Chapter 23

Environmental Chemistry

Major Concepts

23.1 Chemistry of the Troposphere
23.2 Chemistry of the Stratosphere
23.3 Water Pollution and Water Treatment
23.4 Green Chemistry

Learning Outcomes:

Students will be able to:

- Recognize various chemical reactions occurring in the atmosphere. **(Understanding)**
- Recognize that the release of COx, SOx, NOx, VOCs are associated with the combustion of hydrocarbon based fuels. **(Applying)**
- Outline problems associated with release of pollutants including acid rain and the formation by free radical reactions of hazardous inorganic and organic compounds e.g., PAN. **(Analyzing)**
- Describe causes and impacts of urban smog. **(Analyzing)**
- Explain greenhouse effect and global warming as resulting in climate change. **(Analyzing)**
- Explain the build upto and recognize the adverse effects of ozone in the troposphere. **(Applying)**
- Describe the role of CFCs in destroying ozone in the stratosphere. **(Applying)**
- Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth. **(Understanding)**
- List possible alternatives to the use of CFCs. **(Applying)**
- Recognize and describe various water pollutants. **(Applying)**
- Explain the various parameters of water analysis. **(Applying)**
- List some major products of the petrochemicals industry, together with their uses. **(Applying)**

Introduction

Environmental chemistry is the study of various chemical phenomena that occur in the natural places such as air, water and soil. Environmental chemistry can be defined as: the study of sources, reactions, effects, transport and fate of chemical substances in the air, water and soil as well as their effects on human health and natural environment. Environmental chemistry is related with chemistry, physics, agriculture, life sciences, medical sciences, public health, sanitary engineering etc.

Environment and its Segments

Environment is everything that is around us. It belongs to all the living beings and thus is, important for all. The environment consists of four segments: lithosphere (from the Greek "lithos" for *stone*), hydrosphere (from the Greek "hydor" for *water*), biosphere (from the Greek "bios" for *life*, course or way of living) and atmosphere (from the Greek "atmos" for *vapour* and "sphaira" for *globe*).

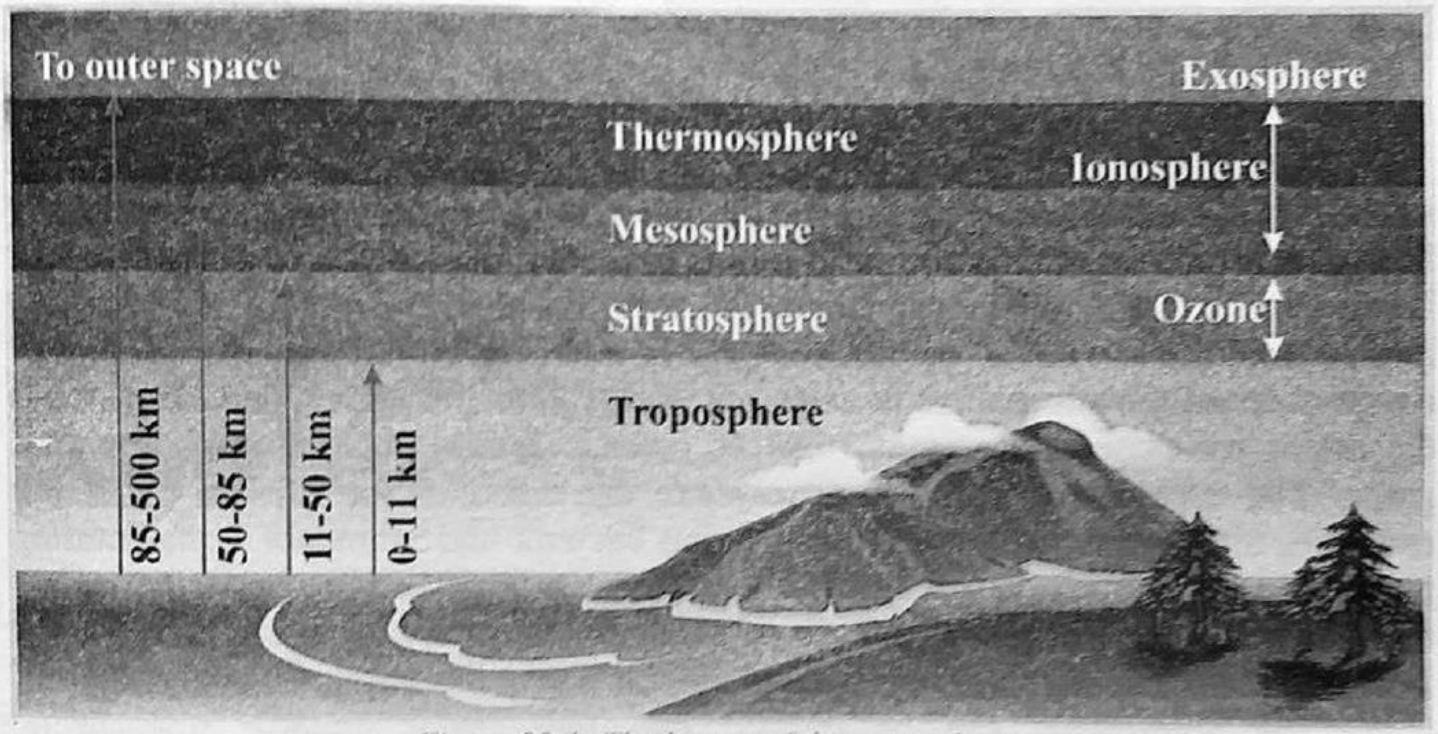

Figure 23.1: The Layers of the atmosphere

Lithosphere

The upper rigid and rocky layer of earth's crust is called lithosphere. It includes soil, earth, rocks and mountains. The soil is the most important part of lithosphere. The soil mainly consists of complex mixture of minerals, organic matter and water. Soil is used as a medium for agricultural production of crops. It extends to the depth of 100 km.

Hydrosphere

The water containing part of our earth is called hydrosphere. It includes oceans, rivers, lakes, streams, polar icecaps, glaciers and groundwater reservoirs. The earth is called blue planet because about 75% of the earth's surface is covered by water that appears blue from space. Oceans are large bodies of salt water and contain about 97% of all water on earth. Salt water is unusable by most land animals, including humans. About 2% of the earth's water is stored in glaciers and polar ice caps. However, only about 1% of the total earth's water is available as a fresh water.

It includes surface water, rivers, lakes, streams and ground water. The fresh water is used for irrigation (30%), thermal power plants (50%), industry (12%) and for domestic purposes (8%).

Biosphere

It consists of the region of earth where all living species exist above as well as below sea level (about 10000 m below sea level to 6000 m above sea level). Thus, the biosphere denotes the entire realm of living organisms and their interactions with other three segments of the environment, viz., lithosphere, hydrosphere and atmosphere.

Atmosphere

Atmosphere is the protective layer of gases surrounding the earth. It helps in sustaining life on the earth and protecting the earth from the dangerous cosmic rays from outer space. It screens the dangerous ultraviolet radiations coming from the sun. It plays an important role in maintaining the heat balance of the earth by absorbing the infrared radiation emitted by the sun and re-emitted from the earth. The major components of the atmosphere are nitrogen (78.08%) and oxygen (20.94%), whereas the minor components are argon (0.93%), carbon dioxide (0.03%) and some trace gases. The component gases of atmosphere are essential for life on earth. For example, nitrogen is used by nitrogen fixing bacteria and ammonia manufacturing plants (for the preparation of fertilizer), oxygen supports life on earth and carbon dioxide is essential for photosynthesis of plants. Furthermore, it is a carrier of water from oceans to land. Its thickness is about 500 km above the surface of the earth.

