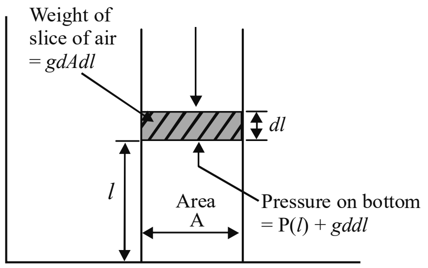


Fig. 4.2 Relationship between Air Pressure and Altitude for a Column of Air in Static Equilibrium.

Consider a static column of air with cross-sectional area *A*. Now, a horizontal slice of air placed at a height of *l* cm from the base in a column with thickness *dl* and density *d*, will have the mass *dAdl*. For air to be static at a given height, internal pressure and external pressure must be equal. The internal pressure (pressure on the bottom of slice) is the atmospheric pressure *P* (1 + *dl*) plus the pressure of the slice *P* (*dl*) due to its weight. Thus,

$$P(l) = P(l + dl) + P(dl)$$

Mass of the slice is *d.A.dl*

The pressure *P* (*dl*) exerted by the slice of air,

$$= \frac{\text{Force}}{\text{Area}} = \frac{d.A.dl.g}{A} = d.dl.g$$

(g = acceleration due to gravity)

Hence,

$$P(l) = P(l + dl) + d.dl.g$$

The incremental pressure dP for an incremental change in elevation *dl* is,

$$dP = P(l + dl) - P(l) = -\,d.dl.g$$

or $$\frac{dP}{dl} = -\,d.g$$

$$\therefore \frac{dT}{dl} = \frac{dT}{dP} \times \frac{dP}{dl} = \frac{V}{C_p} \times -\,dg$$

Now, $V.d$ = mass and for unit mass of gas slice $V.d = 1$ and

$$\frac{dT}{dl} = \frac{-\,g}{C_p}$$

The negative sign indicates that temperature decreases with increasing altitude. Now putting the values of g and C_p

$$= \frac{-\,9.8/\text{m}/\text{sec}^2}{1{,}005\text{J}/\text{kg} - {}^\circ\text{C}} = \frac{-\,9.8\,\text{m}/\text{sec}^2}{1{,}005\left(\text{kg.m}^2/\text{sec}^2\right)/\text{kg} - {}^\circ\text{C}}$$

$$(\because 1\text{J} = 1\,\text{kg. m}^2/\text{sec}^2)$$

The equation predicts that the packet of dry air either up or down will cause its temperature to change by 9.76°C/km or roughly 10°C/ km. This temperature profile if be made reference against which actual ambient air temperature profile is to be compared then a good idea about the stability, instability of the atmosphere can be achieved. Thus, if the actual air temperature decreases faster with increasing elevation than the adiabatic lapse rate, the air will be unstable and rapid mixing and dilution of pollutants will occur. On the other hand, if the actual air temperature drops more slowly than the adiabatic lapse rate, the air will be stable and air pollutants will concentrate.

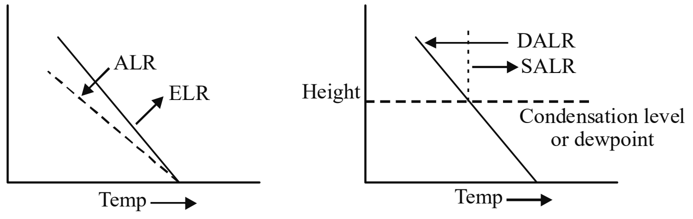
Dry Adiabatic Lapse Rate (DALR)

When the packet of moving air is dry and the temperature is more than the dew point (the temperature at which dew is formed), the adiabatic lapse rate is called Dry Adiabatic Lapse Rate (DALR). The Dry Adiabatic Lapse Rate (DALR) is constant. DALR is constant at – 9.76°C/km.

Saturated Adiabatic Lapse Rate (SALR)

When the packet of moving air contains a very small amount of moisture in it, then C_p change is negligible. On the other hand, if the air is saturated with moisture and temperature is less than the dew point, the adiabatic Lapse Rate is called Saturated Adiabatic Lapse Rate or Wet Adiabatic Lapse Rate (SALR). As the air is saturated with moisture, the movement which leads to cooling, condensation of water vapours occurs, releasing latent heat and the air packet will not cool as rapidly as happened with the dry one. Saturated adiabatic lapse rate is not constant since the amount of moisture that air can hold before condensation begins is a function of temperature. The average value of saturated adiabatic lapse rate in the troposphere is about – 5.4°C/km.

The packet of air moving into the atmosphere is neither absolutely dry nor fully saturated with moisture. The ALR therefore, lies between – 9.76°C/ km and – 5.4°C/km.



(a) (b)

Fig. 4.3 *(a) Graphical Representation of ELR and ALR*
(b) Graphical Representation of DALR and SALR

Atmospheric stability

Atmospheric stability is important because it determines the ability of pollutants to disperse vertically into the atmosphere and its ability to dilute pollution. Difference between the Ambient Lapse Rate and Adiabatic Lapse Rate determines the stability of the atmosphere. There are three different cases of atmospheric stability:

(i) When ELR > ALR, then the atmosphere is unstable, *i.e.*, when the internal temperature of the air packet is higher than the surroundings, its density becomes lower and it keeps on going up.

(ii) When ELR < ALR, then the atmosphere is stable, *i.e.,* internal temperature of air packet is lower than the surroundings, its density becomes higher and it goes down.

(iii) When ELR = ALR, then the atmosphere is neutrally stable, *i.e.,* internal temperature of air packet is same as that of the surroundings, it experiences no forces that can make it continue its motion.

Sub-adiabatic lapse rate/sub-adiabatic condition of atmosphere

When ELR < ALR, the atmosphere is said to be stable and this prevailing lapse rate is called sub-adiabatic lapse rate. Under sub adiabatic condition, dissipation of pollutant into the atmosphere will be slower than the unstable condition.

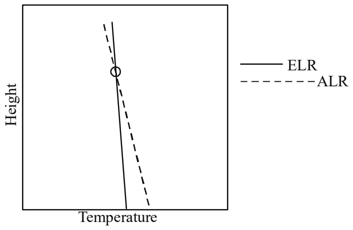


Fig. 4.4 *Sub-Adiabatic Lapse Rate.*

Super adiabatic lapse rate/ super adiabatic condition of atmosphere

When ELR > ALR, *i.e.,* the rate of cooling is faster than theoretical ALR, the condition of atmosphere under such circumstances is called super adiabatic condition of atmosphere. This condition is helpful in the dissipation of pollutants into the upper atmosphere and hence, eliminates air pollution problems.

On a clean summer day, rapid heating of the earth by the sun warms the air near the surface and the lapse rate is super adiabatic. Under this condition, the atmosphere is under unstable equilibrium and results in vertical mixing of air. Under this condition, pollutants are rapidly dispersed.

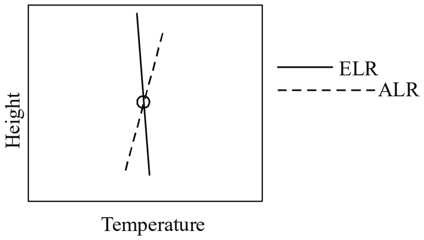


Fig. 4.5 *Super Adiabatic Lapse Rate*

Temperature inversion

Under normal situation, the temperature of air decreases with increasing altitude. In an unusual case, the temperature may increase with increasing altitude. This is known as temperature inversion. Under such condition, the lapse rate becomes inverted or negative from its normal state. This is called negative lapse rate. Temperature inversion represents the extreme cases of atmospheric stability, restraining upward movement of pollutants. Three important causes of temperature inversion are as follows:

(*i*) **Radiation inversion:** During the day, the sun heats the earth and air near it. At night, the ground and the air near it cool faster than that high up, creating an inversion. This is more prominent in winter. Radiation inversions generally start at dusk and with the progress of evening the inversion extends to a higher and higher elevation. At evening, the pollutants thus, get concentrated near the ground level. Without sunlight the photochemical reactions cannot occur and the biggest problem is the accumulation of carbon monoxide (CO). In the morning when the sun rises, inversion starts breaking up, although it may persist for few days in cold and cloudy weather and the pollutants that were trapped in the stable air mass are suddenly brought back to the earth through a process known as fumigation.

(*ii*) **Subsidence inversion:** Subsidence inversion is associated with anticyclones (high pressure weather system). This kind of inversion results when the upper layer of air descends (subsides) during a developing anticyclone. The high pressure compresses the upper layer of air, thereby heating it. The lower layer of air on the other hand, is relatively colder and denser. This cold air cannot rise up due to the lack of any driving force and the atmosphere becomes stable. Thus, in this case of high level inversion, the lower inversion layer forms a lid for pollutants, causing them to accumulate and raise their concentration. Thus, if the subsidence inversion lasts for a long time, it will create a serious air pollution problem.

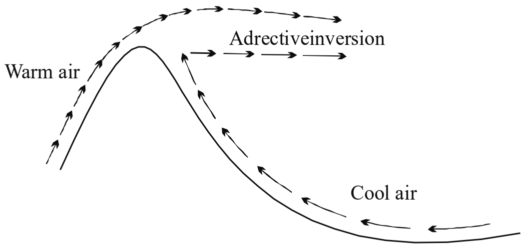


Fig. 4.6 *Development of Advective Inversion*

(*iii*) **Advective inversion:** This type of inversion occurs when warm air moves over cold air or a cold surface. Elevated advective inversion occurs when a hill range forces a warm land breeze to flow at high levels and a cool sea breeze flows at low levels in just the opposite direction.

Maximum mixing depth

The amount of air available to dilute pollutants depends on the wind speed as well as the extent to which the emissions can rise into the atmosphere. The emitted flue gas, being warmer and lighter than the surrounding air moves up. As it moves up, it may get cooled adiabatically at about 10°C/ km. The warmer flue gas will move up to the height where its temperature and density become equal to that of surrounding air. This height is known as maximum mixing height or maximum mixing depth.

The maximum mixing depth can be obtained simply by plotting ELR and ALR in a graph. The vertical distance from the point of intersection to the base is called the maximum mixing depth.

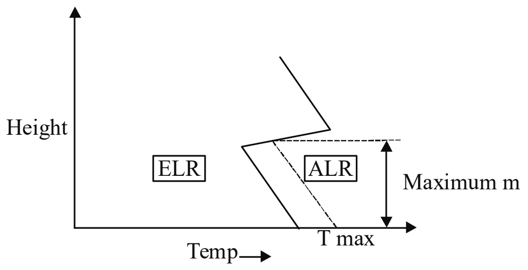


Fig. 4.7 *Maximum Mixing Depth*

Ventilation coefficient

The product of the maximum mixing depth and the average wind speed in a region is called ventilation coefficient. Sometimes, this is used as an indicator of the atmosphere's dispersive capability. Ventilation coefficient less than 6000 m^2/s, is considered to be a bad condition for dispersion of pollutants.

The direction and speed of wind determines the drift and diffusion of polluted gases. The higher the wind speed at or near the point of emission, the greater will be the dispersion of pollutants from the source. If, however, the wind speed is low, the pollutants will concentrate near the area of their emission, indicating poor dispersion. Wind speed and concentration of pollutants are thus, inversely proportional to each other. However, the simple relationship may get jeopardized by the humidity, geographical condition of a place and atmospheric stability and turbulence, etc.

4.7.2 Continuous Monitoring Instruments

Environmental monitoring describes the processes and activities that are essential for characterising and monitoring the quality of the environment. Principally, the term 'Environmental Monitoring' is specifically used for preparing and assessing or measuring the environmental impact and also in different circumstances or situations associated with human activities that cause risk of harmful effects on the natural environment. All the monitoring strategies and programmes have specific reasons and justifications that are precisely designed for establishing the current status of an environment or to establish trends in environmental parameters. For all the circumstances or situations, the results of environmental monitoring has to be reviewed and statistically analysed before it is published. Therefore the designing of an environmental monitoring programme is precisely and carefully done, before the monitoring starts, for the collection of data.

Environmental monitoring methodology is used for measuring and recording the essential measurements that are required for assessing or evaluating the status of an environment. However, for obtaining robust results the methodology and analysis used in environmental monitoring must be pre-defined including the objectives of sample collection strategies. Furthermore, the objectives, plans and strategies of environmental data collection methods must be in conjunction with the target environment, including the physical, chemical and biological variables and any other significant feature that is relevant for the study. Sometimes the environmental monitoring plan can also be developed on the basis of existing information.

Following are the three significant components that are associated with the environmental monitoring:

- **Purpose:** Assess the status of an environment that changes spatially and temporally.
- **Objective:** Define and measure physical, chemical, and biological states, attributes, and processes.
- **Approach:** Collect and analyse a subset of samples (units) that represent the target environment in space and time.

Environmental monitoring is, therefore, the close observation and comprehensive study of the environment. The data obtained after the study of environment monitoring is typically used in risk assessment for creating methodologies of environmental regulations. However, the analysis and interpretation of data for monitoring the environment hazards is critical in making decisions about the possible health risks and corrective actions. Risk assessment methods help in estimating the risks responsible for health effects and diseases caused due to exposure to harmful chemicals and microorganisms that are present in the environment. Environment management is principally referred as a science that manages the environment appropriately, proficiently and efficiently. It includes rational, stable and balanced use of natural environment resources. The government of all developed countries and most of the developing countries have their government departments or agencies that are typically dedicated to monitor and protect the environment.

The environment monitoring and quality management is done using the following methods.

Air quality monitoring

Air pollutants are the atmospheric substances which may potentially have a negative impact on the environment and organism health. Principally the air pollutants include both naturally occurring and anthropogenic substances. Due to the evolution and development of new chemicals and industrial processes there is extreme rise or elevation of pollutants in the atmosphere, which can be life threatening. Hence, it has become essential to monitor the air quality which is typically being done through the environmental research and regulation programs.

Air quality monitoring is a challenging task as it involves the effective integration of multiple environmental data sources, which generally originate from different environmental networks and institutions. These challenges require specialized observation equipment and tools for establishing air pollutant concentrations, including Sensor Networks, Geographic Information System (GIS) models, and the Sensor Observation Service (SOS), a web service for inquiring real-time sensor data. There are specific air dispersion models that combine topographic, emissions, and meteorological data for predicting air pollutant concentrations are also sometimes helpful in interpreting air monitoring data. Additionally, the anemometer data that is collected in the area between sources and the monitor can also be considered as it provides insights on the source of the air contaminants recorded by an air pollution monitor. Figure 4.8 illustrates the model of an air quality monitoring station.

Fig. 4.8 *Air Quality Monitoring Station*

Air quality monitors are regularly functioning and are operated/monitored by citizens, regulatory agencies, and environmental researchers for investigating air quality and the effects of air pollution. Interpretation and analysis of ambient air monitoring data normally considers the spatial and temporal representativeness of the collected/gathered data, and also the health effects associated with exposure to the monitored levels.

Air sampling

The air sampling can be either ‘Passive’ or ‘Diffusive’. Basically, the air sampling depends on meteorological conditions, such as wind to diffuse air pollutants to a sorbent medium. Passive air samplers are considered as less harmful because of typically being small, quiet, and easy to deploy, also they are particularly useful in air quality studies for determining key areas for future continuous monitoring.

Air pollution can also be assessed, measured or evaluated through biomonitoring with organisms that bioaccumulate the air pollutants, such as Lichens, Mosses, Fungi, and other Biomass. One of the key benefits of this type of sampling is that how quantitative information can be obtained through measurements and quantities of accumulated compounds, which are the characteristic representative of the environment from which they originated. However, a guarded and careful considerations are essential while choosing or selecting the particular organism of the biomass, how it is dispersed and what is its relevance/significance to the pollutant. Some other sampling methods are also used which include the use of a denuder, needle trap devices, and micro-extraction techniques.

Check Your Progress

18. Mention any two ways of controlling air pollution.
19. What does SALR stand for?
20. Mention three important causes of temperature inversion.

NOTES

4.8 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The phenomenon, called "the greenhouse effect", keeps the earth warm enough to sustain life on the earth.
2. The major component of the air are nitrogen, oxygen and water vapour.
3. The UV radiations from the sun are mostly responsible for the formation of the ionic species in ionosphere.
4. Polycyclic aromatic hydrocarbons (PAH) are generated from the pyrolysis of higher paraffin present in fuels and in some vegetable matter.
5. The oxides of nitrogen present in the atmosphere are N_2O, NO and NO_2.
6. Photochemical smog is initiated by the photochemical dissociation of NO_2.
7. In the stratosphere, NO_2 may react with the HO• free radical, forming HNO_3.
8. 'Smog' is the combination of smoke and fog.
9. Depending upon the compositions and the methods of formations, smog is of two types—London smog or sulphurous smog and photochemical smog.
10. An example of a secondary pollutant is ground level ozone (O_3).
11. Carbon monoxide combines with haemoglobin, the oxygen carrier of the blood in the body, to form carboxy haemoglobin, a stable compound. The oxygen transportation is thus, disturbed and in extreme cases it can be fatal.
12. It is a reddish brown gas and exists at room temperature.
13. The main source of CFCs include leaking air conditioners and refrigerators, evaporation of industrial solvents, production of plastic foams, aerosols, propellants (CFC-11), etc.
14. The N_2O concentration in atmosphere is 0.3 ppm and is increasing 0.2% annually.
15. The average global temperature is 15°C.
16. The concept of acid rain was first given by a British Alkali Inspector, Robert Angus Smith in 1872.
17. The acid formed in acid rain can be deposited in two ways (i) dry deposition (ii) wet deposition.
18. The ways of controlling air pollution are
    (a) Vehicular emissions must be checked periodically
    (b) Large importance should be given to utilize solar energy.
19. SALR stands for saturated adiabatic lapse rate.
20. The three important causes of temperature inversion are radiation inversion, subsidence inversion and advective inversion.

4.9 SUMMARY

- The atmosphere plays a vital role in maintaining the heat balance on the earth by absorbing the radiation received from the sun and re-emitted by the earth.
- Any major disturbance in the atmospheric composition, either by extraordinary or anthropogenic activities, may lead to disastrous consequences or may even endanger the very survival of life on the earth.
- The various chemical species present in atmosphere are ions, radicals, particles,
- The atmosphere, which extends up to about 500 km above the earth's surface, can be broadly divided into four major regions, namely troposphere, stratosphere, mesosphere and thermosphere.
- The various chemical and photochemical reactions taking place in the atmosphere, mostly depend upon the temperature, composition, humidity and intensity of sunlight.
- The oxides of nitrogen present in the atmosphere are N_2O, NO and NO_2. The most important primary photochemical reaction is the dissociation of NO_2.
- Sulphur dioxide, present in the atmosphere, absorbs solar radiation in the range of 300–400 nm and produces electronically excited states of SO_2.
- Organic compounds such as hydrocarbons, aldehydes and ketones absorb solar radiation and undergo various photochemical and chemical reactions involving free radicals.
- 'Smog' is the combination of smoke and fog. The name was so given because the fog in the atmosphere condenses on the carbon particles of the smoke to form smog.
- The factors responsible for formation of smog are: (1) inversion of temperature (2) mixing of the polluted gases emitted from industries and motor vehicles with foggy air.
- There are six pollutants which have the main contribution in creating air pollution. They are primary pollutants like carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen dioxide (NO_2), lead (Pb) and particulate matters (PM) and secondary pollutants like ground level ozone (O_3).
- There are different sources of pollution such as chemicals, petroleum, minerals and chlorofluorohydrocarbons.
- The gases that are responsible for this greenhouse effect are CO_2, water vapour, CH_4 and man-made chloroflourocarbons (CFCs).
- The study of the dynamics of atmosphere, which ultimately govern the air quality at a given site, is known as meteorology.

- The pH of acid rain generally varies from 3 to 6. Acid rain mainly contains H_2SO_4 and HNO_3 and HCl along with weak H_2CO_3. The oxides of sulphur, nitrogen and carbon interact with other components of the atmosphere and form corresponding acids.
- The rate of change in air temperature with altitude is called lapse rate.
- Atmospheric stability is important because it determines the ability of pollutants to disperse vertically into the atmosphere and its ability to dilute pollution.
- Under normal situation, the temperature of air decreases with increasing altitude.
- Three important causes of temperature inversion are: (i) radiation inversion (ii) subsidence inversion, and (iii) advective inversion.
- The amount of air available to dilute pollutants depends on the wind speed as well as the extent to which the emissions can rise into the atmosphere.
- Air pollutants are the atmospheric substances which may potentially have a negative impact on the environment and organism health.
- The air sampling can be either 'Passive' or 'Diffusive'. Basically, the air sampling depends on meteorological conditions, such as wind to diffuse air pollutants to a sorbent medium.
- Environmental monitoring is a tool used for assessing environmental conditions and trends, to support policy development and its implementation, and to develop information for reporting to the government officials, national policymakers, international forums, etc.

4.10 KEY TERMS

- **Atmosphere:** It is defined as a layer of gases that surrounding the planet.
- **Smog:** It is a kind of air pollution that consists of nitrogen oxides, sulfur oxide, ozone, smoke and other particulates.
- **Chlorofluorocarbons (CFCs):** These compounds are fully or partly halogenated paraffin hydrocarbons consisting of carbon (C), hydrogen (H), chlorine (Cl), and fluorine (F) which are produced as volatile derivatives of methane, ethane and propane.
- **Air Pollution:** It refers to any physical, chemical or biological change in the air.
- **Greenhouse Effect:** It refers to a process which keeps the atmosphere of the earth warm by absorbing radiations.

4.11 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. How is photochemical smog formed?
2. What are the effects of pollution caused by chemicals?
3. Mention some of the common sources of oxides that cause acid rain.
4. How can air quality be monitored?

Long-Answer Questions

1. Discuss the mechanism of formation of PAN and O_3.
2. Explain the major six pollutants and their oxides.
3. Describe the greenhouse effect and its impact on global warming in detail.
4. Analyse various analytical methods used for measuring air pollutants.

4.12 FURTHER READING

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UNIT 5 INDUSTRIAL POLLUTION

NOTES

Structure

5.0 INTRODUCTION

Industrial pollution takes numerous forms and has a wide range of effects on the land, water, and environment, as well as inflicting illness and death all over the world. Coal combustion, fossil fuel combustion (petroleum, oil, natural gas), and chemical solvents used in the tanning and dyeing industries are the primary sources of industrial pollution. Furthermore, when fossil fuels such as coal and oil are used to generate energy and transport, pollutants such as carbon dioxide, nitrogen, and sulphur dioxide, as well as fly ash, are released into the air, water, and soil, polluting the environment. In this unit, we will discuss the concept of industrial pollution and its various sources, along with the disposal of waste and their management. It will also focus on the concept of environmental toxicology and various methods to deal with it, along with the various industrial disasters.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Describe the concept of industrial pollution and its various sources
- Explain the disposal of waste and their management
- Discuss the concept of environmental toxicology and various methods to deal with it
- Evaluate the various industrial disasters

5.2 CONCEPT OF INDUSTRIAL POLLUTION

Pollution is defined as the introduction into the environment of any substance that has a detrimental or poisonous effect. Industrial pollution refers to any type of contamination that may be traced back to industrial activities. Industries take raw materials, process them, and make final products, and certain by-products are discarded as industrial waste in gas, liquid, or solid form, polluting the air, water, and soil. Industrial wastes can be categorised into the following categories:

- **Biodegradable waste:** Textile mills, food processing plants, paper mills, and cotton mills all produce biodegradable waste.
- **Non-Biodegradable waste:** Thermal power facilities, iron and steel mills, and fertiliser industries all produce non-biodegradable waste, posing a serious threat to humanity.

5.2.1 Cement Industry

One of the most major causes to air pollution is the cement industry. Around 7% of global carbon emissions are attributed to the cement industry. Particulate matter (PM) emissions from cement facilities are quite high, and cement is widely regarded as the world's most hazardous pollutant. The Indian cement industry is the world's second-largest cement producer. The Indian cement industry, which is dominated by roughly 30 major businesses, has around 210 big and 365 small cement factories. Despite the pandemic, the sector continues to benefit from strong market demand, as India is the world's second largest cement user. The Indian cement business had a turnover of 64,000 crore in the financial year 2020. However, the pollution caused by the cement industry has the potential to be extremely harmful to human life.

Some of the studies on its impact on humans and human-made systems are included below:

- Random tests on cement workers in Bengal and Tamil Nadu revealed that one-fifth of the workforce suffers from ailments such as bronchitis, asthma, and obstructive pulmonary disease, among others.

- According to a recent study in Sri Lanka, which is ecologically and geographically adjacent to India, over 14% of persons living near cement mills suffer from respiratory problems.
- The economic advantages of lower PM emissions from the American cement sector were predicted to vary between 0.76 and 3.97 million USD year in an intriguing study conducted in the United States. The ramifications of such a discovery in India, which produces three times as much cement as the United States, are obvious.

Despite having established pollution control measures, many cement plants' emissions remain high. We occasionally come across news items showing cement companies paying hefty fines in the tens of lakhs, if not millions, or even shutting down factories for breaking pollution regulations. Even if a facility is shut down for a month, it can have a significant influence on a company's revenue and overall efficiency. Dust or particulate matter, NOx, SOx, carbon oxides, and methane are among the pollutants usually released by cement factories. Because cement is a major source of air pollution, it is estimated that 4, 90, 000 people die each year as a result of emissions from the cement sector. Furthermore, emissions from cement plants endanger the lives of nearby flora and fauna.

Unaccounted or 'fugitive' emissions are one of the cement industry's biggest problems. Fugitive emissions are pollutants that are 'fugitive,' meaning they escape from a source without being counted. Regular emissions from recognised sources are accounted for, making tracking and controlling them easy. The source of fugitive emissions, on the other hand, is unclear, making them difficult to track. As a result, they add to undetectable ambient air pollution. The issue of fugitive emissions arises at every level of the cement manufacturing process, posing a significant challenge. Pollution control technology designed to handle ambient air pollution, i.e., air pollution over a vast area, is the only effective method for stopping fugitive emissions. Technology that deals with air pockets is more or less pointless. The device should be able to cover a vast area while also tackling pollutants emitted by unaccounted-for sources.

5.2.2 Sugar Industry

Sugar production has been demonstrated to have a negative impact on the soil, air, and water, according to research. This is especially noticeable in tropical environments close to the equator. Furthermore, research suggests that, when compared to other crops, sugar production is the leading driver of biodiversity damage. This is largely due to its high use of harmful agricultural pesticides, massive release of polluted wastewater, and destruction of numerous habitats for plantations. Unfortunately, due to the enormous rate of sugar production, these impacts are compounded year after year. For example, 145 million tonnes of sugar are produced each year in over 120 nations. And that's before you include in the over 10 million tonnes produced in Asia.

Bagasse is a major contributor to air pollution in the sugar industry. The odd thing is that this industry also employs bagasse as a source of energy. Bagasse is typically used to power boilers in the sugar industry. Pollutants such as sulphur dioxide, carbon monoxide, and nitrogen oxide are released as a result of this process. Apart from that, evaporators and juice fermenting units are other sources of pollution in the air.

Through wastewater, the sugar sector contributes greatly to water pollution as well. These are, in case you're curious. They are a liquid that is produced as a by-product of sugar manufacture. The following are some instances of wastewater:

- Cane wash water is a by-product of the cane washing process.
- Millhouse effluent refers to the waste produced by milling equipment, floor washes, and spill overs.
- Filter press cloth wash water is a by-product of the filter press washing process.
- Effluent from the vaporisation process
- Overflows and leakages from the molasses storage tank are referred to as molasses effluents.

And, in the vast majority of cases, this wastewater is heavy in solids, chloride, nitrate, magnesium, calcium, and sulphate. These compounds can lower the amount of oxygen in water bodies, putting aquatic life at risk. Furthermore, such water bodies become inappropriate for your usage as a result of this concentration. To safeguard the environment from pollution and other hazardous activities, several norms and restrictions exist. These standards and guidelines are generally applicable to the sugar industry. And this is especially true when it comes to its negative effects on the environment. These numerous standards cover maximum emission and discharge limits, as well as the regulation of a wide range of activities. However, it's quite challenging to measure the extent of compliance by sugar factories with these existing norms.

5.2.3 Distillery Industry

Distillery industries are a major contributor to the global economy, but they are also one of the most significant sources of pollution due to the discharge of large amounts of dark-coloured wastewater. The Biological Oxygen Demand, Chemical Oxygen Demand, total solids, sulphate, phosphate, phenolics, and numerous hazardous metals are all very high in this dark-coloured wastewater. Melanoidins, di-n-octyl phthalate, di-butyl phthalate, benzenepropanoic acid, and 2-hydroxysocaproic acid, as well as hazardous metals, are found in distillery wastewater and have been shown to be genotoxic, carcinogenic, mutagenic, and endocrine disruptive in nature. It has major environmental consequences in aquatic resources because it reduces the penetrating power of sunlight, photosynthetic activities, and dissolved oxygen concentration. If discharged without sufficient treatment, it can also inhibit seed germination and depletes vegetation on agricultural land by lowering soil alkalinity and manganese availability.

5.2.4 Drug Industry

Drug pollution, also known as pharmaceutical pollution, is pollution of the environment caused by pharmaceutical medications and their metabolites that enter the aquatic environment through wastewater (groundwater, rivers, lakes, and seas).

As a result, drug pollution is mostly a form of water pollution. Pharmaceutical contamination has been found in waters all around the world. Aging infrastructure, sewage overflows, and agricultural runoff are all contributing factors. Even when wastewater reaches sewage treatment plants, they are unable to extract pharmaceuticals.

Every year, almost 100,000 tonnes of pharmaceutical products are consumed around the world. Active Pharmaceutical Ingredients (APIs) and other chemical ingredients are released into the environment during their manufacture, use, and disposal. A large portion of pharmaceutical production now takes place outside of the United States. This is especially true when it comes to antibiotics and other generic medications. Antibiotic APIs are produced in China at a rate of 80-90 percent, and final dosage products are produced in India. In both China and India, there have been multiple high-profile pollution incidents at antibiotics production plants, leading in the spread of drug-resistant microorganisms. In the EU and other parts of the world, downstream contamination from manufacturing industries has been detected.

Because between 30 and 90 percent of an oral dose is excreted in urine as an active substance, APIs are released in large proportions into the environment. Over 600 distinct APIs have been found in the environment, some at levels that represent a serious risk to the environment, according to a global review. Drugs have also been found in drinking water, waste water, sewage sludge, and soils. APIs' ecotoxicological impacts include impaired reproduction in exposed fish populations, the effects of various antibiotics on environmental bacteria and algae, and the fall of vulture populations owing to diclofenac toxicity while feasting on animal carcasses. Antimicrobial Resistance (AMR), one of the main increasing risks to human health today, is aided by the presence of antibiotics in the environment.

The impact of AMR in terms of lives lost, morbidity, healthcare costs, and productivity losses is substantially higher than currently available numbers show–25,000 deaths in 2007–and forecasts predict a 15-fold rise in morbidity in Europe by 2050, with 390,000 deaths. Despite widespread awareness about the dangers that drugs represent, their release into the environment is mostly unregulated:

- The public and authorities do not have access to information about API's environmental effects.
- Only a small percentage of medications are subjected to environmental risk assessments.
- For API discharges from manufacturing plants, there are insufficient monitoring standards and no defined emission limitations in place.
- There are no restrictions on the amount of pharmaceuticals that can be found in drinking water, surface water, or waste water, including hospital effluents.
- For the most part, there are no explicit regulations governing the disposal of medical waste.

Pharmaceuticals' emissions into the environment must be regulated to ensure adequate information and transparency about their environmental impacts; adequate and reliable evaluation of pharmaceuticals' environmental risks; prevention of pharmaceuticals' environmental releases throughout their life cycle; and control of pharmaceuticals' environmental emissions when prevention is not possible.

5.2.5 Paper and Pulp Industry

The paper manufacturing process mainly consist of the following three steps:

- **Raw material preparation:** In this the cellulosic raw materials e.g., wood, bamboo, cotton liners, bagasse, rags, straw, jute and hemp are slashed and cut into small chips.
- **Pulping:** In this, the raw materials are digested with chemicals under high temperature and pressure so as to free the cellulose fibres from the binders *viz*., lining, resins etc. Several types of pulping processes are available of which the following three are more common.
    - **Sulphate or craft pulping process:** This is a widely used process suitable for any kind of wood. Since the pulp produced is coloured and difficult to bleach and since long and strong fibres are produced in this process, it is used for preparing strong wrapping papers, bag making papers, wall papers, paper boards for cartons, corrugated boards, etc. The process consists of digesting the raw materials with Na_2S, NaOH and Na_2CO_3 at about 175°C and 120 psi pressure for 2 to 5 hours. During this process, most of the linings are hydrolysed to alcohols and acids. Toxic chemicals such as mercaptans and dimethyl sulphide are also formed. After digestion, the pressure is allowed to drop and the charge (called brown stock) is blown into a pit where the fibres are separated. The remaining waste cooking liquor, known as 'black liquor' is sent to another unit for recovering chemicals such as Na2S, Tall oil, etc.
    - **Acid sulphide pulping process:** This is used for the manufacture of high grade paper such as bond paper, tissue paper, bread wrap papers etc. In this process, the raw material containing mostly coniferous woods is digested with calcium bisulphite or magnesium bisulfite at 125 to 160°C with steam at a pressure of about 100 psi for about 6 to 12 hours. The pulp produced is dull white in colour and easy to bleach but the fibres are weaker than those obtained is case of sulphate kraft pulping process.
    - **Semi-chemical pulping process:** In this process, lesser amounts of NaOH and Na_2S are employed for pulping and $NaSO_4$ is used as the make-up chemical. This process produces high quality bleaching pulp suitable for manufacturing writing paper, bond paper, tissue, offset, newprint papers and corrugated boards. After digestion by any of the above processes, washing of the pulp followed by bleaching (with Cl_2 or ClO_2, NaOH and $CaOCl_2$ in successive stages) must be employed. These steps along with the chemical recovery step contribute to the bulk of the effluents.
- **Paper making:** The pulp is disintegrated in a better along with fillers (*e.g.*, clays, $CaCO_3$, $BaSO_4$ or TiO_2) rosin or wax emulsion and $Al_2(SO_4)_3.18H_2O$ (for providing a gelatinous film on the fibre), dyes and other chemicals are required. Then the pulp is refined. The fibres are cut to the desired size,

passed on to stuffing boxes to get the proper consistency and then passed over a moving belt of fine wire. The water passes through the screen while the fibres form a mat on the surface of the screen. This is the sent on the rolls and then to calendaring machine for final finishing.

NOTES

Wastewater sources and characteristics

All the above steps *viz.*, raw material preparation, pulping, washing, bleaching, chemicals recovery, screening of pulp and paper making contribute to the waste effluents. The important characteristics of combined effluent of integrated pulp and paper mills with chemical recovery system are dark brown colour, characteristic odour, high content of suspended and dissolved solids (about 1350 mg/1 and 1650 mg/1 respectively), high COD (about 1500 mg/1) and resistant to biological oxidation.

Environmental effects

The effects on environment include:

- The dark colour of the effluent is due to the lining compounds which are not easily biodegradable and hence it imparts persistent colour to the receiving water streams and inhibits photosynthesis and other natural self-purification process of the water streams.
- The immediate oxygen demand of the effluent brings about depletion of oxygen of the receiving stream with the concomitant adverse effects to the aquatic life.
- The chemicals present in the effluent, *e.g.,* sulphites, phenols, free chlorine, methyl mercaptan, pentachlorophenol are harmful to fauna and flora of the receiving waters. The settleable materials present may sink to the bottom and interfere with aquatic life.

Treatment options

Recovery of by-products, preliminary screening, coagulation, sedimentation, flocculation and flotation to remove suspended matter, chemical treatment to remove colour, activated sludge treatment to remove dissolved organics, lagooning for storage and biodegradation of organic matter.

5.2.6 Thermal Power Plants

As society progresses, new contaminants are discovered that contribute to harmful climate change consequences and global warming. Many of these pollutants are produced by our industrial and power generation businesses, and no matter how much pollution is reduced, some pollutants will always enter our environment. Thermal power stations are notorious for emitting a wide range of pollutants into the atmosphere. A thermal power plant is a type of power plant that transforms heat energy into electricity. These power plants achieve this by primarily heating fossil fuels, which in turn heats water and turns it into steam. The steam passes through a turbine, which produces energy, before being condensed and recycled back to its pre-heated state. Thermal power plants emit a number of substances that are bad for the environment, but they also emit something called thermal pollution.

The term thermal pollution has been used to indicate the detrimental effects of heated effluents discharged by various power plants. It denotes the impairment of quality and deterioration of aquatic and terrestrial environment. Various Industrial plants like thermal, atomic, nuclear, coal fired plants oil field generators and mills utilize water for cooling purposes. The heated effluents are discharged at a temperature 8 to 10°C higher than the temperature of intake waters, which reduces the concentration of D.O. (Dissolved Oxygen).

Thermal pollution can be defined as:

- The warming up of an aquatic system to the point where desirable organisms are adversely affected.
- Addition of excess of undesirable heat to water that makes it harmful to man, animal, plant or aquatic life or otherwise causes significant dangers to the normal activities of aquatic communities in water.
- Heated effluents (either from natural or man-made sources) contaminated with water supplies, may be harmful to life because of their toxicity, reduction in Dissolved Oxygen (D.O.), and which are aesthetically unsuitable and spread diseases.
- It reduces the number of aquatic species and destroys the balance of life in streams as is evidenced by the biological indices of community and diversity.
- It is a by-product of rapid and unplanned industrial progress and over population.