The atmosphere can be divided into four major regions: troposphere, stratosphere, mesosphere and thermosphere.

Table 23.1: Regions of Atmosphere

Region	Altitude range (km)	Temperature range (°C)
Troposphere	0 to 11	15 to –56
Stratosphere	11 to 50	–56 to –2
Mesosphere	50 to 85	–2 to –92
Thermosphere	85 to 500	–92 to 1200

23.1 Chemistry of the Troposphere

Troposphere is the nearest to the earth's surface extending up to 11 km. It accounts for about 70% of the atmospheric mass. In this region of atmosphere, the humans live and most of the biological activities occur. In this region all the dramatic events of weather (breezes, winds, storms, clouds, lightning, rain, and sunny skies) occur. The jet aircrafts flying at an altitude of about 10 km is still in the troposphere, although near upper limits of troposphere. The temperature in this region decreases uniformly with increasing altitude, reaching a minimum of about −56°C at about 11 km. The important chemical species in this region are nitrogen, oxygen, carbon dioxide and water vapours. Due to the force of gravity, molecules making up the atmosphere are most concentrated near earth's surface. Atmospheric pressure decreases with increasing altitude. The average value of pressure at sea level is 760 torr and at 100 km altitude is 0.0023 torr. The troposphere is the most easily disturbed by human activities and has the greatest effect on the earth's surface conditions. Among those effects, air pollution, acid rain, and global warming are particularly important.

Keep in Mind

Primary pollutants are directly emitted from a source. Examples are total suspended particulates (tiny particles of smoke, dust, fumes, etc.) and oxides of carbon, nitrogen and sulphur. They are emitted from chimneys of industrial units and exhaust of automobiles. **Secondary pollutants** are created in the atmosphere as a result of chemical reactions such as oxidation, photochemical reactions, and oxidation that involve primary pollutants. Examples are: hydrogen peroxide, ozone, peroxyacetyl nitrate (PAN), sulphuric and nitric acids and their salts.

23.1.1 Chemical Reactions in the Atmosphere

The atmosphere contains various gases. The numerous chemical and photochemical reactions occur in the atmosphere. The chemical reactions initiated by sunlight are called photochemical reactions. These reactions depend upon composition, temperature, pressure, humidity and intensity of sunlight. Evidently different processes will be observed under variable atmospheric conditions. Diatomic oxygen (O_2) plays an important role in the troposphere and ozone (O_3) plays an important role in the stratosphere.

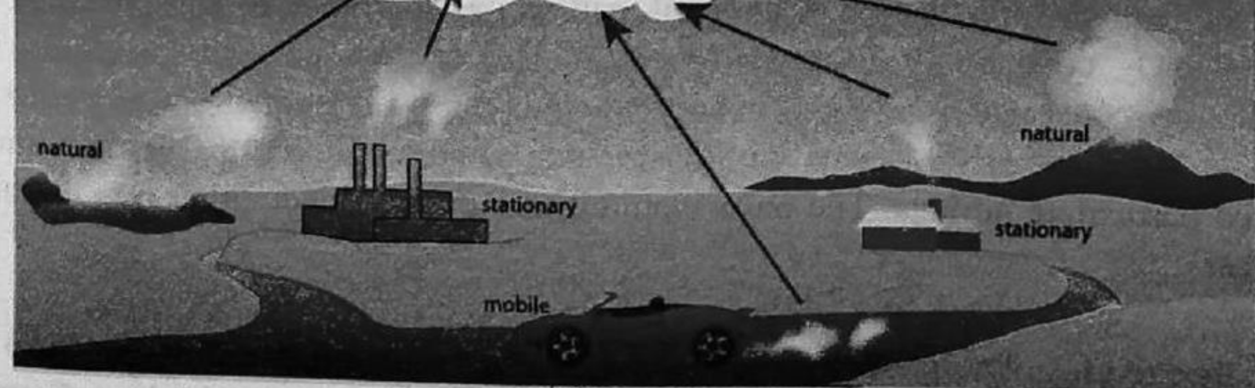

Figure 23.2: Air pollution

The important chemical reactions that occur in the atmosphere are:

23.1.1.1 Reaction of Oxygen

About 21% by volume of the gas in the atmosphere is oxygen. Oxygen plays a key role in the atmosphere (troposphere) because it is very reactive and acts as a strong oxidizing agent. The presence of large amount of oxygen makes the atmosphere thermodynamically oxidizing. In the atmosphere, oxygen is produced by photosynthesis and this oxygen is consumed by animals through respiration. The important chemical reactions of oxygen in the atmosphere are:

Rusting of iron

Iron and steel rust when they come into contact with oxygen and water vapours.

$$\text{Iron} + \text{Oxygen} + \text{Water} \longrightarrow \text{Hydrated iron (III) oxide (rust)}$$

Formation of ozone

Diatomic oxygen absorbs an ultraviolet photon and produces two free radicals such as oxygen atoms.

$$O_{2(g)} \xrightarrow{h\nu} O^{\bullet}_{(g)} + O^{\bullet}_{(g)}$$

These free radicals react with another molecule of diatomic oxygen to produce triatomic oxygen (ozone).

$$O^{\bullet}_{(g)} + O_{2(g)} + M(N_2 \text{ or } O_2) \longrightarrow O_{3(g)} + M$$

Where, M is the third body that absorbs excess energy liberated by the ozone formation, and thereby stabilize the ozone in the stratosphere. The third body may be oxygen or nitrogen.

23.1.1.2 Reaction of Nitrogen Oxides

The important oxides of nitrogen present in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). They undergo many reactions in the atmosphere both in the presence and absence of sunlight. Nitrous oxide is produced through the microbial activities while nitric oxide and nitrogen dioxide are produced from the combustion of coal, oil, natural gas and other human activities. The NO and NO_2, collectively designated as NO_x. Due to photochemical reactions, NO and NO_2 are converted to HNO_3. This nitric acid is removed from air as acid rains. On the other hand, the HNO_3 reacts with bases such as ammonia and particulate lime to produce particulate nitrates. The particulate nitrates comes down either by rain fall or as a dust.

23.1.1.3 Reaction of Sulphur Oxides

The oxides of sulphur present in the atmosphere are sulphur dioxide (SO_2) and sulphur trioxide (SO_3). These are colourless gases and have pungent odour. Some of the oxides of sulphur are originated from biological processes and from volcanoes (67%). The oxides of sulphur are also produced by burning of fuels like coal and petroleum.

$$S + O_2 \longrightarrow SO_2$$

The SO_2 is then oxidized to SO_3 in the atmosphere.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

The sulphur trioxide, in the presence of water vapours, is converted to sulphuric acid (H_2SO_4).

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The rate of photochemical oxidation of sulphur dioxide leading to the formation of H_2SO_4 aerosol is greatly accelerated in the presence of olefins and oxides of nitrogen which are present in photochemical smog.