Effects of thermal pollution

The various effects of the thermal pollution are:

- **Reduction in Dissolved Oxygen:** Concentration of dissolved oxygen decreases with increase in temperature of water. For example, the D.O. content is 14.6 ppm in water at a temperature of 32°F and 6.6 ppm at 64°F. Thus cold-water fish, which requires about 6 ppm to survive, would not tolerate the high water temperatures. If they remained in the area they would die of oxygen starvation. Since the aquatic biota live aerobically, so a healthy stream should have an adequate supply of dissolved oxygen.
- **Change in water properties:** A rise in temperature changes the physical and chemical properties of water. The vapour pressure increases sharply, while the viscosity of water decreases. The decrease in density, viscosity and solubility of gases increases the settling speed of suspended particles, which seriously affect the food supply of aquatic organisms.
- **Increase in toxicity:** The rising temperature increases the toxicity of the poison present in water. A 10°C rise in temperature doubles the toxic effect of Potassium cyanide, while an 80°C rise in temperature triples the toxic effect of O-Xylene causing massive mortality of fish.
- **Interference with biological activities:** Temperature is considered to be of vital importance to physiology, metabolism and biochemical process in controlling respiratory rates, digestion, excretion and overall development of aquatic organisms. The temperature changes totally disrupt the entire ecosystem. Sharp changes in temperature are often destructive. Because, the life of aquatic animals involves several chemical reactions and the rate

of these reactions vary according to changes in temperature.

- **Interference with reproduction:** In fishes, several activities like nest building, spawning, hatching, and migration and reproduction etc. depend on some optimum temperature. For instance, the maximum temperature at which lake trout will spawn successfully is 8.9°C. The warm water not only disturbs spawning but also destroys the laid eggs.
- **Variations in reproductive rate:** The increase in temperature triggers deposition of eggs by female. The triggering is particularly dramatic in estuarine fish, which spawn in four hours after the water temperature reaches critical level.
- **Changes in metabolic rate:** Fishes show a marked rise in basal rate of metabolism with temperature to the lethal point. The respiratory rate, oxygen demand, food uptake and swimming speed in fishes increase.
- **Increased vulnerability to disease:** Activities of several pathogenic microorganisms are accelerated by higher temperature. Hot water causes bacterial disease in certain fishes such that they fail to develop eggs above critical temperature.
- **Invasion to destructive organisms:** Thermal pollutants may permit the invasion of organisms that are tolerant to warm waters and highly destructive e.g. invasion of ship worms into New Jersey's Oyster Creek.
- **Undesirable changes in algae population:** The life in an ecosystem is greatly influenced by the algal growth. Excess nutrients from the washout waters from farmlands, thermal plants cause an excessive algal growth with consequent acceleration of eutrophic and other undesirable changes.
- **Destruction of organisms in cold water:** The volume of water required for cooling purposes from a stream is enormous. Unfortunately many of plankton, small fish, insect larvae that are sucked into the condenser along with cooling water are killed by the thermal shock, increased pressure and water viscosity.
- **Biochemical Oxygen Demand:** When the temperature of stream carrying biodegradable organic matter rises, the intensified action of aquatic organisms causes B.O.D. to be accomplished at a lower temperature. When the temperature of stream carrying biodegradable organic matter rises fish death may occur due to synergistic action, which is caused due to accelerated chemical or biochemical action.
- **Effect on marine life:** Temperature plays an important role in affecting the physiology, metabolism, growth and development of marine animals. Sea organisms are poilkilothermic i.e. their body temperature varies with the surrounding water. Some marine creatures cannot tolerate wide changes of temperature, so they die at higher temperature.
- **Effect on bacteria:** Due to the heated discharges from the industries and plants (industrial), the bacteria are severely damaged. The effect includes coagulation of body Protein, melting of cell fats, toxic action of metabolic products, etc.

Control of thermal pollution

Heat must be removed from the condenser cooling waters prior to their disposal into water bodies. The major principles involved in the process of heat loss are: Conduction, convection, radiation, and evaporation. The following methods can be adopted to control high temperature caused by thermal discharges:

- **Cooling ponds:** The cooling towers are beneficially used in dissipation of heat as shown in Figure 5.1.

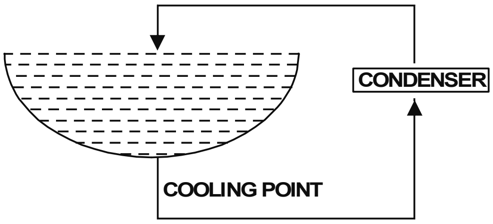

Fig. 5.1 *Cooling Ponds*

The water from the condensers is stored in the earth like ponds where natural evaporation brings down the temperature. The water is re-circulated again. Another method for installation of cooling ponds is shown in Figure 5.2.

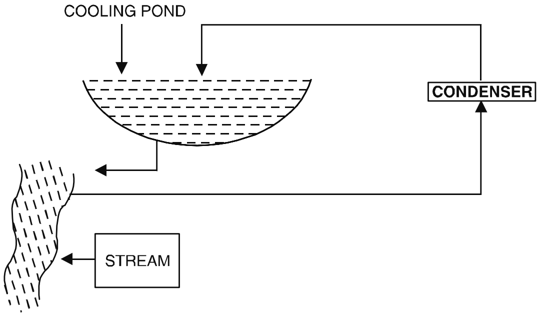

Fig. 5.2 *Method for Installation of Cooling Ponds*

- **Spray ponds:** In spray ponds, the water is sprayed in the cooling ponds with the help of spray nozzles to convert it into fine droplets which provide more surface area to facilitate efficient heat transfer to atmosphere.

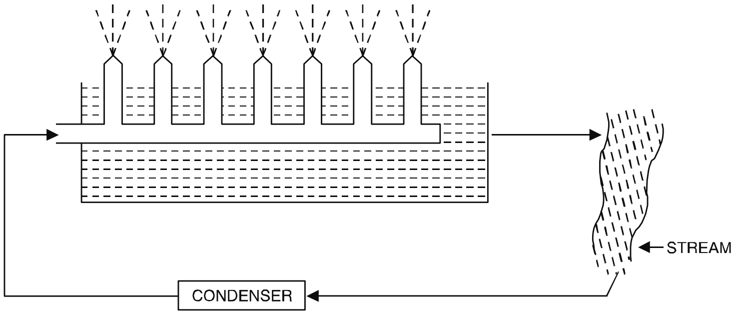

Fig. 5.3 *Spray Ponds*

- **Cooling towers:** In wet cooling towers, the heated water is brought in direct contact with continuously flowing air. The evaporation brings down the temperature. To increase the surface area of contact, the water is broken down into droplets by use of spray nozzles or by splashing it on the packing or baffles in the cooling towers.
- To handle large quantities of heated effluents, large tanks or reservoirs should be constructed to retain the water for a little longer time. When water cool down to a tolerable temperature, it may be released.
- The heated effluents discharged from the chemical industries and thermal power plants can be put in to certain beneficial uses like green house, frost protection during colds, aquaculture, heating the buildings, etc.

5.2.7 Nuclear Power Plants

Nuclear power plants fulfill approximately 17 per cent of electricity needs the world over. Nuclear fission reaction is used to release nuclear energy in these plants.

Subcriticality, criticality and supercriticality

Splitting of a U-235 atom gives out two or three neutrons. These neutrons would collide with other U-235 atoms resulting in more free neutrons. In the absence of U-235 atoms around, the free neutrons form neutron rays.

- **Critical mass:** It is the smallest amount of fissile material required for a sustained nuclear chain reaction. In case, on average, exactly one of the free neutrons from each fission collides with another U-235 nucleus and causes its splitting, then the mass of uranium is said to be critical. The mass will ex-ist at a stable temperature.
- **Subcritical mass:** It is the mass of fissile material that cannot sustain a fission reaction. There will be an exponential decrease in the population of neutrons. A steady rate of spontaneous fissions causes a proportionally steady level of neutron activity. If, on average, less than one of the free neutrons collides with another U-235 atom, then the mass is subcritical. Induced fission cannot continue under these conditions.
- **Supercritical mass**: It is the mass of fissile in case there is an increasing rate of fission. The fissile may enter the state of equilibrium (i.e., become critical again) at an increased temperature/power level or destruct itself. If, on average, more than one of the free neutrons collides with another U-235 atom, then the mass is supercritical. This results in heating up of the reactor.

For developing a nuclear bomb, the mass of uranium should be very supercritical to cause splitting of all of the U-235 atoms in the mass in a single microsecond. In a nuclear reactor all the atoms should not undergo splitting at once. However, the reactor core ought to be a bit supercritical to help plant operators increase and decrease the temperature of the reactor. Control rods of a neutron-absorbing material are used in nuclear reactors to absorb free neutrons to let the operators can maintain the reactor at a critical level.

In addition to mass of U-235, shape of the nuclear material affects the number of free neutrons. If the material is shaped like a very thin sheet, most of the free neutrons will be freed into space rather than hitting other U-235 atoms. A sphere is the optimal shape for nuclear material to be used in nuclear power plant. To accomplish a critical reaction, 2 pounds (0.9 kg) of uranium-235 is required. This amount is therefore referred to as the critical mass. For P-239, the critical mass is about 10 ounces (283 grams).

Interior of nuclear power plants

To use nuclear fission reaction to generate electrical energy, first of all, the energy produced by enriched uranium should be controlled and used to convert water into steam.

A nuclear power plant uses 1-inch (2.5-cm) long pellets of enriched uranium. The pellets are arranged to form long rods, which are grouped together into bundles. The bundles remain submerged in water inside a pressure vessel. Water acts as a coolant in the plant. The plant works only when the submerged bundles are a bit supercritical.

In order to avoid overheating, control rods made of a neutron-absorbing material are used. These rods are inserted into the uranium bundle with the help of a device that can raise or lower the control rods. Raising and lowering the control rods permits the operators to monitor the rate of nuclear reaction. Raising the control rods out of the uranium bundle (thus absorbing fewer neutrons) would help the operator use the uranium core to generate more heat. To generate less heat, these rods are lowered into the uranium bundle. Lowering the rods completely into the uranium bundle would shut the reactor down when an accident occurs or a change of fuel is needed.

Uranium bundle acts as an extremely high-energy source of heat. It heats the water and turns it to steam. The steam drives a turbine, which spins a generator to produce power. Humans have been harnessing the expansion of water into steam for hundreds of years.

Certain nuclear power plants let the steam from the reactor pass through a secondary, intermediate heat exchanger in order to convert another loop of water to steam, which drives the turbine. The merit to this design is that the radioactive water or steam is never allowed to come in direct contact with the turbine. Further, certain reactors use a gas (carbon dioxide) or liquid metal (sodium, potassium) as the coolant fluid that remains in contact with the reactor core. These types of reactors permit operation of the core at higher temperatures.

Exterior of nuclear power plants

Since a nuclear power plant involves emission of hazardous levels of radiation, extra precautions are needed. To make a radiation shield, a concrete liner is built around the pressure vessel of the reactor. This concrete liner, in turn, is covered by a much larger steel containment vessel. This vessel covers the reactor core as well as the equipment plant workers who refuel and maintain the reactor. This vessel acts as a barrier that checks the effusion of any radioactive material from the plant.

The outermost layer consists of a concrete building. This building protects the steel containment vessel and is capable of surviving the great damage that may be caused by natural calamities like earthquake or a crashing jet airliner. These secondary containment buildings are essential to check the emission of radiation/ radioactive steam in case of an accident.

Merits and demerits of nuclear power plants

There are numerous merits as well as demerits of nuclear power plants. The merits of a nuclear power plant are as follows:

- It does not use fossil fuels such as coal and natural gas, which emit carbon dioxide into the atmosphere and result in climate change. CO_2- emissions are minimal in nuclear power plants.
- As it does not depend on fossil fuels, the cost of nuclear power also is not influenced by fluctuations in oil and gas prices.

The demerits of a nuclear power plant are as follows:

- It involves risk of contamination even during transport of radioactive material.
- There is no 100 per cent safe process for the disposal of the radioactive waste generated in a nuclear power plant.
- On average, a nuclear power plant produces 20 metric tons of used nuclear fuel (high-level radioactive waste) per annum. The radiation and heat emitted by this waste has the capacity to eventually corrode any container. It is deadly to nearby life forms. In addition, nuclear power plants generate a huge amount of low-level radioactive waste in the form of radiated parts and equipment.
- Even low-level radioactive waste needs hundreds of thousands of years to reach acceptable levels.

5.2.8 Radionuclide Analysis

The various radionuclides present in the environment originate from the following two sources:

- **Natural radionuclides:** These arise from the all-pervading primordial radioelements such as uranium and thorium along with their daughter nuclides and potassium.
- **Technology related radionuclides:** These arise from the human activities such as nuclear and thermal power generation, uranium mining and milling, use the radiations and radioisotopes for medical applications, etc. Watching of colour television, air travel and other modern amenities also give rise to additional environmental radiation exposure.

Natural radiation environment

An elaborate survey of the environmental radiation using indigenously made sensitive radiation dosimeters by the Bhabha Atomic Research Centre, Bombay revealed that population-weighted all India average environmental external radiation exposure projected to the 1991 census figures works out to 734 m SV/y per person. The average environmental external radiation exposure to the population varies from place to place within our country. For instance, the average exposure value in Andhra Pradesh is 10165 m SV/y (highest), whereas the corresponding figure in Laccadive is 285 m SV/y (lowest). However, in certain isolated parts of the beaches containing monazite deposits, the average radiation exposure value was estimated at 5760 m SV/y per person due to the presence of 232Th and its daughter nuclides. [1 SV (Sievert) = 100 rem = 1 Joule/kg.].

A significant part of the human exposure to environmental radiation arises from inhalation of radon, thoron and their short lived a–emitting daughter nuclides, for example, 212Bi, 212Po, 214Po 216Po and 218Po, which are extremely hazardous to the lung tissues. A recent study on the randon inhalation exposures in different parts of our country indicates an average individual exposure of 1440 m SV/y. The indoor randon levels in western countries are quite high and have been identified as a risk factor for lung cancer similar to smoking cigarattes. However, in our country, thanks to the tropical climate and the consequently high ventilation in our houses, in-door randon exposure is not reckoned to be a serious radiological hazard.

Radiation exposures due to thoron and its short-lived daughter nuclides in air are not usually considered seriously because their concentrations above 1 metre from the ground level are not appreciable. However, in Indian context, these exposures cannot be ignored because a considerable number of people habitually sit and sleep on the Floor. The global average exposure value from this source is estimated at about 260m SV/y as per UNSCEAR 1988. The following Table 5.1 shows the per capita radiation dose received by the people in India from radionuclides in the environment from natural and man-made sources:

Table 5.1 *Per Capital Radiation Dose Received by the People of India*

Sr. No.	Source and types exposure	Contributing Radionuclides	Per capita dose of rate, mSV/Y
1.	**Natural sources**		
	(i) External irradiation	^{238}U, ^{232}Th and their daughters, cosmic radiations and 40K	734
	(ii) Ingestion irradiation	^{210}Po, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K, ^{14}C, ^{7}Be and ^{87}Rb	330
	(iii) Inhalation irradiation	^{232}Rn, ^{218}Po, ^{214}Po, ^{220}Rn, ^{216}Po, ^{212}Bi, ^{212}Po	1600
2.	**Man-made sources**		
	(i) Medical applications	^{131}I, ^{99}(m) T-C, X-ray	48
	(ii) Stack effluents, liquid effluents and fall out	^{14}C, ^{3}H, ^{41}Ar, ^{90}Sr, ^{131}I, ^{133}Xe, ^{239}Pu, ^{137}Cs, etc.	7
	(iii) Watching television, air-travel, etc.	Soft x-rays, cosmic radiations	4

It is clear from the data given in the above table that the population exposures due to environmental radiation from man-made or technological activities including thermal and nuclear power production, mining and milling operations, air travel, TV viewing, etc. together, is quite small as compared to the natural background radiation constantly received by us. Further, comprehensive surveillance programmes recently conducted by BARC, Bombay clearly indicate that there is absolutely no reason for concern regarding the radionuclides released into the environment from the routine operation of the nuclear installations in our country.

5.2.9 Metallurgy

Metallurgy is a branch of science that studies the physical and chemical properties of metals and their mixtures. It's a way of creating metal components that can be used in other processes or consumed. It is also a study of metal properties on the basis of which alloys are formed. Metallurgy is made up of three processes. The breaking down of big pieces of ore, followed by the concentration of valuable particles by removing waste particles, is the process of ore concentration. More than one precious metal can be found in ore. They can be broken down into its essential parts. Ore concentration can take place in two ways: physically and chemically.

Due to the generation of a high number of hazardous wastes, metallurgical activities are the source of environmental concerns such as air, water, and land pollution. The rate of metal extraction is increasing every day, resulting in the generation of waste and contaminants. In recent years, production has risen dramatically. Because of the growth in output, the lands closest to the industries are impacted and are no longer suitable for farming. The particles produced also pose a threat to adjacent flora and animal life.

The concerns generated by metallurgical industries are classified according to the nature of their consequences, and they include the following issues:

- **Air pollution:** Chemical reactions in the metallurgy process result in the development of fumes and smokes, while mechanical attrition produces dust. Dust inhalation causes lungs difficulties by hardening the lungs' parts. Asbestos dust causes cancer by causing damage to the lungs and other organs of the body. Because of their small size and ease with which they might enter the respiratory system of the body, fumes and smoke are more harmful than dusts.
- **Land pollution:** Mining is the process of extracting precious minerals from the earth's surface. It entails the mining of minerals that cannot be synthesised artificially and are non-renewable resources. However, the process has the potential to generate a variety of environmental issues, including soil erosion, sinkhole development, biodiversity loss, and pollution of soil groundwater and surface water.

Pollution issues are caused by the metallurgical industries. The problem must be addressed, and metallurgists must take responsibility for protecting the environment and human health from the toxicity risks associated with the manufacturing of high-quality metal products. By enhancing the quality of industrial by-products and utilising metallurgical slags, the environment can be safeguarded. Keeping the dumps wet at all times is a good strategy to avoid these issues. Planting trees and cultivating bushes are beneficial as they act as a windbreak and reduces pollutants.

5.2.10 Polymers Industry

A polymer is a macromolecule generated by the repeated coupling of a large number of monomer units. Polymer makes up the physical structure of the world we live in. Natural and synthetic polymers are the two primary types of polymers. Proteins (wool, silk), carbohydrates (starch, cellulose, cotton, etc.), lipids, and nucleic acids are all natural polymers found in living systems (DNA, RNA, etc.). Synthetic polymers, such as plastic, on the other hand, are man-made and produced in the polymer industry. Polymers have a lengthy life span since they are difficult to biodegrade in the environment due to their water repellent properties.

The polymer sector is linked to the following environmental issues in terms of manufacturing, use, and disposal of synthetic polymers.

- **Air pollution:** Synthetic polymers are a permanent waste because they are non-biodegradable. Plastic bags and bottles that have been used cannot be disposed of in sanitary landfills. These synthetic waste items are then burned in incinerators, releasing toxic gases and polluting the atmosphere. Carbon dioxide, nitrogen oxides, and carbon monoxide are among the gases created during burning. All of these gases are hazardous in nature and contribute to global warming and acid rain generation. In addition, dust particles are released during burning. Because polyvinyl chloride includes chlorine, it produces HCl gas when it is burned. It is transformed to HCl acid in the presence of moisture, resulting in corrosion of neighbouring buildings and structures. It also has an impact on the growth of vegetables in the area.
- **Water pollution:** When polymeric wastes are released into the marine environment, they quickly degrade into smaller particles. Sea organisms absorb the microscopic plastic particles, which cause intestinal blockage in fish larvae. These are not only harmful to sea creatures, but they also have a tendency to bioaccumulate in the food chain.
- **Occupational hazards:** Workers in the polymer and plastic industries have been documented to have a variety of health issues. Workers in the poly vinyl chloride sector are thought to be exposed to serious health risks since the monomer causes a rare type of liver cancer. As a result, a limit for vinyl chloride exposure in industry is set at 1ppm over an 8-hour period.

Check Your Progress

1. What is the major contributor to air pollution in the sugar industry?
2. What is the composition of wastewater produced by distilleries?
3. Mention any two effects of paper and pulp industry on the environment.
4. How is the rate of nuclear reaction monitored in nuclear power plants?
5. What do you mean by natural radionuclides?
6. What is the difference between natural and synthetic polymers?

5.3 DISPOSAL OF WASTES AND THEIR MANAGEMENT

There are four steps involved in the hazardous management program:

(1) Identification of the waste
(2) Handling of waste
(3) Minimization of hazard
(4) Administrative control

5.3.1 Identification

As discussed in Unit 3, hazardous waste should have at least one of the following characteristics: (1) Reactivity (2) Ignitability (3) Corrosivity (4) Toxicity. Thus, if any waste is found satisfying the above criterions it will be identified to follow further steps.

5.3.2 Handling

Proper handling is very essential as far as hazardous waste is concerned. Any mistake may lead to explosion, ignition and release of toxic gases polluting the air. For proper handling several methods need to be followed:

(a) Packaging: Special packaging in accordance with the characteristics of the waste.

(b) Labelling: After packaging, the package needs to be marked properly with labels giving details about the characteristics of that waste, *i.e.*, chemical composition, date of generation and safety data sheet.

(c) Segregation: Segregation is required to avoid chemical reaction if it is found to have that possibility.

(d) Storage: After segregation, it needs to be stored in an isolated area of the site where it is generated and the area is known as 'Hazardous Storage Area'. Afterwards, it needs to be transferred to the disposal site.

(e) Transportation Hazardous waste needs transportation in special type of vehicles marked with the details of waste that are transported.

Waste of low level may be buried underground at a properly selected site, on the other hand, for waste of high level, disposal in the underground might be a catastrophe and in the long run it might be fatal. It is thus, wise to think about destruction of waste to reduce toxicity to the maximum possible extent and then safely dispose it. There are basically three processes by which it can be done:

(*i*) Physical Processes
(*ii*) Chemical Processes
(*iii*) Biological Processes

Physical processes

In physical processes, the solid and liquid components can be separated through sedimentation of the solid in a sedimentation tank, followed by filtration for solids which do not settle and float. Liquid wastes which do not settle or float can be separated through adsorption in granular activated carbon having surface area as large as 1000 m^2/g. Removal of some specific components can be achieved by reverse osmosis, ion exchange process, dialysis, electro-dialysis and simple distillation process.

Chemical processes

In chemical treatment, various techniques adopted are:

(*a*) **Neutralization:** Acidic waste water (pH<2) is neutralized by adding lime slurries, ($Ca[OH]_2$) and alkaline waste water (pH<12.5) is neutralized by adding either acid directly or by passing CO_2 through the solution, the H_2CO_3 thus formed catalyses the reaction. When the pH of the solution approaches 7 (near neutrality), it becomes less hazardous.

(*b*) **Oxidation – reduction:** Materials with some elements of variable oxidation states differ in toxicity. In other words, the oxidation states of some specific elements in a material determines its toxicity. Under such conditions, if the lower oxidation states of that element shows greater toxicity, it needs to be converted to higher oxidation states by oxidation. On the other hand, if the higher oxidation states of that element show greater toxicity, it needs to be converted to lower oxidation states by reduction. For example, cyanide containing waste needs to be oxidized to cyanate to reduce toxicity and finally to nitrogen and CO_2 for complete reduction of toxicity.

$$\overset{+1}{Na}\,\overset{+2}{C}\,\overset{-3}{N} + Cl_2^{\,0} + NaOH \rightarrow \overset{+4}{Na}\,\overset{+4}{C}\,\overset{-3}{N}\,\overset{-2}{O} + \overset{+1}{Na}\,\overset{-1}{Cl} + H_2O$$

Partial reduction of toxicity,

$$\overset{+1}{Na}\,\overset{+4}{C}\,\overset{-3}{N}\,\overset{-2}{O} + 3Cl_2^{\,0} + 5NaOH \rightarrow 2\overset{+4}{C}\,\overset{-4}{O_2} + \overset{0}{N_2} + 6\overset{+}{Na}\,\overset{-}{Cl} + 2H_2O$$

Complete reduction of toxicity,

In NaCN, the oxidation states of C and N are respectively +2 and –3 and when converted to NaCNO (cyanate) by alkaline chlorination, oxidation states of C changes to +4 and finally with excess chlorination oxidation states of N become zero and there is a complete reduction of toxicity. The wastes containing benzene, toluene, phenol, arsenic as toxic materials can be detoxified through oxidation. In case of material with hexavalent chromium, Cr^{6+} is found to be more toxic compared to trivalent chromium Cr^{3+}. Thus, hexavalent chromium is reduced to trivalent chromium by passing SO_2 in the medium.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2\overset{+6}{Cr}\,\overset{-6}{O_3} + 3H_2SO_3 \rightarrow \overset{2\times 3}{Cr_2}\,(\overset{-6}{SO_4})_3 + 3H_2O$$

More toxic Less toxic

The oxidation states of chromium changes from +6 to +3, reducing toxicity. The wastes containing chromium (IV), lead, silver, mercury can be detoxified through reduction.

(*c*) **Chemical precipitation:** In this process, the soluble toxic heavy metals like Pb, Hg are precipitated out as sulphides due to their low solubility. Although this is an efficient process, there remains the possibility of formation of toxic H_2S gas. The other alternative process could be precipitation as hydroxide at a specific pH. Thus, the metal ion (M^{2+}) reacts with $Ca(OH)_2$ and removes $M(OH)_2$,leaving Ca^{2+} ion in the solution which is not toxic.

$$M^{2+} + Ca(OH)_2 \rightarrow M(OH)_2 + Ca^{2+}$$

The precipitate so formed can be removed by settling and filtration.

(*d*) **Ion-exchange:** In this technique the hazardous liquid waste is forced through a column of solid resin beads of zeolites or any synthetic resin. In the ion-exchange unit, the toxic heavy metals get exchanged with sodium ion of resin.

$$\underset{\text{(Toxic metal ion)}}{M^{2+}} + Na_2R \rightarrow \underset{\text{(Resin)}}{MR} + 2Na^{+}$$

(*e*) **Ultraviolet radiation/oxidation:** This is an excellent technique of destruction of dissolved organic compounds. In this case, a potent oxidizer, hydroxyl free radical ($OH^{\bullet}$) is generated. Ozonized solution is exposed to UV rays and $OH^{\bullet}$ forms readily which simultaneously oxidizes organic molecule to CO_2 and water.

$$OH^{\bullet} + HR \rightarrow H_2O + R^{\bullet} \rightarrow CO_2$$

Biological processes

In the biological process, the microorganism (bacteria, fungi) mainly bacteria, decomposes the organic substances like oils, phenols and refinery waste to CO_2. Although the living organisms are generally susceptible to toxic substances in hazardous wastes, for some microorganisms under specific temperature, pH of solution and concentration of toxic chemicals is an ideal condition for survival. They consume the heavy metals and as well as decompose organic wastes into CO_2 and H_2O, thereby reducing over all toxicity.

Land disposal of hazardous waste

The land disposal techniques are:

(1) Secure landfills

(2) Underground injection wells

(3) Surface impoundments

(4) Waste piles

Secure landfill is however widely accepted for its convenience and low cost. Preventive measures guided by Resources Conservation and Recovery Act (RCRA) need to be taken care of before such disposal. Thus, in the first stage hazardous liquids are extracted, in the second stage the solid wastes are kept in properly designed containers of proper composition to prevent leakage of liquid wastes and finally disposed off in suitable hydrologic condition, at an appreciable distance (2km) from water resources being used for domestic purpose.

The hazardous waste is thus, treated first and then taken for final disposal. The hazardous waste containing organic wastes is treated physically, as well as biologically to reduce toxicity of organic wastes. The inorganic wastes are neutralized, oxidized or reduced to reduce toxicity of inorganic waste and to finally incinerate. The solidified mass is then ready for land disposal.

Secure landfill

The main objective of a secure landfill is to protect ground water from pollution apart from explosion, fires and degradation of organics. The secure landfill consists of three dimensional cells with a double liner system. The double liner system prevents the leakage of liquid wastes (leachate) protecting groundwater from pollution. The upper liner is flexible and is made up of plastic (Polyvinyl Chloride [PVC] or Polyethylene of high density [HDPE]) or rubber (Chlorosulphonated polyethylene [CSPE] or ethylene propylenediene monomer [EPDM]).

After dumping the wastes in the cells, they are covered with soil. The leachate collected on each double liner is pumped to the surface by drainage pipes for further treatment. For possible burial of organic wastes, gas venting is provided. To check the possibility of contamination from the site, monitoring facilities are provided in many landfill designs.

However, a secure landfill must not be considered as the sole means of hazardous waste disposal, rather it is a part of overall system minimizing the volume of hazard through physical, chemical, biological treatment, incineration and solidification.

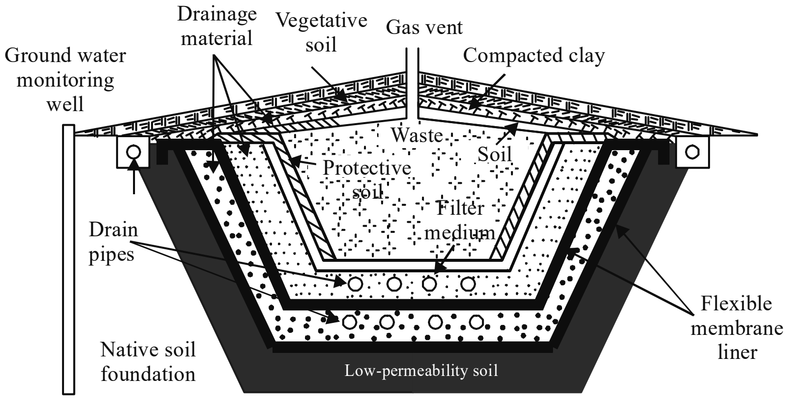

Fig. 5.4 Schematic diagram of hazardous waste landfill

Underground injection walls

The most popular way of disposal of liquid hazardous waste is to force them underground through deep injection wells. Typical injection depths are more than 700m below the surface. Even with such a depth, there still remains the possibility of contamination of underground water. To avoid such problem, one has to dispose the waste below the lowest formation containing underground sources of drinking water. But yet, the contamination of underground water cannot be prevented completely and requires more stringent rules to follow such as construction, operation and monitoring while continued reliance on this technology should be discouraged.

One of the cheapest ways of hazardous waste disposal could be co-disposal. In this case, the hazardous waste can be mixed with large amount of Municipal Solid Waste (MSW) so that the inorganic and organic liquid wastes get absorbed and their concentration is reduced. Under such circumstances landfill disposal will not be that hazardous. However, this is not the best way of disposal.

Surface impoundments

The treatment technologies involved in surface impoundments are neutralization, precipitation, setting and biodegradation. Surface impoundments are excavated areas used to store liquid hazardous wastes. Generally, the storage is made temporarily but may also be used for permanent storage and eventually closed as a landfill. The main advantage of this technology is that the wastes remain accessible, allowing some treatment to be carried out during storage.

The conventional surface impoundments were poorly constructed and loosely monitored. The maximum were located over very thin or very permeable soil that would allow easy transport of leachate to ground water. Recent regulations are very stringent now and require new surface impoundments equipped with two or more liners, a leachate collection system and monitoring system, similar to those required for landfills.

Waste piles

Waste piles are ground level mounds of hazardous wastes. The piles are completely open and lined underneath with impermeable materials and so that the waste does not contact the ground and contaminate surface or ground water. In waste piles the materials that emit toxic fumes cannot be stored. The storage of a hazardous waste plant is always temporary. Once the plant treats the waste to make it less hazardous it must be disposed in a protected landfill or underground injection well or a surface enclosure or waste piles designed to handle hazardous materials.

5.3.3 Minimization of Hazardous Waste

Considering the consequence of hazardous waste, the first thought must be given to its reduction in generation and then we can think of technologies regarding the disposal.

The first priority must be to find ways of eliminating the use of hazardous substances. This can be achieved by changing manufacturing process or by substituting the products which satisfy the same need, without creating hazards. For example, instead of using steel and aluminum cooking utensils, one can use products made up of earth.

The second priority is to reduce the amount of hazardous waste generated. This again can be done by changing manufacturing process.

The third priority is to recycle the hazardous substances, such as solvents and acids to maximize their use before their treatment and disposal. The final priority is to treat the hazardous waste to reduce its volume and toxicity.

All these operations are economically beneficial.

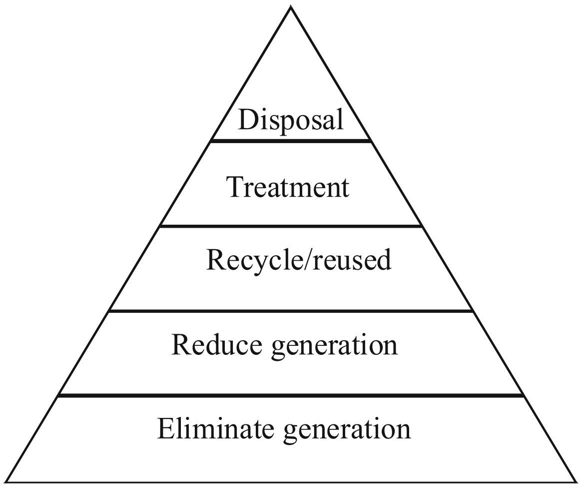

Fig. 5.5 *The sequence of Priorities in Hazardous Waste Management*

5.3.4 Administrative Control

Administrative responsibilities are very important in hazardous waste management. The responsibilities are:

(*a*) To ensure that the container of hazardous waste is properly marked.
(*b*) To choose correct disposal methods.
(*c*) To treat the hazardous waste correctly.
(*d*) To check the right kind of vehicle used for transportation.

Check Your Progress

7. Why is proper handling of waste essential?
8. Mention any three administrative responsibilities when it comes to hazardous waste.

5.4 ENVIRONMENTAL TOXICOLOGY

The study of the adverse effects of diverse chemical, biological, and physical agents on living organisms is the subject of environmental toxicology, a multidisciplinary discipline of science. Ecotoxicology is a subfield of environmental toxicology that focuses on the detrimental effects of toxicants on humans and ecosystems. Rachel Carson is known as the 'Mother of Environmental Toxicology', as she established it as a separate field within toxicology with the release of her book *Silent Spring* in 1962, which examined the consequences of unchecked pesticide use. Carson's work was heavily influenced by a series of reports by Lucille Farrier Stickel on the pesticide DDT's ecological impacts.

The relative potential of a substance or combination of different substances in causing injury or harm to living organisms is called toxicity. If chemical substances are responsible for toxicity then it is called chemical toxicity and the chemical substances are known as chemical toxicants, or toxins.

Most chemical substances are poisons or toxins and it is the right dose which differentiates a poison and a remedy. The dose is expressed as milligram of chemical ingested per kilogram of body weight. One measure of toxicity of something is the amount needed (dose) to cause some acute response, such as injury of organ, coma or even death. However, not every member of an exposed population will react the same way to a toxin and the response depends on condition of health, age, food habits, etc.

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Toxicity can be both acute and chronic. Acute toxicity refers to effects that are caused within a short period of time, after a single exposure to the chemical and chronic toxicity refers to effects that take place after prolonged exposure.

The transmission or flow of toxic substances or toxins, through the body of living organisms follows a definite path and is known as 'pharmocokinetics'. There are four steps in pharmocokinetics such as:

1. Absorption
2. Storage
3. Distribution
4. Excretion

All these steps occur simultaneously. The absorption of toxins can be through ingestion with food or drink, through inhalation or by dermal (skin) contact or other exterior surfaces such as eyes. Once in the body, it can be absorbed by the blood and distributed to various organs and systems. The toxicant or toxin may then be stored (*e.g.*, DDT in fat) or may be eliminated from the body by excretion or by biotransformation.

On the basis of target organs, toxicity can be classified as:

- (***a***) **HepatotoxicityL** Target is liver and the chemicals responsible are $CHCl_3$, C_2HCl_3, $CCl_{4;}$ DDT; metals like As, Fe, Mn; drugs like anabolic steroids, acetaminophen, etc. The chemicals are called hepatotoxins.
- (***b***) **Nephrotoxicity:** Target is kidney and the chemicals responsible are chlorinated hydrocarbons and heavy metals like Pb,Cd and Hg. The chemicals are called nephrotoxins.
- (***c***) **Hematotoxicity:** Target is blood and the chemicals responsible are CO and nitrates in ground water (water pollution). The chemicals are called hematotoxins.
- (***d***) **Pulmonotoxicity:** Target is lungs and the chemicals responsible are cigarette smoke, O_3, asbestos, etc. The chemicals are called pulmonotoxins.
- (***e***) **Genotoxicity:** Target is gene (*DNA*) and the chemicals responsible are called genotoxins.

5.4.1 Health Effects

The health effects of industrial toxicology are as follows:

- Acute poisoning is represented by quick absorption of the substance and the exposure is severe and sudden. Usually, a single large exposure is enough to cause damage. For examples, cyanide poisoning or carbon monoxide.
- Chronic poisoning is represented by prolonged or recurring exposures of a duration measured in days, months or years. Symptoms may not be apparent right away. Examples include mercury or lead poisoning or pesticide exposure.
- 'Local' means the spot of action of an agent and means that the action occurs at the point or area of contact. The site or location may be skin, gastrointestinal system, eyes, mucous membranes, the respiratory tract, etc. Absorption does not essentially occur. Examples include some strong alkalis or acids.
- 'Systemic' means a location or spot of action other than the point of contact and presupposes absorption has occurred. For example, an inhaled substance may act on the liver. For examples, arsenic has an effect on the nervous system, blood, liver, skin and kidneys.
- Cumulative poisons are represented by substances, which have a tendency to develop in the body due to chronic exposure. The effects are not visible till a critical body burden is attained. Example includes heavy metals such as lead.
- When two or more than two hazardous substance exposures take place, the resulting effect can be bigger than the effect of the individual exposures. It is known as *synergistic response (e.g.,* exposure to tobacco, smoke and asbestos leading to lung cancer or mesothelioma).

Other factors affecting toxicity

The route of exposure and rate of entry (i.e. by what means the toxic is delivered and how fast does it react) are significant factors that affect toxicity. A person's age can certainly affect the capacity to restore the damage of tissue. Previous exposures can result in increased sensitivity or tolerance. Normal state of health, life style and physical condition can influence the toxic response. Pre-existing disease can lead to raised sensitivity.