23.1.1.4 Reaction of Organic Compounds

Generally, organic compounds such as hydrocarbons, aldehydes and ketones undergo redox and photochemical reactions. The reactions of organic compounds through a series of steps produce secondary pollutants in the atmosphere. The organic compounds in the lower atmosphere produce photochemical smog.

23.1.2 Air Pollutants (CO_x, NO_x, VOCs, SO_x, O_3, PANs) and their Harmful Effects

Pollutants can be defined as any substance in air that has harmful effect on living organism or their environment. Some of the important air pollutants are: (i) oxides of carbon (ii) oxides of nitrogen (iii) volatile organic compounds (VOCs) (iv) oxides of sulphur (v) ozone.

23.1.2.1 Oxides of Carbon (CO_x)

The oxides of carbon present in the atmosphere are carbon monoxide (CO) and carbon dioxide (CO_2).

Carbon Monoxide

Carbon monoxide is a colourless, odourless and tasteless gas. It is lighter than air and is insoluble in water. It is produced by:

(i) Incomplete combustion of fuel, namely coal, gas, charcoal, oil etc.

$$2\,C + O_2 \longrightarrow 2\,CO$$

(ii) It is also produced by forest fires and incineration of biomass (burning of forest debris, bushes, crop residue, weeds, and vegetation).

(iii) Industrial operations such as petroleum refining, paper industry, coal mining, electric and blast furnaces.

Harmful Effects of CO

It is extremely toxic and causes suffocation if inhaled. Exposure of high concentration of CO causes headache, fatigue, unconsciousness and eventually death may occur if such exposure is experienced for a longer time.

Carbon Dioxide

It is a colourless gas. It is odourless at low concentrations and has a sharp and acidic odour at high concentrations. It is soluble in water. It is added to the atmosphere through human activities such as the burning of fossil fuels, biomass and the production of cement. It is added to the atmosphere naturally through respiration system of plants and animal cells, forest fires and eruption of volcanoes. The high rate of CO_2 emissions is because of the deforestation, increase of automobiles and high population growth, etc.

Harmful Effects of CO_2

It is usually considered nontoxic and harmless. But more than 65% of the anthropogenic greenhouse effect is attributed to CO_2 gas.

23.1.2.2 Oxides of Nitrogen (NO_x)

There are eight possible oxides of nitrogen. Out of these only three oxides namely, N_2O, NO and NO_2 are the important components of atmosphere. N_2O is high in concentration in atmosphere but it is not generally considered a pollutant. NO and NO_2 are more significant pollutants and they are usually represented together as NO_x. NO is a colourless, odourless gas, but NO_2 has a reddish-brown colour and pungent suffocation odour. The major man-made sources of oxides of nitrogen are combustion of coal, oil, natural gas, gasoline and other organic matter. The oxides of nitrogen can also be discharged by natural bacterial activity. The average residence time of NO is about 4 days and that of NO_2 is 3 days in the atmosphere.

Harmful Effects of NO_x

Nitric oxide (NO) and nitrogen dioxide (NO_2) both gases are toxic but NO is less toxic than NO_2. NO_x gases cause irritation in the airways and lungs. Long term exposure may cause asthma. These gases also contribute to the formation of fine particles and ground level ozone, both of which are associated with adverse health effects. Nitrogen dioxide, ozone and hydrocarbon in sunlight form peroxyacetyl nitrate (PAN) responsible for photochemical smog.

23.1.2.3 Volatile Organic Compounds

Volatile organic compounds (VOCs) include a variety of chemical gases emitted from certain liquids and solids. They are released from burning fuel, such as diesel, gasoline, wood, coal, or natural gas. They are also released from solvents, paints, glues, and other products that are used and stored at home and at work. They also found in paint thinners, varnishes, air fresheners, cosmetics, Tobacco smoke, flooring, carpet, wood preservatives, aerosol sprays and dry cleaning fluids. Some common examples of VOCs that are present in our daily lives are benzene, formaldehyde, toluene, xylene, styrene, tetrachloroethylene and ethylene glycol.

Harmful Effects of VOCs

Short-term exposure to high levels of some VOCs can cause headaches, dizziness, light-headedness, drowsiness, nausea, and eye and respiratory irritation. Long-term exposure to high levels of some VOCs has caused cancer and affected the liver, kidney and nervous system.

23.1.2.4 Oxides of Sulphur (SO_x)

Sulphur dioxide and small amounts of sulphur trioxide are formed during combustion of sulphur-containing materials such as fossil fuels. The most important and predominant form of sulphur oxides present in the lower atmosphere is SO_2. It is a colourless gas and has pungent odour. It is moderately soluble in water, forming weakly acidic sulphurous acid and tends to form aerosols. It is heavier than air. SO_3 is a colourless solid and has low melting and boiling points. It reacts quickly with water to form sulphuric acid tending to form aerosols. These acidic aerosols are eventually precipitated as acid rain, snow, sleet or fog but only when they encounter the right meteorological conditions.

Harmful Effects of Oxides of Sulphur

SO_2 causes irritation of the eyes, nose, and throat and premature mortality. Sulphur dioxide also causes damage to vegetation, including forests and agricultural crops.

23.1.2.5 Ozone (O_3)

Ozone is an allotrope of oxygen. It is a pale yellow gas and is fairly soluble in water. It is sweetish in taste. It occurs both in the earth's upper atmosphere and at ground level. Ozone affects life on earth in either good or bad ways, depending on where it is found. It acts as pollutant in the biosphere and as protector in the stratosphere.

Harmful Effects of Ozone

Ozone is a familiar component of photochemical smog. It causes various health problems. It cause eye irritation, throat irritation, coughing and asthma. It is harmful to plants. It reduces the durability and appearance of paint and fabrics.

23.1.2.6 Peroxyacetyl Nitrate (PAN)

The peroxyacetyl nitrates (PANs) is a photochemical oxidant and is the major component of photochemical smog. PANs are both toxic and irritating, as they dissolve more readily in water than ozone.

Harmful Effects of PANs

At lower concentration, they cause eye irritation and at higher concentration, they cause extensive damage to vegetation.

23.1.3 Automobile Pollutants and the Catalytic Converter

The complete combustion in the petrol (or diesel) engine of automobile produce carbon dioxide and water vapours. The incomplete combustion leads to emissions of the poisonous carbon monoxide gas, and a wide range of various unburnt volatile organic compounds (VOCs), including hydrocarbons, aromatics and oxygenated species. Automobile also generate some oxides of nitrogen i.e. NO and NO_2. The nitric oxide is produced when atmospheric nitrogen and oxygen combine at the high temperatures present in an automobile engine. The NO released into the atmosphere further reacts with O_2 to form NO_2. The unburnt hydrocarbons produce photochemical smog and nitrogen dioxide form photochemical smog and acid rain.

The pollution that all the cars produced together can cause lung cancer, respiratory problems, urban smog and acid rain. In order to reduce air pollution, modern automobiles are equipped with a device called a catalytic converter that reduces emissions of harmful compounds such as CO, NO_2 and VOCs. These compounds are converted into less harmful compounds such as carbon dioxide, water, nitrogen, and oxygen before leaving the car's exhaust system. Catalytic converters can also be found in generators, buses, trucks, and trains; almost everything with an internal combustion engine has a form of catalytic converter attached to its exhaust system.