5.4.2 Target Tissues

When an organism reacts to a contact to a foreign material, it results in the incidence of biological effect, at least in the starting, in the cells of either one or more tissues, which are named the target cells. The tissues and organs of which the target cells form parts are named target tissues and target organs, respectively. The scale and the type of biological effect are finally based on the amount of concentration of foreign substance present at the target location, which implies, within the target cells or in the fluid which encloses them.

Assimilation by the organism raises the concentration within the body, whereas excretion has a contrary effect. The storage inside some tissues can either raise or reduce the level of concentration at the target site(s); also, biotransformation of the compound will reduce its concentration but will result in a raise in the concentration of its metabolites. Eventually, the volume of body fluid within which the compound is distributed is also accountable for influencing the concentration at target sites.

Body fluid compartments

As it is normally known that 60 per cent of the adult human body weight is water, which is one of the most necessary constituents of body fluids. Thus, if a man weighs 70 kg, it will be 42 kg, or say about 42 litres of water which is distributed inside three main compartments of his body. Approximately two-thirds of water is contained inside the cells in the form of intracellular fluid, and one-third is stored in the spaces between the cells (in the form of extracellular fluid). These so-called compartments are separated from one another by cell membranes. The extracellular compartment is further divided into two parts—first part is plasma, which is about three litres of fluid that is contained inside the blood vessels in which the blood cells remain suspended; second part comprises the interstitial fluid, which remains outside the vessels. Also, the interstitial fluid and plasma are separated from one another by walls of the blood vessels, and most of the capillaries add to their surface area. In spite of being distributed all through the body, the fluid compartments are uniform as far as the chemical composition is concerned and therefore can be assumed as single, well-mixed collections of fluid. An interstitial fluid in one organ, possibly, is similar in composition to an interstitial fluid in another. Hence, there are major differences in composition among the three compartments which eventually reflect the selective permeability of barriers, which divide these compartments. Figure 5.6 illustrates the same.

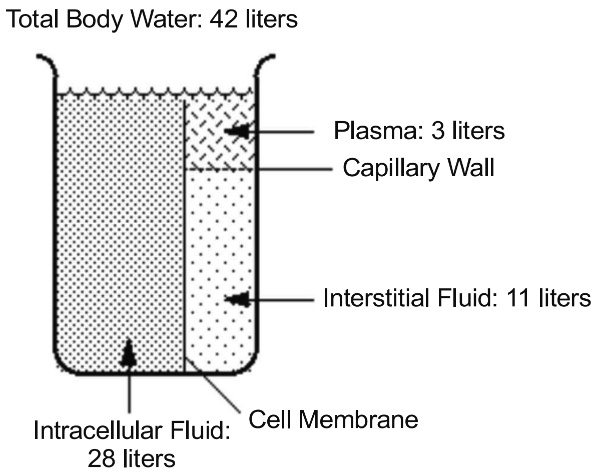

Fig. 5.6 *Body Fluid Compartments for a 70 kg Person*

Just think that a definite quantity of a foreign material is injected into the bloodstream (through injection). If the size of the molecules of this material is similar to that of the size of the normal plasma proteins then they will not break through the vascular walls, nor will they break through the cell membrane; as a result, they will be distributed, although at first, only in the plasma compartment of body fluid. If, however, the molecules of this material are smaller in size in comparison to that of plasma proteins but larger than the urea molecules, then they will generously break through and cross the capillary walls and get into the interstitial fluid although without entering the cells. Therefore, the foreign material is quickly distributed in the whole extracellular fluid compartment. Eventually, if the molecules of the material are similar in size to that of molecules of urea then they may perhaps break through or cross the cell membrane as well and enter into the body fluid throughout the body.

The knowledge pertaining to the volume of distribution of an absorbed material is necessary, if it is restricted to the plasma; while, the concentration of this foreign material will be almost 15 times higher where the same absorbed amount is distributed in the whole body fluid. Thus, it with no trouble impacts the concentration of a foreign chemical at the target site. In addition, other factors apart from the size of the molecule often affect the movement of the same across the barrier between the fluid compartments. This involves the existence of electric charge, which slows down the movement across cell membranes, and high lipid (oil) solubility that boosts cell membrane penetration.

Homeostatic mechanism

Birds and mammals have a highly evolved and complicated system of maintaining constant inner environment. The extracellular fluid compartment demonstrates more or less constant pressure, temperature and chemical composition contained by tremendously narrow limits. This feature of inner stability, or homeostasis, permits the various types of cells, which create the body organs and tissues, to carry out highly specialized functions. It is controlled by two significant systems—the nervous system and the endocrine system. The former, being the most significant and the autonomic component, manages the involuntary functions of all the organs through production and transmission of electrical impulses. The latter improves nervous control through the secretion of chemical substances named hormones, which are discharged to the organs under control through blood. Both the systems together supervise the waste products, water content, metabolic raw materials and various other significant molecules in body fluids and help in regulating their production, storage, intake and excretion that is required to preserve constant conditions.

Review of physiology of major organs

Respiratory system maintains close contact of air with blood circulating in the body to help transfer of oxygen and carbon dioxide to body cells. A thin and extremely broad barrier separates oxygen from blood. This barrier allows adequate transfer of oxygen into blood and carbon dioxide into air. The process of respiration involves the following two steps:

1. **Ventilation:** It is the bulk movement of gas through tracheobronchial tree, which passes several defensive structures mainly meant to protect lungs from airborne hazards to alveolar region.
2. **Gas exchange:** It is the process of diffusion of solutes under partial pressure gradient between alveolar gas and capillary blood.

Under normal conditions, only oxygen, carbon dioxide and water vapour are exchanged between air and blood. If there is a diffusible gas in the air, which is soluble in blood, can freely pass through the respiratory barrier.

The main functions of circulatory system are as follows:

- Distributing blood to all the tissues and organs
- Collecting returning deoxygenated blood and passing it through the lungs before starting the new cycle

When at rest, the volume of blood pumped by heart in 1 minute is equal to the entire blood volume. For example, as a consequence of rapid blood circulation, equilibration between plasma and interstitial fluid for all the solutes except protein molecules is maintained. There are certain limits to the distribution of the flow of blood to various organs. Blood circulation to central nervous system remains nearly constant under all the conditions. However, circulation of blood to other organs may change with the changing environment. Heart muscles receive blood via coronary arteries. These muscles do not use from the blood present in the chambers of heart. Red blood cells are continuously produced in the bone marrow and removed in the spleen, liver and the bone marrow. The red blood cells possess haemoglobin, a pigment molecule having important chemical properties: it binds reversibly with many small molecules, out of which oxygen, carbon dioxide, carbon monoxide and hydrogen ions are the most important.

The volume of water in blood and other tissues of the body is maintained by kidneys. Thus, kidneys monitor the concentration of several solutes in the plasma. In the state of rest, kidneys receive a large part of the total blood flow and remove water and solutes smaller than protein called albumin dissolved in by the process of filtration. The average rate of filtration by kidneys is 180 litres per day. Kidneys permit reabsorption of water and required solutes selectively and let the undesired molecules to be excreted through urine. Out of total water filtered per day, 99 per cent or more is reabsorbed and only less than 2 litres per day is removed in the form of urine. Kidneys reabsorb glucose, amino acids and ions for maintaining plasma concentrations within close limits. Further, foreign substances may get further concentrated in urine, relative to their concentration in the plasma, by the process known as secretion.

Gastrointestinal (GI) tract breaks down ingested material both physically and chemically. The substances, which are able to permeate through the lining of this tract, are absorbed into the circulation. The membrane of the GI tract cannot monitor absorption. This tract absorbs all the material that is digested. As the surface area of the inner walls of small intestine is the greatest, it performs maximum absorption. There is a very strong acidic environment in the stomach where charged molecules get converted into electrically neutral molecules, which helps in absorption at that site, for example, aspirin.

The blood leaving the intestinal capillaries enters liver via the portal circulation prior to moving back to heart for recirculation. Cellulose and the complex proteins are the ingested material, which are not absorbed. These molecules do not get broken down by digestive chemicals in the gut into smaller species, which are able to permeate through blood vessels or lymphatic system. These materials are then passed into the large intestine where most of the remaining water is absorbed before excretion.

Liver is one of the most significant regulators of chemical composition of plasma and body fluid. Its main function is to convert most of the absorbed

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molecules into certain fundamental nutrients (especially glucose, amino acids, lipids and vitamins) to be utilized by all the cells. Enzymes existing in the liver catalyse the process of chemical transformation of foreign substances into compounds, which are more easily excreted. Another function of liver is secretion of bile, which contains complex salts. These salts have the principal role in final digestion and absorption of ingested material that enters small intestine. 0.25 to 1.0 litres per day of bile is secreted by liver. Most of the bile is reabsorbed in the intestine and re-circulated to the liver—this permits conservation of bile salts. Bile also acts as a carrier of fluid for excretion of foreign compounds or their breakdown products.

Dose-Response relationships

The potential toxicity (harmful action), which is an intrinsic property of a substance, is manifest only when that substance comes in contact with a susceptible living biological system. A chemical usually considered to be harmless may cause a toxic response if it is added to a biological system in significant quantity. The toxic potency of a chemical is defined by the relationship between the dose (the amount) of the chemical and the response that is produced in a biological system.

The interaction of any foreign chemical with an organism is based on the principle that there is a steadily increasing effect as the amount absorbed is increased. This is completely consistent with the notion of a group of target cells affected by the concentration of foreign compound in the surrounding extracellular fluid. General examples of dose-response relationships are shown in Figure 5.7.

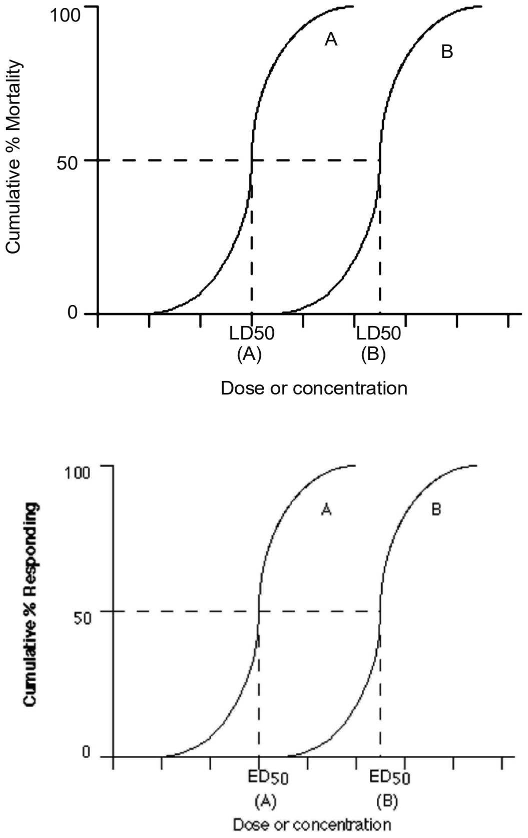

Fig. 5.7 General Examples of Dose-Response Relationships

Both dose and response can be characterized in several ways. The response can be described as the number of exposed animals that display a specified effect, such as development of tumour, liver failure or death. In a less common but more advanced study, response can be determined as the magnitude of an impact in an exposed individual (e.g., degree of functional impairment of one or more than one organ). Measurement of dose can be done as concentration in the external environment (e.g., milligrams of compound per cubic meter of air). The purpose is to determine the amount of the material ingested or injected as dose. These measures of dose are not related to the extracellular fluid concentration, but these are the simplest to determine.

The dose-response curves for numerous compounds have similar shapes but their position and slope varies. The position of curve on the dose axis depicts the toxic potency. The curves that indicate lower doses depict relatively high toxicity as only small doses are needed to generate measurable responses. If the exposed population is relatively homogeneous, you will obtain steep dose-response curves owing to the following reasons:

- The target tissue in an individual has comparatively little adaptive or reserve capacity
- All the individuals respond at nearly the same dose

Gradual dose-response curves are more common. This indicates the following facts:

- There are few relatively sensitive individuals who respond at low doses.
- Few relatively resistant individuals respond at high doses.
- Most of the individuals respond at doses close to middle of the range.

There are numerous ways of quantifying the information obtained from the dose-response relationship for the purpose of comparison and regulation. The classical method, which may be considered the simplest, is determination of the dose at which the response is one half the maximum. This method classifies the dose as follows:

- The dose which kills half of the exposed animals is known as the median lethal dose (LD50).
- The dose at which half the exposed animals develop tumours is called the median effective dose (ED50).
- The air concentration at which half the exposed persons report respiratory irritation is called the median effective concentration (EC50).

These median measures offer an accurate way of comparing the toxicity among different chemicals—the higher the LD50 the lower the toxicity.

It should also be noted that the slope of the dose-response curve can also have an important influence on the relative toxicity comparisons. The two curves as shown in Figure 5.8 indicate that the compounds have similar median effective doses, but the results at lower doses are different—compound B elicits reaction in a significant portion of the exposed group at doses well below the median, whereas compound A does not. In an industrial setup, it may be more important to consider the response at lower doses than at the doses near the median.

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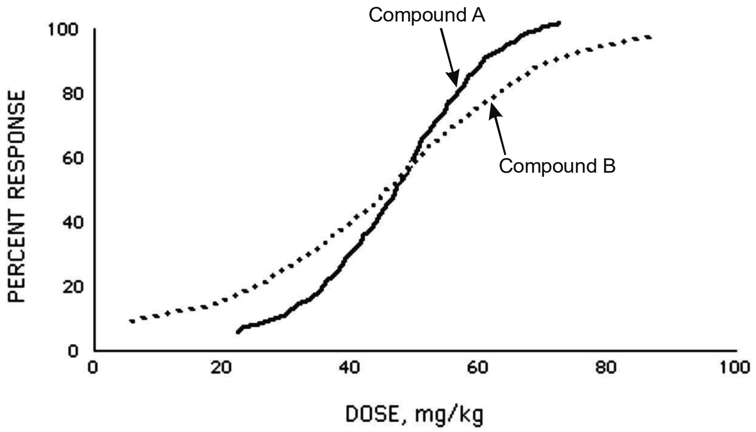

Fig. 5.8 Dose-Response Relationships

In many instances, the dose-response relationship for a chemical seems to cross the dose axis at a non-zero value of the dose. This particular point is called the threshold, and it identifies the highest dose at which no response takes place. By assuming that the threshold can be assessed for an industrial chemical, it seems that the safety can be ensured by maintaining each worker's dose below that level. The broad popularity of threshold as the goal of industrial environmental control is based on this concept. Unfortunately, it is practically difficult to assess the threshold value that can be applied to a group of workers exposed to a chemical under numerous, actual working conditions. As the individual sensitivity varies, and there exist differences among physiological variables in the workers, a wide range of doses over which responses will start appearing have been noticed. That is why, the best practical approach is a stochastic one, in which the fraction of workers responding at lower doses is determined. It is not possible to determine an absolutely safe dose. However, identification of a dose, which affects only a small proportion of workers, would be helpful.

5.4.3 Toxicokinetics

As you know, a large number of factors play an important role in determining the dose of chemical subsequent to the exposure at work. All factors affect the motion of a foreign material from the extrinsic environment into and through the human system; therefore, these factors are known as toxicokinetic factors. The various elements of toxicokinetic pathway are as follows:

- Surface contact
- Uptake
- Distribution
- Storage
- Biotransformation
- Excretion

The toxicokinetic pathways mentioned in the preceding list have been described here.

Surface contact

Surface contact implies the event of contact of a foreign material with a part of the body's external surface. Skin constitutes the main external surface of the body. The surface of respiratory and gastrointestinal system is also included in the boundary that separates the internal and external environments. Hence, a chemical, which is inhaled or ingested does not actually enter the body till it makes contact with a part of the surface and is absorbed. The bulk liquids and solids may come in contact with the skin or with the gastrointestinal mucosa after ingestion. Finely divided solids and liquids, along with gases and vapours, are capable of contacting respiratory surfaces. The main routes of entry taken by the workplace chemicals are as follows (refer Unit 2):

- Ingestion
- Skin contact
- Inhalation

The other routes of entry are specialized opening such as eyes and ears. The area of skin in an average adult male is approximately 1.8 to 2.0 m^2. Gastrointestinal tract comprises approximately 15 m^2, while the respiratory surface covers an area of 50 to 70 m^2. The most frequent route of entry for industrial chemicals is skin contact. However, inhalation is also a significant route of entry for chemicals. Ingestion exposure is very rare in the workplace, with some important exceptions result from food contamination and suicide attempts.

Inhaled gases, vapours and solid particles may access the surface by a process known as deposition. They may be exhaled without deposition and subsequently fail to enter the body. The following factors determine the deposition of airborne material:

- Retention on the surface once contact occurs
- Time spent in the respiratory airways
- Mobility relative to the air

Movement of gases and vapours occurs by diffusion, which is quite fast for virtually all chemicals (it is inversely related to the weight of molecules, but its impact is negligible for the large majority of volatile chemicals). The major factors, which affects gas and vapour deposition, is retention at the surface, which is heavily dependent on solubility in the fluid lining respiratory surface. High aqueous solubility of chemicals results in high respiratory deposition for gases and the vapours. Low molecular weight of alcohols and ketones have respiratory deposition rates of 80 per cent or more, which means that 4/5 or more of the molecules inhaled will deposit and will be retained on the respiratory surfaces. Further, the gases and the vapours, which react chemically with the body surface have an extremely high effective solubility as well (e.g., all acidic and basic gases such as SO_2, C_{l2}, NH_3).

For the airborne particles and droplets, the deposition depends almost completely on mobility and residing time in the respiratory system, while retention is nearly 100 per cent, once contact occurs. Mobility of particles/droplets, in turn, depends on size. For diameters greater than about 0.5 micrometers (μm), mobility rises with the diameter and is caused by the forces of gravity and inertial acceleration. Therefore, inhaled particles from 0.5 μm up to about 50 μm reach the airway surfaces with very high efficiency when they have time to get settled under gravity, or else when they are forced to navigate sharp turns at high speed. Above 50 μm in diameter, the particles are so much influenced by gravity that they do not remain airborne for long enough to be inhaled, except under very unusual circumstances. As the particle diameter decreases below 0.5 μm, the diffusion becomes the dominant mechanism for deposition, and its magnitude increases when diameter further decreases. The diffusive deposition is important in the lungs where speeds of air are negligible and hence there is time for the particles to diffuse to the surface. Figure 1.11 summarizes dependence of deposition on the particle size for the human respiratory system. Between 1 and 10 μm the efficiency of deposition (the fraction of inhaled particles depositing) rises rapidly to nearly 100 per cent. Much of this deposition takes place in the head—nose, mouth, pharynx and larynx. Above 10 μm, high deposition is seen. It is more concentrated in the head. Below 1 μm, there is minimum deposition at about 0.5 μm, then a gradual rise in deposition occurs as the diameter decreases. The sub-micrometer particles deposit on the surface of airways and on the deeper portions of the lungs.