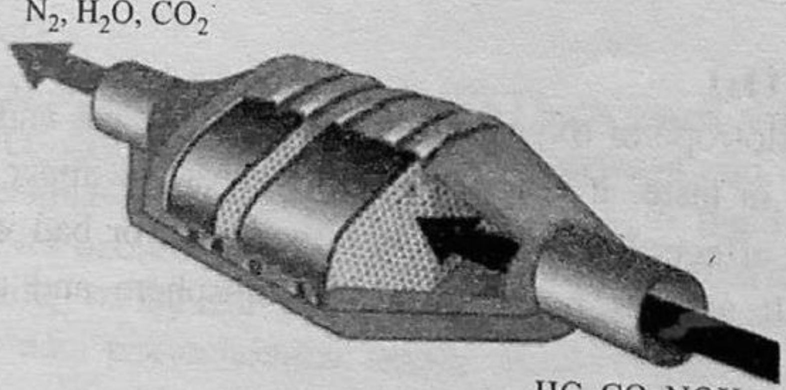

Figure 23.3: Catalytic Chamber

An efficient catalytic converter (three way catalytic converter), perform three functions: (i) it oxidizes CO and unburnt hydrocarbons to CO_2 and H_2O (ii) it reduces NO and NO_2 to N_2 and O_2 (iii) it oxidized hydrocarbons to carbon dioxide and water:

$$2\,CO_{(g)} + O_{2(g)} \longrightarrow 2\,CO_{2(g)}$$

$$2\,NO_{(g)} \longrightarrow N_{2(g)} + O_{2(g)}$$

$$VOCs + O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(g)}$$

Keep in Mind

Catalytic converters are effective at removing hydrocarbons, carbon monoxide, and nitrous oxides from car exhaust. But they do not reduce emission of carbon dioxide (CO_2), which is one of the most common greenhouse gases and contributes significantly to global warming.

Catalytic converters contain porous honeycomb structures made of ceramic materials that are coated with the catalysts. The catalyst used in a catalytic converter is a combination of platinum (Pt), palladium (Pd), and rhodium (Rh). Catalytic converter contains two different types of catalysts at work: (i) reduction catalyst (ii) oxidation catalyst. The reduction catalyst uses platinum and rhodium to reduce harmful pollutants such as nitrogen oxides in the exhaust whereas the oxidation catalyst uses platinum and palladium to reduce harmful pollutants like the carbon monoxide (CO) and VOCs in the exhaust of automobiles.

23.1.4 Industrial Smog

The word smog is a combination of smoke and fog. There are two types of smog: the industrial smog and the photochemical smog.

The industrial smog (sometimes known as London smog or gray smog) is created when SO_2 (from combustion of coal and oil) and particulate matter (larger solid particles such as metal oxides, soil particles, sea salts, fly ash, elemental carbon and small metal particles in the atmosphere) combine with the moisture in fog at suitable conditions. It produces a yellow-brown colour near ground level. It is a mixture of fly ash, soot, SO_2, smoke and some VOCs. One of the worst cases of industrial smog was the Great Smog of 1952 in London, where the smog was so thick it killed thousands of people (about 4000 people). This industrial smog is common in many cities in the world where heavy industry and power plants are found. Examples of such countries are India, China and European countries. This smog has serious negative effects on people, plants, and animals. Various human health problems such as emphysema, asthma, chronic bronchitis, lung infections, and cancers are caused by the effects of smog. It is formed in those cities where the weather is cold and wet. In many urban areas of developing countries, industrial smog is still a major problem.

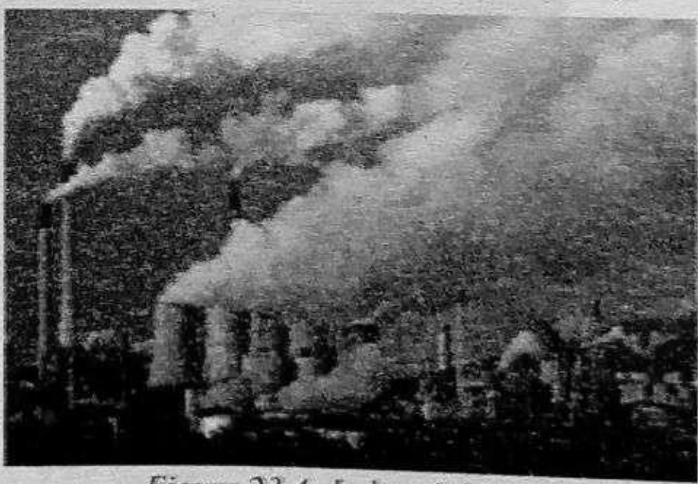

Figure 23.4: Industrial Smog

23.1.5 Photochemical Smog

Photochemical smog (sometimes known as Los Angeles smog or brown smog) is created when oxides of nitrogen reacts with volatile organic compounds (VOCs) in the presence of sunlight. This reaction produces a mixture of hundreds of dangerous secondary pollutants, such as ozone, peroxyacetyl nitrate (PAN), aldehydes, and peroxybenzoyl nitrate (PBZN). It also appears to be yellow-brown haze. Photochemical smog is common in those cities that have a lot of automobiles along with a sunny, warm and dry climate. Examples of such cities are Los Angeles (California, USA), New York (USA), Sydney (Australia), Jakarta (Indonesia), Shanghai (China), Bangkok (Thailand), Rome (Italy) and Vancouver (Canada). Photochemical smog has serious negative effects on people, plants, and animals as well. It causes health hazards such as headache, eye irritation, asthma, lung tissue damage, bronchial infections and pulmonary edema (collection of fluids in lungs).

23.1.6 Greenhouse Effect and Global Warming

The greenhouse effect is the process during which radiation (thermal infrared radiation) from the sun is trapped by the gases such as carbon dioxide, water vapours, methane, nitrous oxide, and ozone and prevent the heat from escaping back into space. Although some of the energy passes back into space, most of it remains trapped in the atmosphere, which causes the earth to heat up. This natural process of maintaining the average temperature of our earth, and keeping it warm, is known as the greenhouse effect.