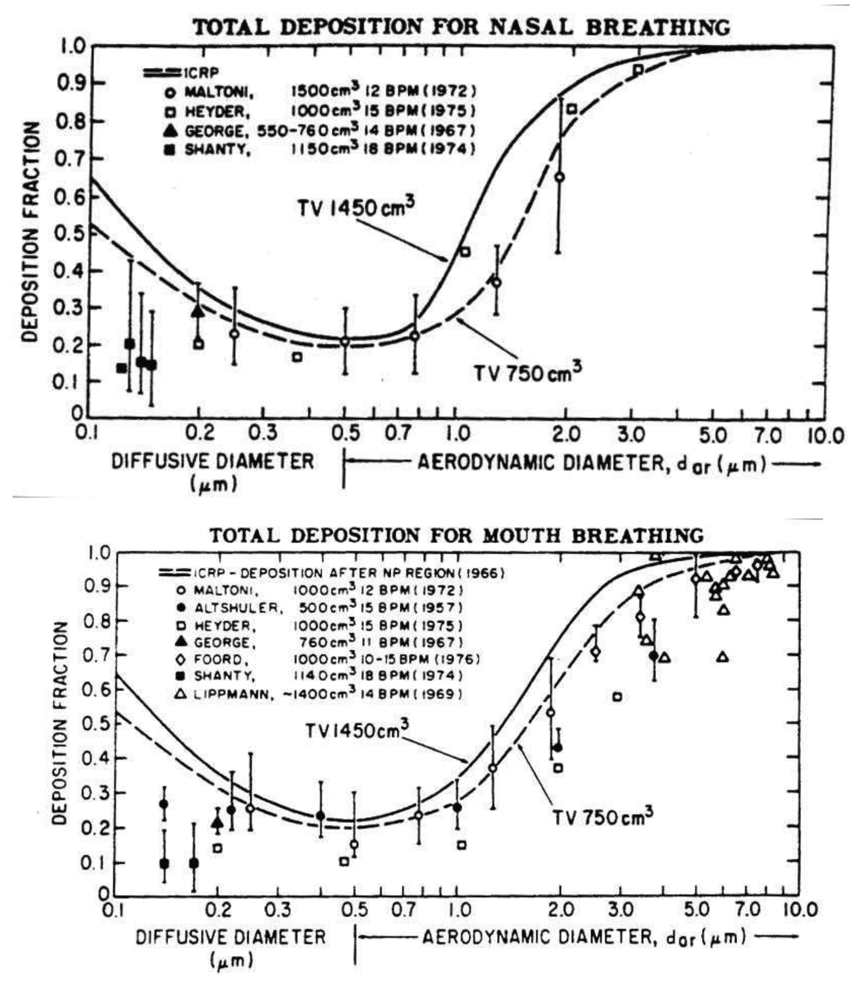

Fig. 5.9 *Dependence of Deposition on the Particle Size for the Human Respiratory System*

Uptake

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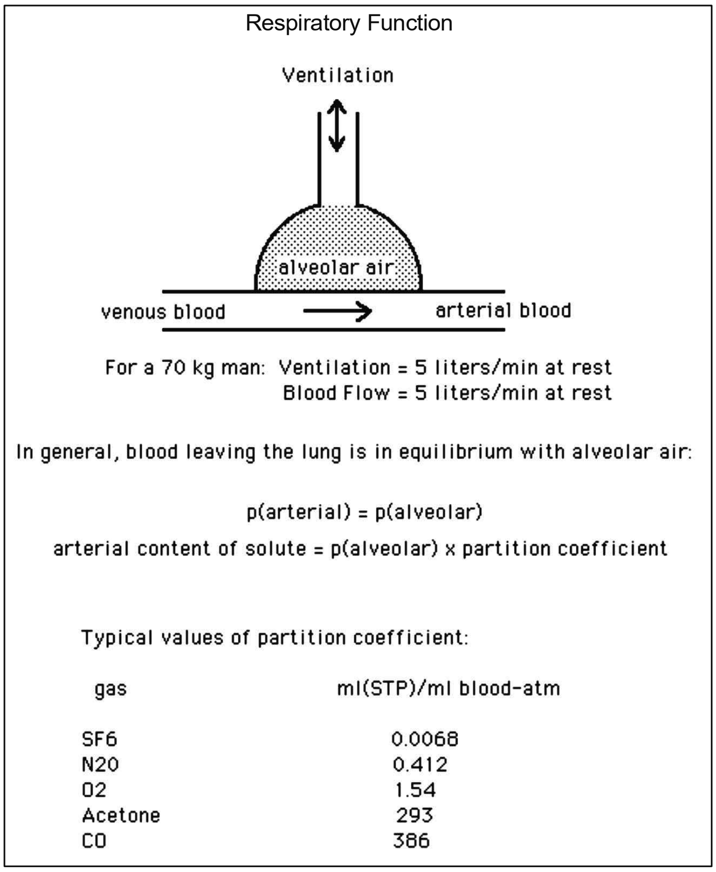
The relationship of the chemical and physical properties of a foreign substance to the physiology of the body surface where the contact is made has a significant impact on absorption, or uptake. The permeability of respiratory surface increases tremendously if contact takes place in the alveolar zone where the exchange of gas takes place. The average thickness of the barrier between alveolar air and circulating blood is less than 1 ìm thick. That is why, the uptake of several substances takes place in this particular region. As illustrated in Figure 5.10, for the gases the extent of uptake is dictated by the equilibrium solubility in the capillary blood, since exchange is so efficient that the partial pressure of the gas is equal in both alveolar air and blood.



For a 70 kg man: Ventilation = 5 liters/min at rest
Blood Flow = 5 liters/min at rest

In general, blood leaving the lung is in equilibrium with alveolar air:

p(arterial) = p(alveolar)

arterial content of solute = p(alveolar) x partition coefficient

Typical values of partition coefficient:

gas	ml(STP)/ml blood-atm
SF6	0.0068
N20	0.412
02	1.54
Acetone	293
CO	386

Fig. 5.10 *Respiratory Function*

The examples of the equilibrium solubility in blood are given for many gases of interest. It must be noted that the solubility values for oxygen and carbon monoxide include the effect of the haemoglobin. Apparently, there are many gases and vapours, which have higher blood solubility than the oxygen, and their uptake via the respiratory system will be quite efficient. For the particles and droplets, the solubility in the blood is also one of the major factors in determining the uptake, but the diffusive mobility is very low. So the uptake is delayed until the particles or the droplets are broken down into finer components or until they enter, by extremely slow processes, into the epithelial cells of the respiratory surface or the lymphatic system.

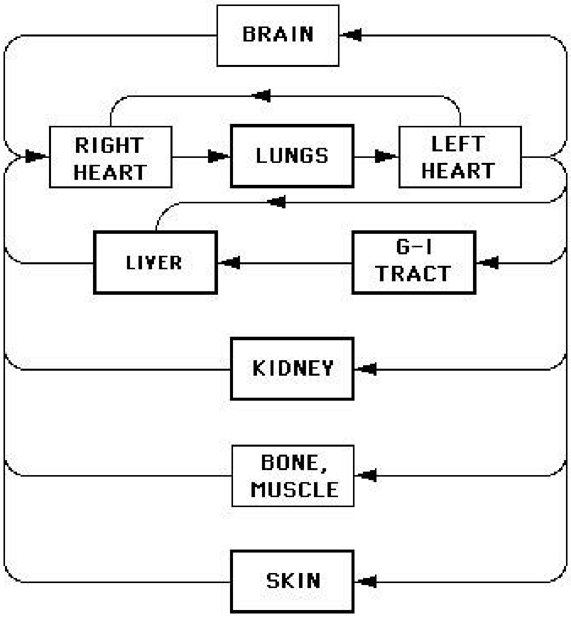
The skin consists of complex layers. The thickness of these layers between its surface and the circulation provides an effective barrier against uptake for most of the foreign compounds. Epidermis (i.e., the outermost layer of skin) comprises many sub-layers, which cannot be permeated by water and water-soluble chemicals. The lower parts of the epidermis, and the subsequent layer below that, known as dermis, are more permeable to aqueous materials. Dermis forms effective barriers against oils and other oil-soluble materials. Intact skin is therefore not very permeable, except for compounds which are water-soluble and oil-soluble both, to modest. Skin is not completely intact, as it has numerous pores through the epidermis for hair follicles and sweat glands. It can be pierced by foreign objects or damaged by the chemicals so that permeation at local areas of may take place.

Surface of the gastrointestinal tract is adapted for the process of absorption of a wide variety of nutrients, and have relatively lesser selective ability to exclude the ingested material from uptake. Foreign compounds, which can be broken down by chemical attack from acidic, basic and the enzymatic agents, are usually absorbed to certain extent, until and unless they retain an electrical charge, which causes inhibition of membrane transport. Small intestine can absorb both aqueous and the oil-soluble compound (fats), irrespective of whether they are essential nutrients or not.

Distribution

Blood circulatory system forms the main distribution system for all the absorbed chemicals. Figure 5.11 depicts organization of the circulation with the important routes of entry and the target organs. The different entry routes are related to the various target organs on the basis of the route taken by blood after the uptake. The exposure through inhalation results in the delivery of the absorbed compounds first of all to the heart, especially to the left side. The compound that is absorbed by skin is taken to the right heart at first, and then to the lungs. (It should be noted that, if compound is volatile, then it will be partially excreted via lungs before it reaches arterial circulation.) Ultimately, the material absorbed across the gastrointestinal barrier is delivered to the liver first. The perfusion rates have been given in the Figure 5.11 for various organs to show relative distribution of blood flow to organs and variation in distribution under different physiological conditions. Circulation of blood to the central nervous system remains constant. Blood circulation to kidneys, GI tract and liver is relatively higher at rest, in comparison to their weights. This helps kidneys and liver perform the regulatory function. Perfusion to these organs decreases temporarily when more blood is needed by skeletal muscles for exercise or skin for thermoregulation. An incessant supply of blood to heart muscles through coronary artery is essential as these muscles never stop working, and they do not get nourished by blood contained in the heart chambers.

NOTES



For a 70 kg person, at rest:
Cardiac output = 5 liter/min, higher when needed
Flow to brain = 0.74 liter/min, closely regulated
kidney = 1.2 liter/min, variable
GI tract = 1 liter/min, variable
liver = 1.5 liter/min, variable
coronary arteries = 0.23 liter/min, higher when needed
skeletal muscles = variable
→ skin = variable: 5-10% of Cardiac output at neutral temperatures; can increase 7 fold in heat stress

Fig. 5.11 *Organization of Circulation with Important Routes of Entry and Target Organs*

Storage

Once chemical compounds enter blood circulation, they may be sequestered (i.e. stored) at one or more than one locations in the body. The main sites for storage are listed as follows:

- Liver
- Bone
- Adipose tissue (fat)
- Plasma proteins, which are capable of binding themselves to a particular compound

Storage increases the duration of the residence of foreign compound inside the body. However, it modifies the duration and concentration of the compound in blood positively. For example, compounds with adequate solubility of oil will be absorbed selectively by adipose tissue on the basis of higher chemical affinities. Storage continues for as long as there is the gradient in concentration between the blood and the fat, until and unless, fat tissues are saturated. This process keeps the chemical concentration in the blood during the process of absorption from rising to harmful levels. Once absorption is over, the compounds, which are stored in the form of fat, are released back into blood circulation. This process is dependent on reversed concentration gradient. On the other hand, blood continues to contain the compounds long after the exposure ends. In addition to this, the preferential storage can lead to an exposure of the target organ (e.g., bones store lead and other metals). Quite a few heavy and the transition metals may replace calcium to a little extent in crystal matrix of bone. When this happens, bone marrow gets exposed to a relatively high level of lead causing damage to the production of blood cells, or haematopoietic system. The liver can store various types of absorbed compounds, sometimes to its own disadvantage.

Biotransformation

After a compound is absorbed, a big part of the foreign compound becomes susceptible to the process of biochemical transformation in one or more than one organ. Most of these occur mainly in the liver reactions and are catalysed by enzymes. The variety and the quantity of enzymes present are greatly affected by heredity and environment. That is why, there may be marked difference in the biotransformation activity towards a foreign compound amongst various persons and even in the body of a person in different conditions. In addition, there are big differences amongst various species with regard to biotransformation activity, making inter specific comparison and the extrapolation difficult. The biotransformation can be classified into the following groups of chemical reactions:

- **Hydrolysis:** It can be defined as the process of separation of a molecule into two parts in the presence of water. This reaction is chiefly helpful in the breakdown of ester and the amide linkages.
- **Oxidation:** It is defined as addition of one or more atoms of oxygen, or removal of hydrogen atoms from a molecule. It is probably the reaction, which is most frequently used as the first step on modifying foreign compound (e.g., benzene gets oxidized to phenol).
- **Reduction:** It is defined as the process of removal of oxygen atoms, or addition of hydrogen atoms (e.g., conversion of nitrobenzene into aniline).
- **Conjugation:** It is defined as the process by which an endogenous molecule is added to partially transformed compounds (e.g., addition of sulfonic acid or glucuronic acid to oxidized or the reduced aromatic solvent). This reaction nearly always takes place as last step in metabolic pathway.

Generally, a metabolite is more soluble in water than parent compound and, therefore, is easily excreted by kidneys or liver. In addition, the biotransformation of compound can lead to reduction in toxicity, which is often due to more fast excretion. On the other hand, there are other compounds for which a metabolite is more toxic than a parent, and in such cases, the toxicological property of a compound is completely a consequence of the biotransformation after absorption. The example is a parathion, an insecticide, whose neurotoxicity depends on the enzyme-catalysed oxidation to a paraoxon.

Excretion

NOTES

There are numerous excretory pathways by which the compounds and the metabolites are removed from the body fluid. The compounds in the plasma, which are soluble in water, leave mainly by filtration in the kidneys. High rate of filtration in these organs, together with an ability to selectively re-absorb the desirable constituents, permit very proficient removal of the aqueous material. Additionally, kidneys are capable of removing some compounds such as organic acid and the organic bases by way of active secretion. The cells which line the renal tubules are capable of helping in the transfer of these compounds from plasma to the urine directly.

The volatile ingredients of the blood would reach an equilibrium between capillary blood and the alveolar air during the passage through lungs. This could be the essential route of excretion after the exposure has been put to an end. The solvents with lower molecular weight, for example acetone and the benzene, can be easily traced in the breath of the workers after being exposed for a day. Some other solvents, for example, the tetra chloroethene, are excreted almost completely by this way.

The development of the bile in liver and the bile transport by way of the bile duct to the small intestine serves as the route of excretion for the conjugated metabolites of the foreign compounds. These materials can be seen in feaces. It must be observed that this route may be associated with recirculation. As small intestine contains a highly proficient absorptive surface, recirculation takes place which refers to the process in which the material being transported in the bile may get absorbed in small intestine and then circulated again to the liver, just the way bile salts are. The potential entero-hepatic recirculation might lead to a very long exposure, at least for liver, and to compounds or the metabolites.

The other routes for excretion include the milk of the lactating mothers, the sweat, the saliva and other secretions which includes semen. These are normally considered as minor means of the eliminating compounds from an exposed individual although the appearance of the toxic compounds or the metabolites in the lactating mothers' milk can be an important route of a secondary exposure for an infant.

Figure 5.12 is a summary of the important distribution pathways identified for exposure to industrial chemicals. Routes of exposure and absorption are shown at the top of the diagram, and subsequent distribution pathways are indicated by the arrows. The major storage compartments are shown at the right, in communication with the extracellular fluid compartment. The entero-hepatic recirculation may be traced from the liver via bile to the GI tract, to the blood and back to the liver. Finally the major routes of excretion are shown together with their relationships with target organs and body fluids. Note, for example, that the appearance of a foreign compound in feaces may not reflect absorption, if exposure was by ingestion.

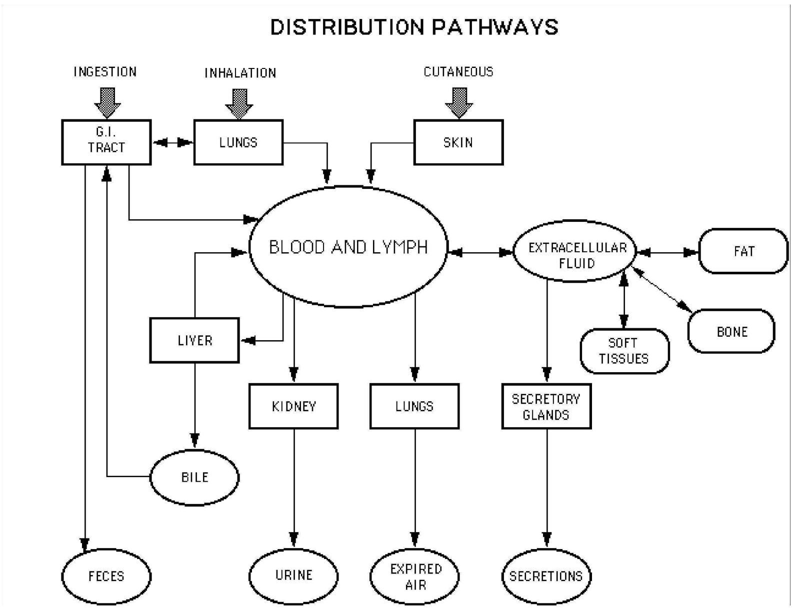


Fig. 5.12 *Important Distribution Pathways for Exposure to Industrial Chemicals*

5.4.4 Solution to Environmental Chemical Problems

Consumers are exposed to chemicals in a variety of products, ranging from toys and childcare items to food contact materials, cosmetics, furniture, and textiles, to mention a few. Furthermore, chemical pollution is one of the major factors endangering the world, influencing and aggravating planetary problems such as climate change, ecosystem degradation, and biodiversity loss. Chemicals, materials, and products must therefore become fundamentally safe and sustainable from the point of manufacture to the point of disposal, avoiding the most harmful qualities and causing the least amount of damage to the environment, resource consumption, ecosystems, and biodiversity.

The Chemicals Strategy lays out the measures that must be taken to attain a toxic-free environment and ensure that chemicals are manufactured and used in a way that maximises their contribution to society while minimising harm to the earth and future generations. The Strategy envisions a world in which the most dangerous chemicals are avoided for non-essential societal usage and all industrial chemicals are used more safely and sustainably. Simultaneously, it is critical to continue to encourage the chemical sector's and value chain's green transformation.

Chemical use has a number of advantages for civilization. Making them safe and sustainable is a huge economic opportunity – there are already frontrunners in the EU, especially SMEs, in this area – but many still face financial and technological challenges. The Strategy identifies a collection of regulatory and non-regulatory policies aimed at boosting industrial innovation and productivity. Chemicals that are 'safe and sustainable by design' will be defined and used as criteria for public and private investments. The Strategy outlines incentives to stimulate novel chemical research, development, and market adoption, as well as the overall greening of manufacturing processes in industries that produce and use chemicals. The EU industry's competitiveness will be bolstered by regulatory improvements in chemical regulations that maintain a level playing field between EU and non-EU businesses.

Once a persistent chemical has reached the environment, its effects will last for a long time, even if no fresh emissions are released. The technique tries to evaluate chemicals based on their persistence and act fast to regulate those with another potentially harmful attribute (such as mobility in the environment, bioaccumulation, and toxicity). Those chemicals should only be used if they are absolutely necessary for society and if there are no other options. Chemicals, materials, and processes that are safe and sustainable-by-design should avoid quantities and chemical qualities that may be hazardous to human health or the environment at any stage of their existence during the design phase. These are substances that are likely to be (eco) toxic, persistent, bio-accumulative, or mobile in the environment.

Check Your Progress

9. Who is considered as the 'Mother of Environmental Toxicology'?
10. Define toxicity.
11. What do you mean by target cells?
12. What are the main functions of circulatory system?
13. What is the average rate of filtration by kidneys?

5.5 BIODEGRADABILITY

Biodegradability refers to the ability of a material to decompose after interactions with biological elements. This process is known as the biodegradation that is, the breakdown of organic substances by microorganisms such as bacteria and fungi. The biodegradation process can be broken down into three stages: biodeterioration, biofragmentation, and assimilation.

Biodeterioration is defined as a surface-level degradation that alters the material's mechanical, physical, and chemical properties. When a material is exposed to abiotic elements in the outdoors, it goes through this stage, which weakens the material's structure and allows for further degradation. While biodeterioration is usually the initial stage of biodegradation, it can also occur concurrently with biofragmentation in some situations. Biofragmentation is a lytic process in which links within a polymer are cleaved, resulting in the formation of oligomers and monomers. The methods necessary to fragment these materials vary depending on whether or not oxygen is present in the solution. When bacteria break down materials in the presence of oxygen, this is called aerobic digestion; when oxygen is not present, this is called anaerobic digestion. The biofragmentation products are subsequently incorporated into microbial cells during the assimilation stage. Membrane carriers move some of the fragmentation products easily within the cell. Others, on the other hand, must go through biotransformation events in order to produce compounds that can then be transferred within the cell. Once inside the cell, the products enter catabolic pathways leading to the generation of adenosine triphosphate (ATP) or structural elements of the cell.

5.5.1 Principles of Decomposition

Decomposers are the living components of ecosystem and they are bacteria and fungi. The dead remains of producers and consumers are attacked by the decomposers and these decomposers degrade the complex organic substances into simpler compounds. Decomposers play important role in maintaining the dynamic nature of ecosystem. Main site for decomposition processes in the ecosystem is the upper layer of soil.

Decomposition is concerned about breakdown of complex organic matter by decomposers to inorganic raw materials, such as the Carbon Dioxide, water and various Nutrients. Dead animal remains and plant parts are called detritus. Aboveground detritus, which is also known as litter fall composed of dried plant parts, such as leaves, stems, bark, flowers, etc., and dead remains of animals, including faecal matter, drop over the soil. Contrary to it, belowground detritus also known as root detritus is composed of dead roots.

Process of decomposition

The following are three significant processes of decomposition which involves interrelated components:

(a) **Comminution or Fragmentation of Detritus:** Fragmentation of detritus is the first step in the process of decomposition. In this process by the action of detritivores, such as earthworm's detritus broke down into smaller pieces. During the course of feeding, the detritus (decomposer animal community) utilize the energy and nutrients for their own growth (secondary production). In due course, the decomposers themselves die and contribute to the detritus.

(b) **Leaching:** Leaching is a physical phenomenon. Soon after litter fall leaching starts, and during this process, by the action of water soluble matter, such as sugars and several other nutrients is removed from detritus. Sometime over 20% of the total Nitrogen content of litter maybe leached off.

(c) **Catabolism:** In the catabolism, the enzymatic conversion of the decomposing detritus to simpler compounds and inorganic substances during the process of decomposition carried out by extracellular enzymes released by bacteria and fungi. The process in a plant or animal by which living tissue is changed into waste products.

All the above described three decomposition processes simultaneously operate on the detritus or organic matter. The decomposing detritus first losses its weight and then completely disappears or vanishes. In an ecosystem, if the decomposition is retarded, slow or stopped then huge amount of partially decomposed organic matter will accumulate in the ecosystem.

In addition, the following two processes humification and mineralisation are also significant for the decomposition process in the soil, as shown in Figure 5.13.

- **Humification:** It leads to the accumulation of a dark coloured amorphous substance called humus that is highly resistant to microbial action and undergoes decomposition at an extremely slow rate. Humus functions as a reservoir or storehouse of nutrients.

- **Mineralization:** Microbes further degrade the humus and release inorganic substances from the humus. This process of releasing inorganic nutrients from the humus is known as mineralization. Mineralization results in release of inorganic substances in the soil, such as CO_2, H_2O and other nutrients like NH^{4+}/Ca^{++}, Mg^{++}, K^+, etc.

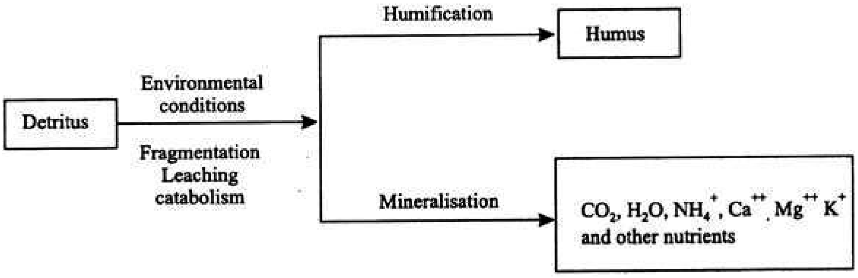


Fig. 5.13 *Humification and Mineralisation*

Functions of decomposition

The two major functions of decomposition within ecosystems are:

(1) The mineralization of essential elements.

(2) The formation of Soil Organic Matter (SOM) to inorganic forms.

Trophic level interaction

A trophic level can be described as the level in which a specific organism occupies the position in a food chain. A food chain is a succession of organisms that eat other organisms and may, in turn, be eaten themselves. It was developed by zoologist Charles Elton. The study of trophic level interaction in an ecosystem gives us an idea about the energy flow through the ecosystem. Three concepts are involved in trophic level interactions, namely the food chain, the food web and the ecological pyramids. Figure 5.14 illustrates the cycle representing the relationship between trophic level in the nature.

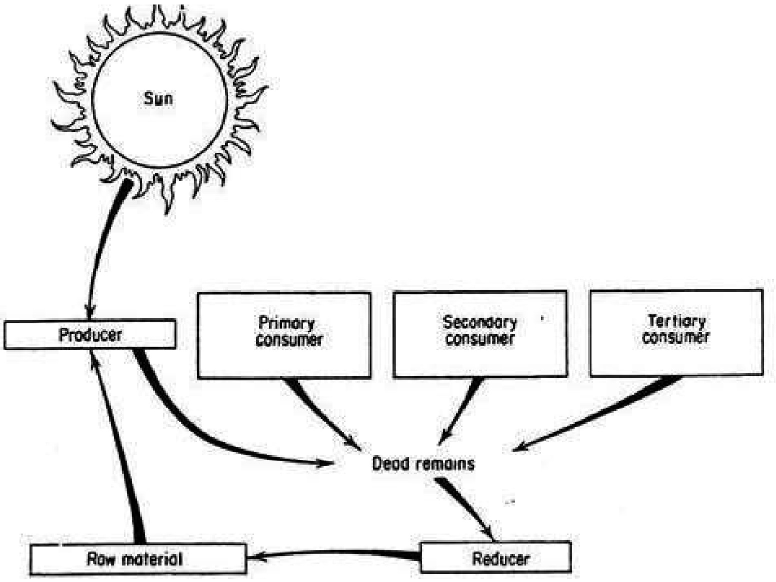


Fig. 5.14 *Cycle Representing the Relationship between Trophic Level in Nature*

Check Your Progress

14. What are the stages involved in the biodegradation process?
15. What are the major functions of decomposition within ecosystems?

5.6 BETTER INDUSTRIAL PROCESSES

Industry has long been seen as the primary source of pollution, and as a result, it was one of the first areas to receive government attention. For example, Israeli legislation allowed the environmental administration to compel plants to install pollution-prevention equipment, treat waste, transport hazardous trash to a central site in Ramat Hovav, and reduce noise pollution. The decline of raw resources as a result of industrial processes, land deterioration, loss of species, harm to human health, and climate change all demonstrate that industrial development as it is currently practised is not sustainable. Sustainable development is based on the idea of allowing the biosphere to provide 'environmental services' to the population through renewable processes rather than non-renewable materials. Nutrients are transported from organism to organism, while materials and energy are circulated and transferred in the natural environment. By decreasing waste and optimising material and energy cycling, industrial ecology attempts to reproduce this state. Both within the context of industrial operations and as separate industries, reuse and recycling are becoming more common.

In the future, the following innovations are predicted to have a favourable impact on industry:

- Increased industrial responsibility for environmentally friendly products and "clean" manufacturing techniques.
- All industrial plants, not just individual units, are subject to comprehensive supervision and treatment.
- In the first stage, increased spending in pollution prevention and waste treatment.
- In the second stage, adjustments to production procedures and material usage are implemented.
- Government and public opposition to rising environmental dangers is growing.
- Increased sway of powerful environmental organisations (such as Green Peace) over industrial decisions.
- Costs of insurance to cover environmental harm have increased.

As environmental issues become more integrated into industrial planning and construction processes, future industrial development is expected to take the following paths:

- Industrial production relying on locally sourced materials, such as those obtained through mining and quarrying, will decline. The higher cost of construction raw materials will make it easier to introduce new materials (such as plastics, aluminium, and glass) and recycle old ones.

- All industrial plants will be equipped with effluent treatment facilities, allowing them to link to municipal sewage systems. New solutions for industrial water conservation and reuse will be introduced as water prices rise. Improved domestic wastewater treatment will produce huge quantities of high-quality effluents suitable for industrial reuse. Water of high quality will continue to be allocated to industries such as the food industry.
- Industrial plants that generate gases or particulate matter will be outfitted with the required infrastructure and manufacturing processes to ensure strict adherence to emission regulations.
- Energy conservation and the usage of cleaner fuels like gas and electricity will be encouraged.
- New methods for lowering material consumption and enhancing recycling will be developed as a result of rising raw material costs around the world. Increased waste disposal prices will force considerable modifications in manufacturing processes in order to reduce waste.

Sustainable industrial practices

For sustainable industrial growth, the following practices can be adopted:

- Reduce the amount of material utilised to a basic minimum to make any product.
- Reduce the amount of energy used in the manufacturing process to a bare minimum. Use fewer energy-intensive materials, enhance manufacturing processes, and move to alternative or renewable energy sources.
- Replace harmful items with non-toxic alternatives, such as lead-free gasoline and biodegradable pesticides.
- Change from coal and oil to natural gas and solar energy.
- Waste products from one industry or stage of production can be used as raw resources in another.
- Use energy-efficient products, such as low-wattage lamps and energy-efficient refrigerators.
- Design things like modular computers that can be reused or upgraded instead of being thrown away as waste.
- Produce items out of recyclable resources like aluminium beverage cans or recycled plastic cans.
- Create items that are biodegradable and have non-toxic byproducts.
- Design items that have a low environmental impact over their life cycle and are recyclable at the end of it.
- Shift away from product manufacturing and toward service provision. For example, the pesticide business should offer integrated biological and chemical control services.

- Prepare and publish a list of all materials that enter and depart the manufacturing process. Publish emission data in order to encourage both the community and the industrial facility to reduce emissions.

5.7 INDUSTRIAL DISASTERS

It's helpful to define the phrase 'industrial accident' before moving on to the term 'industrial disaster'. An industrial accident occurs when an industrial worker is wounded or killed on the job, or when an industrial company causes an accident that injures one or more persons. An industrial disaster occurs when one of these events causes widespread injury to a significant number of people.

5.7.1 Bhopal Gas Tragedy

Bhopal gas tragedy has been the worst man-made catastrophe for India. It occurred on the 2nd December 1984 late in the night at a pesticide plant of Union Carbide of India (UCIL) in Bhopal. Huge quantities of a toxic gas called methyl isocyanate (MIC) leaked from the plant resulting in the exposure of hundreds of thousands of people. The death toll was in the range of 2,200 to 3,700. Another 8,000 died from other gas-related diseases within weeks of the leakage. More than 550,000 people were injured out of which 38,000 were temporary partially injured and 4,000 were severely and permanently disabled.

The UCIL produced the pesticides called carbaryl and methyl isocyanate. On the fateful night, water is claimed to have leaked into a tank containing 42 tons of MIC. The reaction between water and MIC raised the temperature of the gas to over 200°C increasing the pressure inside the tank to such limits that it released the toxic gas into the atmosphere. The gas was blown by north-westerly winds over the city and beyond.

There are various versions on how the water entered the tank. One of those is that workers were using water to clean a clogged pipe some 400 feet away from the tank. Perhaps, due to bad maintenance and leaking valves, water leaked into the tank, but there are doubts about this theory as water entry route could not be reproduced. Officials of the company also maintain that this route was not possible. They hold that the leakage was the result of sabotage by a disgruntled worker.

Risk factors identified

Some of the risk factors identified are:

- Use of a dangerous method of manufacturing the pesticide
- Storing huge quantities of the toxic gas unnecessarily
- Poor maintenance that could fail several safety systems
- Switching off of safety systems as a measure of economy, and this includes the MIC tank's refrigeration system
- Location of the plant near a densely populated area
- Resort to manual operation

- Deficiency in plant management
- Lack of emergency action plans

The chemical process used was mixing methylamine with phosgene to form methyl isocyanate, which was then reacted with 1-naphthol to form carbaryl. This process is different from those followed elsewhere, where phosgene is first reacted with naphtha to form a chloroformate ester, which is then reacted with methyl amine. Since the demand for pesticides had dropped in 1984, there was accumulation of unused MIC which was filled and kept in large tanks beyond recommended levels.

Some reports claimed that working conditions were pathetic at the plant. Attempts to reduce expenses affected the factory's employees and their conditions. According to the report of Kurzman, cuts in expenses resulted in lowered levels of quality control. If a pipe leaked, the employees were told to avoid replacing it, and on the suggestion that MIC workers needed more training, they were told to do with whatever they had. Bad working conditions lowered the morale of the employees forcing some of the skilled ones to move over. No maintenance supervisor was placed on the night shift and frequency of instrument readings was reduced to half— to every two hours from the required hourly. Workers complaints to the unions about the reduction of maintenance and security were ignored. Strangely, employees were even fined before the disaster for refusing to deviate from the proper safety regulations. So much so, that once an employee was even sacked when he went on a 15-day hunger strike against the management pressure in this regard. Some researchers found serious communication problems and managerial gaps between the mother company and its Indian operation. The personnel management policy led to an exodus of skilled personnel to better and safer jobs.

No planning for contingencies

Investigations also revealed that the plant was not prepared to handle problems. There were no clear cut plans to handle such big incidents. Even local authorities were not informed of the quantities of chemicals handled or dangers involved. The list of lapses is long:

- The MIC tank alarms had not worked for four years.
- There was only one manual back-up system, compared to a four-stage system used in the US.
- The flare tower and the vent gas scrubber had been out of service for five months before the disaster. The gas scrubber therefore did not treat the escaping gases with caustic soda to bring down the concentration to a safe level. Even if the scrubber were operating, the maximum pressure it could handle was only a quarter of the pressure during the leak.
- To reduce costs, the refrigeration system was shut down for long durations. The gas was kept at a much higher temperature of 20°C, as compared to the recommended 4.5°C.
- The steam boiler meant for cleaning the pipes was out of action.

- Slip-blind plates of the storage tanks were not installed. Provision for them had even been deleted from the checklist.
- The water pressure to spray the escaping gases from the stack was too weak. It could not spray high enough.
- The pressure gauge of the MIC tank was malfunctioning for quite some time. Instead of repairing the gauge other tanks were used.
- Carbon steel valves were used at the factory, even though they corrode when exposed to acid.
- Following government guidelines the design of the MIC plant was 'Indianized' by UCIL engineers so that more indigenous materials and products could be used.

Many prior warnings were given about the possibility of an accident. However, the reports never reached UCC's senior management. On one occasion, UCC was warned by American experts who visited the plant after 1981 of the potential of a "runaway reaction" in the MIC storage tank. Some local Indian authorities warned the company of problems on several occasions from 1979 onwards.

Aftermath of the leakage

The aftemath of the leakage involved:

- Medical staff was not prepared for such a large number of casualties happening suddenly.
- Doctors did not know of methods for the treatment MIC inhalation as they did not know about its properties.
- Ecology of the area was affected too. Thus, leaves from the trees started falling soon afterwards.
- Problem of disposing animal carcasses of some 2,000 bloated animal.
- Emptying of the remaining two tanks of MIC on December 16 forced another mass exodus of people from Bhopal.
- There was widespread misinformation and rumour.
- The health care system became so much overloaded that the State Government had to establish dedicated hospitals as 'Gas Affected'.
- As an opportunity, a large number of private practitioners have mushroomed in Bhopal many not even professionally qualified.
- The Bhopal Memorial Hospital and Research Centre (BMHRC), a 350-bedded super specialty hospital is the result of the Bhopal gas tragedy.

Health effects

Apart from MIC, the gas cloud may not have contained only MIC. Many other toxic gases like phosgene, hydrogen cyanide, carbon monoxide, hydrogen chloride, monomethyl amine, carbon dioxide and oxides of nitrogen, may have produced either in the storage tank or in the atmosphere.

The gas cloud composed of material that was denser than the surrounding air, so it did not rise up into the atmosphere away from the living world. The exposure caused coughing, vomiting, suffocation and irritation of the eyes. People woke with these symptoms and tried to flee homes. Those who ran, inhaled more air and thus more pollution! Some people were trampled in the stampede. About 170,000 people were treated at hospitals in special wards named 'Gas affected'.

Almost the whole of the city was affected by the morning. There mass cremations, bodies were also disposed of in the Narmada river. Cadavers of thousands of cattle and other animals were collected and buried. Leaves on trees started yellowing within hours. Supplies of commodities became scarce. Fishing was prohibited for fears of contamination causing further supply shortages.

The acute symptoms were burning in the respiratory tract and eyes, spasms, breathlessness, stomach pains and vomiting. The causes of deaths were choking, reflexogenic circulatory collapse and pulmonary oedema. Findings during autopsies revealed changes not only in the lungs but also in brain, kidneys, liver, and stomach. The stillbirth rate increased three times and neonatal mortality rate doubled.

Long-term symptoms are eye problems, respiratory difficulties, immune and neurological disorders, cardiac failure, female reproductive difficulties and birth defects among children born to affected women.

Bhopal gas tragedy is of such horrific proportion that not only will it be remembered for ever by all those who lived at that time, but also the future generations who will read about it—in the same way as the incident of the sinking of Titanic.

Generally, the toxicity of any specific chemical can be ascertained by the study of various animals which are exposed to one chemical only. The testing of mixtures of toxicity is very infrequently conducted as it is practically impossible to judge the probable combinations of various chemicals which may be present in an exposure to multiple chemicals.

The xenobiotics, either administered or received concurrently, can act independently of one another. Though, in a few cases, the presence of a chemical may significantly affect the response of another chemical. Toxicity of a multi-chemical can be less or more than that may be predicted by the known effects of the chemicals independently. Interaction is an effect that a chemical poses to the toxic effects of another chemical.