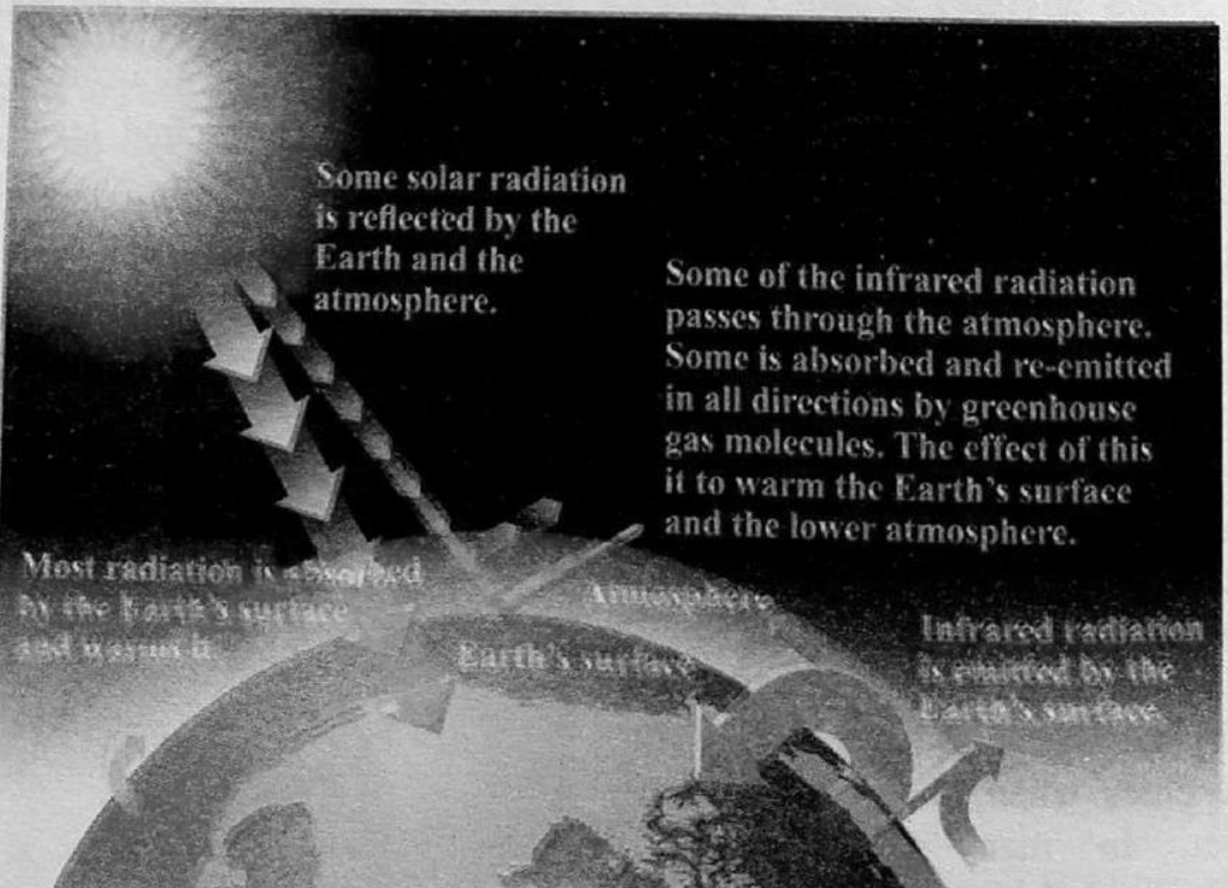

Figure 23.5: Greenhouse Effect

Global warming (Scientists often use the term *climate change* instead of *global warming*) is the gradual increase in the overall temperature of the earth's atmosphere caused by gases that are collecting in the air around the earth and stopping heat escaping into space. The gases that are responsible for causing the greenhouse effect are known as greenhouse gases and they are carbon dioxide, water vapours, methane, nitrous oxide, and ozone. Average global temperatures are maintained at about 15°C due to natural greenhouse effect. Without this phenomenon, average global temperatures might have been around –17°C and at such low temperature life would not be able to exist.

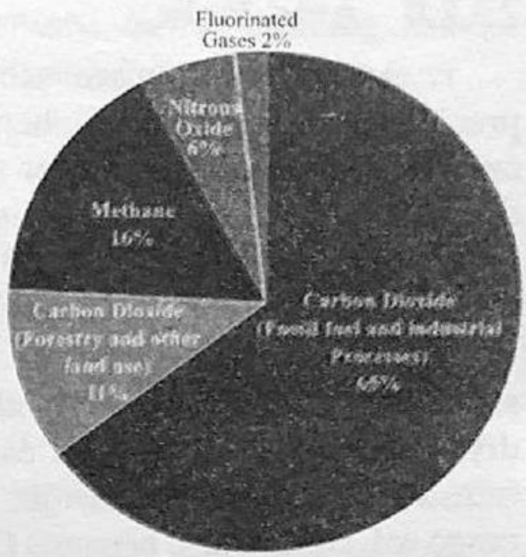

Figure 23.6: Global Greenhouse Gas Emissions

Actually, the greenhouse gases mainly carbon dioxide and water vapours are responsible for keeping the earth warm and thus sustaining life on it.

Consequences of Global Warming

If the amount of energy from the sun and the amount of greenhouse gases in the atmosphere remain the same, then the average temperature on earth will also be constant. If the greenhouse gases are very less or totally absent, the earth would be far colder and life on earth would not be possible. But, however, if the amounts of these gases exceed a certain limit, then the earth would be hotter. If global warming continues unchecked, by the turn of the century the temperature may rise by 5°C. Scientists believe that this rise in temperature will lead to deleterious changes in the environment and resulting in rise in sea levels, increasing ocean acidification, extreme weather events and other severe natural and societal impacts. Relative contribution of various greenhouse gases to total global warming is as:

- CO_2 contributes 76%
- CH_4 contributes 16%
- N_2O contributes 6%
- Fluorinated gases contributes 2%

The concentrations of methane and fluorinated gases are much lower than that of carbon dioxide, but they absorb heat much more effectively than carbon dioxide. Hence they make significant contributions to warming earth.

Carbon dioxide is the only greenhouse gas whose contribution is rising rapidly. It can be removed from the atmosphere when it is absorbed by plants. Removal of carbon dioxide from the atmosphere reduces the greenhouse effect and global warming.

23.1.7 Acid Rain

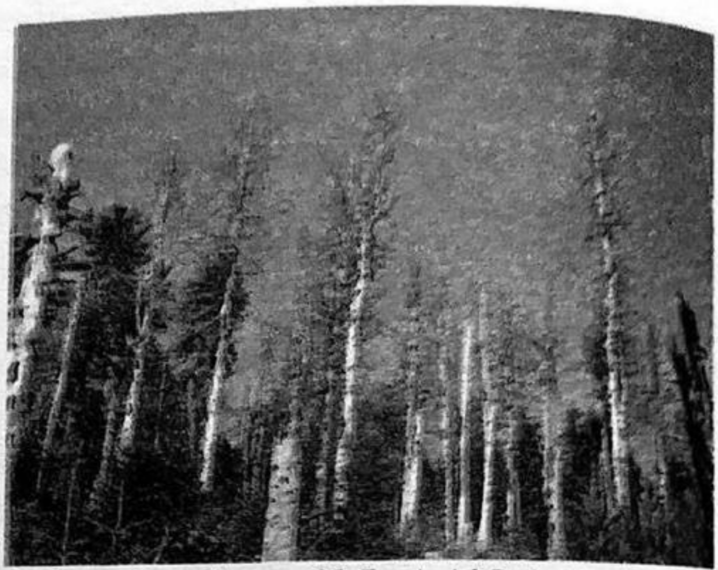

Figure 23.7: Acid Rain

Acid rain, or more accurately acid precipitation, is created when SO_2, NO_2 and CO_2 combines with water molecules in the atmosphere and result in producing mild solutions of sulphuric acid, H_2SO_4; nitric acid, HNO_3 and carbonic acid, H_2CO_3. It can also occur in the form of snow, sleet, fog, dew, hail and tiny bits of dry material that settle to earth. Normal rain water is slightly acidic with a pH range of 5.3 to 6.0, because CO_2 and H_2O present in the atmosphere combine together to produce carbonic acid, which is a weak acid. When the pH level of rain water drops below this range, it becomes acidic rain.

Harmful Effects of Acid Rain

Acid rain has negative effects on the environment and public health.

i) Acid rain can increase the acidity of rivers, dams, streams, lakes and oceans and significantly affect the aquatic life.

ii) Acid rain can increase the acidity of the soil, water and shallow groundwater that results in killing of plants and animals. Acidity may cause death of fish populations and other aquatic species including frogs, snails and crayfish.

iii) Acid rain makes water acidic, and causes them to absorb the aluminium that makes its way from soil into lakes and streams. This combination makes waters toxic to crayfish, clams, fish, and other aquatic animals.

iv) Acid rain affects trees. Acid rain can make them lose their leaves, damage their bark, and stunt their growth. Acid falling on a forest's soil is also harmful because it disrupts soil nutrients, kills microorganisms in the soil, and can sometimes cause a calcium deficiency.

v) Acid rain erodes buildings, monuments and stone statues. It corrodes steel structures such as bridges, towers etc. It also corrodes ceramics, textiles, plastics and paints.

vi) Acid rain adversely affects human health by creating particles in the air that can cause respiratory problems to humans and animals. Children and those who already have respiratory health conditions such as asthma are badly affected. Headaches and irritations of the nose, throat and eyes are some of the minor effects. Intensified levels of the acidic depositions are linked to risks of developing heart and lung problems such as asthma and bronchitis, and even cancer. When we drink tap water contaminated with acid rain, it can damage our brains.

The harmful effects of acid rain may be minimized by minimizing the emissions of nitrogen oxides, sulphur oxides and other harmful gases from power plants, industries and automobile exhausts.

23.2 Chemistry of the Stratosphere

Stratosphere, is the region (second region) from 12 km to 50 km (approximately) above the earth's surface. It consists of nitrogen, oxygen and ozone. No weather takes place in the stratosphere. The stratosphere has over 15% of the total mass of the atmosphere, and is where the ozone layer is located. This layer is about 38 kilometres thick.

The ozone layer is present about 20–40 km above the earth's surface. Ozone (O_3) is a hazardous pollutant at low altitudes but is significantly important in the upper atmosphere because it helps protect us from hazardous ultraviolet radiation (UV) from the sun. The life on earth would not be possible without the protection of this layer. At earth's surface, it can cause various health problems such as skin cancer, effect immune system and may cause blindness.

Air temperature slowly increases with height in the stratosphere, in contrast with the troposphere where the temperature quickly decreases with height. This unusual temperature structure is caused by absorption of sunlight by ozone.

Production and Destruction of Ozone

Ozone is produced by photochemical reactions in the stratosphere when the rays of sun split oxygen molecules into single atoms. These atoms combine with nearby oxygen to form a tri-oxygen molecule, called **ozone**.

$$O_{2(g)} \xrightarrow{\text{UV (220nm)}} O_{(g)} + O_{(g)}$$

$$O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$$

The ozone molecules, in turn absorb ultraviolet rays between 220 to 330 nm, and thus prevent these harmful radiations from entering the earth's atmosphere.

$$O_{3(g)} \xrightarrow{\text{UV (220 to 330 nm)}} O_{2(g)} + O_{(g)}$$

UV radiation at wavelength longer than 220 nm cannot be absorbed by O_2 and it cannot break the oxygen molecule into two oxygen atoms.

$$O_{2(g)} \xrightarrow{\text{UV (> 220 nm)}} \text{No Action}$$

Thus, the total amount of ozone is maintained by this continuous process of destruction, and regeneration.

Ozone Depletion

The ozone layer protects the Earth from harmful ultraviolet radiation by absorbing these radiation. As the layer is reduced, the amount of harmful ultraviolet radiation that reaches the Earth increases. The ozone depletion (reduction) in the stratosphere is caused by ozone depleting chemicals. Examples of these chemicals are CFCs, halons, carbon tetrachloride, methyl bromide, hydrobromonfluorocarbons (HCFCs), and bromochloromethane (BCM).

Keep in Mind

The chemicals that are produced or influenced by human activities are known as anthropogenic (man-made) compounds. For example, chlorofluorocarbons are anthropogenic compounds in the atmosphere that are produced by aerosol propellants, refrigerator coolants and air conditioners. Many of the organic compounds that are produced by the human activities such as CO_2 and CH_4, also occur naturally, and in sufficient quantities. Some anthropogenic organic compounds such as DDT (insecticide) do not have a natural source. Anthropogenic compounds can have harmful effects on human health and the environment.

Chlorofluorocarbons (CFCs) are anthropogenic compounds containing atoms of carbon, chlorine and fluorine. CFCs are also called Freons. They can be readily converted from a liquid to a gas and vice versa. Examples are trichlorofluoromethane and dichlorodifluoromethane.

Halons are also anthropogenic compounds containing atoms of carbon, bromine, chlorine and/or fluorine.

The CFCs and halons are very stable compounds. They are inert. The chlorofluorocarbons take 50 to 1700 years whereas halons take 65 years to breakdown. The CFCs are very important compounds and prepared on large scale in the world. These are non-toxic, non-flammable, and non-corrosive. CFCs are used as coolants in refrigerators and air-conditioners. They are also used as repellents in aerosol sprays. The halons also used as fire extinguishing agents.

CFCs contain chlorine atoms while halons contain bromine atoms. Chlorine and bromine atoms of these compounds cause chemical reactions that breakdown ozone molecules and in turn, reduce the ozone's ultraviolet radiation-absorbing capacity. Bromine is many times more effective at destroying ozone than chlorine. These compounds have been banned since 1996 in advanced countries.

Substitutes of CFCs

Chlorofluorocarbons, halons and methyl bromide are ozone depleting substances (ODS). When these gases are carried to the stratosphere layer of atmosphere, where ultraviolet radiations from the sun break them to release chlorine (from CFCs) and bromine (from methyl bromide and halons). The chlorine and bromine react with the oxygen atoms in ozone and rips apart the ozone molecule. The ozone layer acts as a filter for highly hazardous ultraviolet radiation from the sun, protecting life on earth from its potentially harmful effects.

The protection of ozone layer is only possible by developing alternatives to ozone depleting chemicals. The scientists developed three primary substitutes for CFCs and these are: (i) HCFCs (ii) HFCs (iii) HCs.

Hydrochlorofluorocarbons (HCFCs)

They contain hydrogen, chlorine and fluorine atoms. They are just like CFCs, except hydrogen atoms have replaced some chlorine atoms. They were the first substances used as replacements for CFCs. HCFCs are less stable in the lower atmosphere, enabling them to break down before reaching the ozone layer. However, they still diffuse into the stratosphere and cause significant ozone destruction. They have shorter lifetime (2-25 years) in the lower atmosphere than CFCs (more than 100 years). But the problem is that they still contain chlorine that can attack the ozone layer. The HCFCs can contribute to global warming and are more expensive to make than CFCs.

Hydrofluorocarbons (HFCs)

They contain hydrogen and fluorine atoms. They are chlorine free. They are like CFCs, except hydrogen atoms have replaced the chlorine atoms. Due to absence of chlorine, they have no ozone depletion potential. They are now widely used as replacements for CFCs. They have shorter lifetime (2-25 years) in the lower atmosphere than CFCs (more than 100 years). But the problem is that the HFCs can contribute to global warming and are more expensive to make than CFCs.