5.7.2 Nuclear Accients: Chernobyl and Three Mile Island

Nuclear energy is increasingly being used as a source of electricity. In fact, in Europe, nuclear power supplies about 35 per cent of the electricity. It is considered a clean source of power and an alternative to fossil fuels. But nuclear power, because of the possibility of radiation hazard, requires extreme precautions. Therefore nuclear power plants are designed to anticipate every possible fault and withstand accidents and technical faults. The design ensures that if something fails, there is a back-up system to limit the damage, and if that system also fails, there is another back-up system for it and so on. Risks such as earthquakes are factored in the design, especially in earthquake-prone countries like Japan. Thus, the risk is low, but nuclear accidents have taken place, the most recent one being the meltdown of a reactor at the Fukushima nuclear plant after a catastrophic 9.0 earthquake and tsunami in March 2011.

NOTES

The International Atomic Energy Agency rates nuclear accidents on a scale of 0-7, with Chernobyl in the former Soviet Union rated 7, the most dangerous. Fukushima, where the steel vessels at the heart of the reactors did not rupture, was rated a class 5, the same category as the 1979 partial reactor meltdown at Three Mile Island in the US. The most well-known nuclear accidents are as follows:

- **Three Mile Island:** On 28 March 1979, a loss of coolant and a partial core meltdown occurred at the Three Mile Island nuclear reactor in Pennsylvania, USA. A partial nuclear meltdown is when the uranium fuel rods start to liquefy, but they do not fall through the reactor floor and breach the containment systems. The accident is considered to be the worst nuclear disaster in US history. The cause was said to be simple human error and the failure of a minor valve in the reactor. While the reactor was extensively damaged on-site radiation exposure was not serious. There were no fatalities.
- **Chernobyl disaster:** The worst reactor accident in nuclear history took place on 26 April 1986 at the Chernobyl nuclear power plant, about 130 km north of Kiev, in what is now Ukraine. The accident occurred mainly due to the disregard for normal safety guidelines during an experiment on reactor safety—there was an uncontrolled power excursion, causing a severe steam explosion, meltdown and release of radioactive material. About 50 people, mostly clean-up personnel, were the first fatalities. The effects of the Chernobyl disaster were very widespread. The World Health Organization (WHO) found that the radiation released from the Chernobyl accident was 200 times that of the Hiroshima and Nagasaki nuclear bombs combined. The fallout was also far-reaching. The plume of radioactive material spread over much of Europe. For a time, radiation levels in a place as far as Scotland were 10,000 times the normal. The radiation released also had long-term effects, leading to increased rate of thyroid cancer in children of the area. This is because much of the radiation was emitted in the form iodine-131, which collects in the thyroid gland, especially in young children.

Nuclear Holocaust

Nuclear holocaust refers to the possibility of nearly complete annihilation of the human civilization by nuclear warfare. Under such a scenario, all or most of the Earth will be made uninhabitable by nuclear weapons in future world wars. Today, the world has the deadliest and most destructive weapons of mass destruction—not just in the hands of one or two countries, but many countries. It is certain that if all these weapons were to be used, humanity would be wiped off from the face of the earth. The cities and towns would be destroyed by incoming warheads, the remaining areas would not escape the large amount of radioactive fall-out blown by the wind.

There would be other consequences—a nuclear winter in which global temperatures would drop significantly, as well as the amount of sunlight received by the earth. This would be caused by the dust that would be raised up by impacting nuclear warheads and their explosions. Besides blocking the sun, the dust would be radioactive. The combination of radioactivity, lack of food, and lowering temperatures would cause a nuclear holocaust, with little chances of any humans surviving.

Holocaust in Hiroshima and Nagasaki

In Japan, the citizens of Hiroshima and Nagasaki experienced a nuclear holocaust at the regional level—on 6 August 1945, during World War II, the United States dropped a massive atomic bomb on the Japanese city of Hiroshima. This bomb, the equivalent of 20,000 tons of TNT, destroyed two-thirds of the city. A mushroom cloud of purple-gray smoke covered a whole city, rising to a height of 40,000 feet. Three days later, another bomb was dropped on the city of Nagasaki, scorching the city in an instant. The large amount of radiation seeped deeply into people's bodies, destroying cells, causing diseases and deformities. About 70,000 people died in Nagasaki.

5.7.3 Minamata Disaster

It all started with the neighbourhood cats. The citizens of Minamata, Japan, began to realise their cats were going insane and falling into the sea in the mid-1950s. Some believed the cats were attempting suicide. Soon later, a mysterious ailment began to spread throughout the village. Minamata residents complained of numbness in their limbs and lips. Some people had trouble hearing or seeing. Others experienced tremors in their arms and legs, walking difficulties, and even brain damage. And, like the cats, some people appeared to be going insane. Something was causing their neurological system to malfunction. Finally, in July 1959, Kumamoto University researchers uncovered the cause of the illness: high levels of mercury poisoning, which they dubbed Minamata disease.

Minamata is a small fishing town on the Shiranui Sea's coast. Townspeople eat a lot of fish because of their location. The fish-based diets of Minamata's people and cats seemed to be a common thread among those who were exhibiting symptoms, leading scientists to believe the fish in Minamata Bay were being poisoned. Chisso Corporation's massive petrochemical factory in Minamata was immediately suspected. However, Chisso kept denying the accusations, claiming that their mercury waste was not causing any illnesses. Chisso Corporation was later determined to have dumped an estimated 27 tonnes of mercury compounds into Minamata Bay. Poisoned women gave birth to poisoned babies as the mercury dumping continued. These children were born with deformed limbs, mental retardation, deafness, and blindness. In 1968, Chisso stopped contaminating Minimata's waters. According to the Japanese government, 2,955 persons were infected with Minamata illness, with 1,784 of them dying.

The Supreme Court of Japan ordered the government to pay 71.5 million yen ($703,000) in damages to Minamata disease victims on October 16, 2004. The Environment Minister apologised to the plaintiffs. The plaintiffs succeeded in forcing those responsible for Japan's worst case of industrial pollution pay for their negligence after 22 years. In 2010, Chisso was forced to pay 2.1 million yen in compensation and monthly medical allowances to people who were not initially diagnosed with the disease by the government.

5.7.4 Seveso Disaster

The Seveso disaster occurred on July 10, 1976, at 12:37 p.m. in a small chemical manufacturing factory about 20 kilometres (12 miles) north of Milan in the Lombardy area of Italy. It resulted in the highest known residential exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), prompting several scientific research and standardised industry safety requirements. The Seveso II Directive governs EU industrial safety requirements. In 2010, Time magazine ranked this catastrophe eighth on a list of the worst man-made environmental disasters.

In order of decreasing TCDD surface soil concentrations, the impacted area was divided into zones A, B, and R. Zone A was subdivided into seven sub-zones. The residents of the area were told not to touch or eat any locally grown fruits or vegetables.

- Zone A, which contained 736 inhabitants, had a TCDD soil content of more than 50 micrograms per square metre (g/m2).
- Zone B, which had roughly 4700 people, had a TCDD soil content of between 5 and 50 g/m2.
- Zone R, which had 31,800 residents, had a minimal concentration of TCDD or up to 5 g/m2.

Within days, 3,300 animals, predominantly chickens and rabbits, were discovered dead. To prevent TCDD from entering the food chain, emergency killing began, and by 1978, over 80,000 animals had been slaughtered. Fifteen children were rushed to the hospital with skin inflammation.

A scientific examination, economic aid, medical monitoring, and restoration/ decontamination action plan was finished in January 1977. Shortly after, ICMESA began distributing the first compensation checks to those who had been harmed. Decontamination efforts began later that spring, and in June, an epidemiological health monitoring system for 220,000 people was inaugurated. They next employed trichlorophenol to create a skin-infection-fighting medication, which they tested on dogs. The Italian government increased its special credit from 40 to 115 billion lire in June 1978. Most individual compensation claims had been settled out of court by the end of the year. Paolo Paoletti, ICMESA's Director of Production, was shot and assassinated in Monza by a member of the Italian radical left-wing terrorist organisation Prima Linea on February 5, 1980. In the presence of Italy's Prime Minister, Arnaldo Forlani, representatives of the Region of Lombardy/Italian Republic and Givaudan/ICMESA signed a compensation agreement on December 19, 1980 amounting to 20 billion lire.

NOTES

Check Your Progress

16. Mention any two positive innovations in industry.
17. Who discovered the cause of mysterious illness at Minamata?
18. Which compound was released into the environment in the Seveso disaster?

5.8 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Bagasse is a major contributor to air pollution in the sugar industry.
2. The composition of wastewater produced by distilleries includes: Biological Oxygen Demand, Chemical Oxygen Demand, total solids, sulphate, phosphate, phenolics, and numerous hazardous metals.
3. The effects of paper and pulp industry on the environment are:
   a. The immediate oxygen demand of the effluent brings about depletion of oxygen of the receiving stream with the concomitant adverse effects to the aquatic life.
   b. The chemicals present in the effluent, *e.g.,* sulphites, phenols, free chlorine, methyl mercaptan, pentachlorophenol are harmful to fauna and flora of the receiving waters. The settleable materials present may sink to the bottom and interfere with aquatic life.
4. The rate of nuclear reaction is monitored in nuclear power plants by raising and lowering the control rods.
5. Natural radionuclides arise from the all-pervading primordial radioelements such as uranium and thorium along with their daughter nuclides and potassium.
6. The natural and synthetic polymers are the two primary types of polymers. Proteins (wool, silk), carbohydrates (starch, cellulose, cotton, etc.), lipids, and nucleic acids are all natural polymers found in living systems (DNA, RNA, etc.). Synthetic polymers, such as plastic, on the other hand, are man-made and produced in the polymer industry.
7. The proper handling of waste is very essential as far as hazardous waste is concerned. Any mistake may lead to explosion, ignition and release of toxic gases polluting the air.
8. The administrative responsibilities when it comes to hazardous waste are:
   a. To ensure that the container of hazardous waste is properly marked.
   b. To choose correct disposal methods.
   c. To treat the hazardous waste correctly.
9. Rachel Carson is known as the 'Mother of Environmental Toxicology', as she established it as a separate field within toxicology with the release of her book *Silent Spring* in 1962.

10. The relative potential of a substance or combination of different substances in causing injury or harm to living organisms is called toxicity.
11. When an organism reacts to a contact to a foreign material, it results in the incidence of biological effect, at least in the starting, in the cells of either one or more tissues, which are named the target cells.
12. The main functions of circulatory system are as follows:
    a. Distributing blood to all the tissues and organs
    b. Collecting returning deoxygenated blood and passing it through the lungs before starting the new cycle
13. The average rate of filtration by kidneys is 180 litres per day.
14. The biodegradation process can be broken down into three stages: biodeterioration, biofragmentation, and assimilation.
15. The two major functions of decomposition within ecosystems are:
    a. The mineralization of essential elements.
    b. The formation of Soil Organic Matter (SOM) to inorganic forms.
16. In the future, the following innovations are predicted to have a favourable impact on industry:
    a. Increased industrial responsibility for environmentally friendly products and "clean" manufacturing techniques.
    b. All industrial plants, not just individual units, are subject to comprehensive supervision and treatment.
17. The cause of mysterious illness at Minamata was discovered in July 1959 by Kumamoto University researchers.
18. The Seveso disaster resulted in the highest known residential exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), prompting several scientific research and standardised industry safety requirements.

5.9 SUMMARY

- Industrial pollution takes numerous forms and has a wide range of effects on the land, water, and environment, as well as inflicting illness and death all over the world.
- Industries take raw materials, process them, and make final products, and certain by-products are discarded as industrial waste in gas, liquid, or solid form, polluting the air, water, and soil.
- One of the most major causes to air pollution is the cement industry. Around 7% of global carbon emissions are attributed to the cement industry.
- Unaccounted or 'fugitive' emissions are one of the cement industry's biggest problems. Fugitive emissions are pollutants that are 'fugitive,' meaning they escape from a source without being counted.
- Sugar production has been demonstrated to have a negative impact on the soil, air, and water, according to research. This is especially noticeable in tropical environments close to the equator.

- Distillery industries are a major contributor to the global economy, but they are also one of the most significant sources of pollution due to the discharge of large amounts of dark-coloured wastewater.

- Drug pollution, also known as pharmaceutical pollution, is pollution of the environment caused by pharmaceutical medications and their metabolites that enter the aquatic environment through wastewater (groundwater, rivers, lakes, and seas).
- Pharmaceuticals' emissions into the environment must be regulated to ensure adequate information and transparency about their environmental impacts.
- The important characteristics of combined effluent of integrated pulp and paper mills with chemical recovery system are dark brown colour, characteristic odour, high content of suspended and dissolved solids, high COD and resistant to biological oxidation.
- Thermal power stations are notorious for emitting a wide range of pollutants into the atmosphere. A thermal power plant is a type of power plant that transforms heat energy into electricity.
- The term thermal pollution has been used to indicate the detrimental effects of heated effluents discharged by various power plants. It denotes the impairment of quality and deterioration of aquatic and terrestrial environment.
- Nuclear power plants fulfil approximately 17 per cent of electricity needs the world over. Nuclear fission reaction is used to release nuclear energy in these plants.
- Radiation exposures due to thoron and its short-lived daughter nuclides in air are not usually considered seriously because their concentrations above 1 metre from the ground level are not appreciable.
- Metallurgy is a branch of science that studies the physical and chemical properties of metals and their mixtures. It's a way of creating metal components that can be used in other processes or consumed.
- Due to the generation of a high number of hazardous wastes, metallurgical activities are the source of environmental concerns such as air, water, and land pollution.
- A polymer is a macromolecule generated by the repeated coupling of a large number of monomer units. Polymer makes up the physical structure of the world we live in.
- There are four steps involved in the hazardous management program: Identification of the waste, Handling of waste, Minimization of hazard, and Administrative control.
- Removal of some specific components can be achieved by reverse osmosis, ion exchange process, dialysis, electro-dialysis and simple distillation process.
- Secure landfill is widely accepted for its convenience and low cost. Preventive measures guided by Resources Conservation and Recovery Act (RCRA) need to be taken care of before such disposal.

NOTES

- The most popular way of disposal of liquid hazardous waste is to force them underground through deep injection wells. Typical injection depths are more than 700m below the surface.
- The treatment technologies involved in surface impoundments are neutralization, precipitation, setting and biodegradation. Surface impoundments are excavated areas used to store liquid hazardous wastes.
- Considering the consequence of hazardous waste, the first thought must be given to its reduction in generation and then we can think of technologies regarding the disposal.
- The study of the adverse effects of diverse chemical, biological, and physical agents on living organisms is the subject of environmental toxicology, a multidisciplinary discipline of science.
- When an organism reacts to a contact to a foreign material, it results in the incidence of biological effect, at least in the starting, in the cells of either one or more tissues, which are named the target cells.
- Respiratory system maintains close contact of air with blood circulating in the body to help transfer of oxygen and carbon dioxide to body cells. A thin and extremely broad barrier separates oxygen from blood.
- The potential toxicity (harmful action), which is an intrinsic property of a substance, is manifest only when that substance comes in contact with a susceptible living biological system.
- All factors affect the motion of a foreign material from the extrinsic environment into and through the human system; therefore, these factors are known as toxicokinetic factors.
- Surface contact implies the event of contact of a foreign material with a part of the body's external surface. Skin constitutes the main external surface of the body.
- The relationship of the chemical and physical properties of a foreign substance to the physiology of the body surface where the contact is made has a significant impact on absorption, or uptake.
- The different entry routes are related to the various target organs on the basis of the route taken by blood after the uptake. The exposure through inhalation results in the delivery of the absorbed compounds first of all to the heart, especially to the left side.
- After a compound is absorbed, a big part of the foreign compound becomes susceptible to the process of biochemical transformation in one or more than one organ. Most of these occur mainly in the liver reactions and are catalysed by enzymes.
- The Chemicals Strategy lays out the measures that must be taken to attain a toxic-free environment and ensure that chemicals are manufactured and used in a way that maximises their contribution to society while minimising harm to the earth and future generations.
- Biodegradability refers to the ability of a material to decompose after interactions with biological elements. This process is known as the

biodegradation that is, the breakdown of organic substances by microorganisms such as bacteria and fungi.

- Decomposers play important role in maintaining the dynamic nature of ecosystem. Main site for decomposition processes in the ecosystem is the upper layer of soil.
- A trophic level can be described as the level in which a specific organism occupies the position in a food chain. A food chain is a succession of organisms that eat other organisms and may, in turn, be eaten themselves.
- The decline of raw resources as a result of industrial processes, land deterioration, loss of species, harm to human health, and climate change all demonstrate that industrial development as it is currently practised is not sustainable.
- An industrial accident occurs when an industrial worker is wounded or killed on the job, or when an industrial company causes an accident that injures one or more persons. An industrial disaster occurs when one of these events causes widespread injury to a significant number of people.
- Bhopal gas tragedy has been the worst man-made catastrophe for India. It occurred on the 2nd December 1984 late in the night at a pesticide plant of Union Carbide of India (UCIL) in Bhopal.
- Bhopal gas tragedy is of such horrific proportion that not only will it be remembered for ever by all those who lived at that time, but also the future generations who will read about it—in the same way as the incident of the sinking of Titanic.
- The International Atomic Energy Agency rates nuclear accidents on a scale of 0-7, with Chernobyl in the former Soviet Union rated 7, the most dangerous.
- Nuclear holocaust refers to the possibility of nearly complete annihilation of the human civilization by nuclear warfare. Under such a scenario, all or most of the Earth will be made uninhabitable by nuclear weapons in future world wars.
- Due to Chisso Corporation's illegal dumping of mercury compounds into Minamata Bay, the locals suffered mercury poisoning. This was known as Minamata Disaster.
- The Seveso disaster occurred on July 10, 1976, at 12:37 p.m. in a small chemical manufacturing factory about 20 kilometres (12 miles) north of Milan in the Lombardy area of Italy.

5.10 KEY TERMS

- **Calendering:** It is the process by which the surface of the paper is rendered less fibrous and spongy in appearance. This is accomplished by means of pressure applied to the paper at the end of its manufacturing process.

- **Sievert:** It is a derived unit of ionizing radiation dose in the International System of Units and is a measure of the health effect of low levels of ionizing radiation on the human body.
- **Thoron:** It is a heavy radioactive isotope of radon of mass number 220 that is formed as a decay product of thorium, decays by emission of an alpha particle, and has a half-life of less than a minute.

5.11 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. How is metallurgy harmful to the environment?
2. What is the impact of drug industry on the environment?
3. What are the priorities involved in the minimization of hazardous waste?
4. Classify toxicity on the basis of target organs.
5. Write a short note on the dose-response relationships of toxins.
6. What are the significant processes of decomposition?

Long Answer Questions

1. Discuss the pollution caused by thermal power plants and its solution.
2. 'Around 7% of global carbon emissions are attributed to the cement industry.' Explain.
3. Discuss the processes involved in the handling of the hazardous waste.
4. Describe the various elements of toxicokinetic pathway in detail.
5. Explain the practices which can be adopted for sustainable industrial growth.
6. Discuss the causes and ramifications of Bhopal Gas Tragedy in detail.

5.12 FURTHER READING

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