The HCFCs and HFCs substitutes are six to fifteen times more expensive than CFCs. It is better to use HFCs as compared to HCFCs because HFCs have no ozone depletion potential.

Hydrocarbons (HCs)

They contain hydrogen and carbon atoms. They are free from halogens. They (a propane/isobutane blend) replaced CFCs and are extensively used in mobile air conditioning systems as refrigerants in many countries. They are also used in domestic and commercial refrigeration applications worldwide. They are used as propellants in spray cans.

23.3 Water Pollution and Water Treatment

Any physical, chemical and biological change in the quality of water by the addition of other substances that badly affect the living organisms is called water pollution. Water is essential for life on earth. We use water for drinking, washing, cooking, agriculture, industry, transport and recreation. Marine life is also impossible without water. Hence it must free from deadly chemicals and bacteria in order to be drinkable.

The method in which raw water is made fit for drinking and other domestic purposes by removing foreign materials is called water treatment. The goal of water treatment is to remove contaminants and organisms through a combination of biological, chemical, and physical processes to make it safe for drinking. Contaminated water is the main source of infectious diseases such as amoebiasis, dysentery, cholera, typhoid, jaundice, malaria and paratyphoid fever.

23.3.1 Types of Water Pollutants

There are three major types of water pollutants: (i) Suspended Solids and Sediments, (ii) Dissolved Solids (iii) Thermal Pollution.

23.3.1.1 Suspended Solids and Sediments

The small solid particles that remain suspended in water and act as collide are known as suspended solids. They include silt, coal dust, plankton and industrial wastes. The loose sand, clay, silt and other soil particles that settle to the bottom of liquid are called sediments.

The process of natural erosion of soil and the decomposition of plants and animals gives rise to sediments and suspended solids in water. Sediment is subsequently transported by the action of winds, water or ice. Sediment is the most common pollutant in rivers, lakes, streams and other water reservoirs. The suspended particles and sediments produce turbidity in water and consequently reduce the amount of sunlight available to the aquatic life, which is required for the photosynthesis by bottom vegetation. They reduce the storage capacities of reserves.

23.3.1.2 Dissolved Solids

Dissolved solids are a mixture of different organic and inorganic compounds contained in a water. These solids are mostly minerals, salts, organic matter, metals, cations or anions dissolved in water. The major components of dissolved solids are the cations such as calcium, magnesium, sodium and potassium, and the anions such as bicarbonate, carbonate, sulphate and chloride. Dissolved solids may come from organic sources such as leaves, silt, plankton and industrial waste and sewage. Other sources come from runoff from urban areas, road salts and/or fertilizers and pesticides. Dissolved solids may come from runoff rain water and inorganic materials such as rocks. A constant level of minerals is essential for aquatic life in the water. Changes in the quantities of dissolved solids can be damaging. The amounts of dissolved solids, which are too low or too high limit the growth and lead to the death of aquatic life.

23.3.1.3 Thermal Pollution

Thermal pollution is the increase or decrease in the temperature of a natural body of water caused by human influence. The rates of biological and chemical processes depend on temperature. Thermal power plants, nuclear power plants and industries use large amounts of water for cooling purposes. They used coolant water, which is hot, is usually discharged directly into water bodies. As a result of this hot water discharge, the temperature of water body increases, which reduces the dissolved content of the water and adversely affects the aquatic life.

Various Parameters of Water Analysis

There are six major categories of parameters of water analysis:

i) Physical Tests

Colour, turbidity, total solids, dissolved solids, suspended solids, odour and taste are estimated.

ii) Chemical Tests

The pH, hardness, presence of a selected group of chemical parameters, biocides, highly toxic chemicals, and BOD are estimated.

iii) Toxic Element Tests

Toxic elements such as iron, calcium, copper, chromium, manganese, magnesium, mercury, cadmium, molybdenum, selenium, arsenic, lead, zinc, aluminium, nickel, boron, etc. are estimated.

iv) Bacteriological Tests

In these tests, the presence of harmful bacteria such as *E.coli* bacteria and Total coliform bacteria are checked.

v) Pesticides Tests

Here the pesticides such as alachlor, atrazine, aldrin/dieldrin, alpha HCH, beta HCH, butachlor, chlorpyrifos, delta HCH, DDT, endosulfan, etc. are estimated.

vi) Volatile Organic Compounds (VOCs) Tests

Benzene, toluene, xylenes, bromobenzene, butylbenzense, chlorotoluenes, dichlorobenzenes, phenolic compounds, polyaromatic hydrocarbons etc. are estimated.

> **Keep in Mind**
>
> Biological oxygen demand (BOD) also known as biochemical oxygen demand is a measure of the amount of dissolved oxygen (DO) used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter when dissolved into a body of water. BOD is measured experimentally by calculating the amount of oxygen at the beginning and at the end of five days period at 20°C.
>
> A small amount of oxygen up to 10 ppm is actually dissolved in water. This dissolved oxygen is required by fish and other aquatic life to survive. Dissolved oxygen is also important for us because it is an important indicator of quality of water. If water has 4ppm or less dissolved oxygen, some fish and other organisms may not be able to survive. Dissolved oxygen is used by bacteria when large amounts of organic matter are present in the water.

The physical, biological, and chemical properties of drinking water have great importance because a minor variation in these parameters affects the human health. The defined standards of drinking water in Pakistan have been developed by the Pakistan Standards Quality Control Authority. The permissible limits, as laid down by the World Health Organisation (WHO) and Pakistan Standards Quality Control Authority (PSQCA) are listed for comparison. A parametric value may be a count such as 500 E. coli per litre or a statistical value such as the average concentration of copper is 2 mg/l.

Table 23.2: Parameters and National Standards for Water Quality

Parameters	WHO Standards	PSQCA Standards
Colour	≤15 TCU (true colour units)	≤15 TCU
Odour	Odourless	---
Taste	Tasteless	---
Turbidity	<5 NTU (Nephelometric Turbidity Unit)	<5
Hardness as $CaCO_3$	—	<500mg/L
Total Dissolved Solids	<1000 mg/L	<1000 mg/L
pH	6.5–8.5	6.5–8.5
	mg/L	mg/L
Aluminium	0.2	<0.2
Antimony	0.02	≤0.005
Arsenic	0.01	≤0.05
Barium	0.7	0.7
Boron	0.3	0.3
Cadmium	0.003	0.01
Chloride	250	<250
Chromium	0.05	≤0.05
Copper	2	2
Cyanide	0.07	≤0.05
Fluoride	1.5	≤1.5
Lead	0.01	≤0.05
Manganese	0.5	≤0.5
Mercury	0.001	≤0.001
Nickel	0.02	≤0.02
Nitrate	50	≤50
Nitrite	3	≤3
Selenium	0.01	≤0.01
Zinc	3	5
Phenols	≤0.002	—
PAH (Polyaromatic hydrocarbons)	2	—

23.3.2 Waste Water Treatment (or Sewage Treatment)

Waste water (or sewage) is the mixture of wastes from the human body and used water. It includes domestic waste water (or domestic sewage), industrial waste water (or industrial sewage) and storm waste water (or storm sewage). The waste water come from sinks, showers, bathtubs, toilets, washing machines, kitchen, and bathrooms is called domestic waste water. It is also called sanitary sewage. Industrial waste water is produced from industrial activities such as manufacturing or chemical processes. Storm waste water is rainfall runoff and other drainage that is collected in a system of pipes or open channels. The sewage that is carried away from buildings by pipes under the ground called a sewerage system. Waste water treatment (or Sewage treatment) is the process of removing contaminants from wastewater. The major aim of wastewater treatment is to remove the contaminants to acceptable levels to make the water safe for discharge back into the environment. The wastewater that flows into a treatment plant, basin, or reservoir is called influent.

Waste water treatment consists mainly of three steps: primary, secondary and tertiary treatments. Primary treatment removes around 40–60% and secondary treatment removes around 90% of suspended solids.

Primary Treatment

Primary treatment is also called physical treatment because it is a mechanical process by which large suspended and floating material such as sand, silt and large lump of organic matter are removed. Primary treatment removes around 40–60% suspended solids and about 35% BOD (biochemical oxygen demand or biological oxygen demand). We are unable to remove water dissolved substances and pathogens by this process.

Secondary Treatment

Secondary treatment is also known as biological treatment because it involves the use of bacteria and other microbes. These process may be aerobic or anaerobic. **Aerobic wastewater treatment** is a process where bacteria utilize oxygen to degrade organic matter (generally quantified as BOD) and other pollutants involved in various production systems. **Anaerobic treatment** is a process where wastewater or material is broken down by microorganisms without the aid of dissolved oxygen. However, anaerobic bacteria can and will use oxygen that is found in the oxides introduced into the system or they can obtain it from organic material within the wastewater. Anaerobic systems are used in many industrial systems including food production and municipal sewage treatment systems. The sludge left after decomposition of sewer by aerobic and anaerobic bacteria is rich in phosphorus, nitrogen and minerals. After drying, it is used as manure.

Secondary treatment may require a separation process to remove the microorganisms from the treated water prior to discharge or tertiary treatment. Secondary treatment removes around more than 85% of suspended solids and BOD.

Tertiary Treatment

This is the third and last step of waste water treatment. Tertiary treatment consists of advanced physical, chemical and biological processes. Tertiary wastewater treatment is used when particular wastewater components which cannot be removed by secondary treatment must be removed. The major objectives of tertiary treatment are the removal of bacteria, dissolved inorganic solids, fine suspended solids and final traces of organic compounds if needed.

The water at this stage is almost free from harmful substances and chemicals. The water is allowed to flow over a wall where it is filtered through a bed of sand to remove any additional particles. The filtered water is then used for the irrigation of a golf course, green way or park, or released into the stream, river, bay, lagoon or wetland.

Disinfection

There are still some microorganisms and pathogen contaminants in the remaining treated wastewater. To kill them, the wastewater must be disinfected for at least 20-25 minutes in tanks that contain a mixture of chlorine and sodium hypochlorite. Chlorination is done during tertiary treatment.

23.4 Green Chemistry

Green chemistry, also called sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green Chemistry is based on a set of twelve principles that can be used to design or re-design molecules, materials and chemical transformations to be safer for human health and the environment.

Goal of Green Chemistry

The goal of green chemistry is:

i) To choose the most efficient ways to synthesize the chemicals.

ii) To make safe, sustainable and non-polluting chemicals that consumes minimum amount of materials and energy while generating little or no waste material.

iii) To prevent and minimize the production and use of hazardous chemicals.

Principles of Green Chemistry

In 1998, two US chemists, Paul Anastas and John Warner sketched Twelve Principles of Green Chemistry and these are:

i) Prevention: It is better to prevent the generation of waste than to treat or clean up waste after it has been produced.

ii) **Atom Economy:** Synthetic methods should be planned to maximize the incorporation of all materials used in the synthesis into the desired product.

iii) **Design less Hazardous Chemical Syntheses:** Synthetic methods should be designed to use and generate substances with little or no toxicity to either humans or the environment.

iv) **Designing Safer Chemicals:** Chemical products should be developed to affect their desired function while considerably reducing their toxicity.

v) **Safer Solvents and Auxiliaries:** The use of auxiliary substances such as solvents, separation agents, and others, should be avoided wherever possible. If you must use these chemicals, use harmless auxiliaries.

vi) **Design for Energy Efficiency:** Chemical synthesis should be performed at ambient temperature and pressure, if possible.

vii) **Use Renewable Feedstocks:** A raw material or feedstock should be renewable rather than depleting whenever feasible in technological and economic terms.

viii) **Reduce Chemical Derivatives:** Minimize or avoid unnecessary derivatization, e.g. protection / deprotection, use of blocking groups, temporary modification of physical/chemical processes) if possible, because such steps require additional reagents and can generate waste.

ix) **Use Catalysts:** Catalytic reagents are superior to stoichiometric reagents. Catalysts are effective in small amounts and can carry out a single reaction many times. Hence, minimize waste by using catalytic reactions.

x) **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the biosphere.

xi) **Real-time analysis for Pollution Prevention:** Advanced analytical methods have to be developed to allow for real-time, in-line process monitoring and control prior to the generation of hazardous substances.

xii) **Accident Prevention:** Reagents and solvents used in a chemical process should be chosen to minimize the risk for chemical accidents, including explosions, fires and releases.

Summary of Facts and Concepts

- Environmental chemistry is the branch of chemistry in which study about the sources, reactions, transportations and effects of the pollutants on the environment.
- The environment consists of four components: (i) atmosphere (ii) hydrosphere (iii) lithosphere (iv) biosphere.
- The layers of gases surrounding the earth is called atmosphere. It consists of nitrogen, oxygen, carbon dioxide and trace amounts of hydrogen, ozone, methane, carbon monoxide, helium, neon, krypton, xenon, and water vapours.

- The water containing parts of our earth is called hydrospheres. It includes all water resources like oceans, rivers, streams, lakes, polar ice caps.
- Biospheres consists of the region of earth where all living species exist above as well as below sea level.
- Lithosphere is the upper rigid and rocky layer of earth's crust. It includes soil, earth, rocks and mountains.
- Troposphere is the nearest to the earth's surface extending up to 11 km. It accounts for about 70% of the atmospheric mass.
- The substance in the environment that has adverse effects on human health, quality of life and natural functioning of ecosystem is called environmental pollutant.
- Global warming is the gradual increase in the overall temperature of the earth's atmosphere caused by gases that are collecting in the air around the earth and stopping heat escaping into space.
- The rain having pH value less than 5.3 is termed as acid rain. It is due to presence of carbon dioxide, sulphur dioxide and NO_2 which get mixed with rain water in the presence of pollutants to form carbonic acid, nitric acid and sulphuric acid.
- Ozone is the protective layer in the atmosphere which absorbs harmful ultraviolet radiations and cosmic rays of the sun and thus blocks them to reach on the earth.
- The addition of any harmful substance in water is called water pollution. Water is essential for all the living beings on the earth. The process of removing contaminants from wastewater is called Waste water treatment. Waste water (or sewage) is the mixture of wastes from the human body and used water.

Multiple Choice Questions

Q. Select one answer from the given choices for each question:

i) The segments of environments are
   (a) One
   (b) Two
   (c) Three
   (d) Four

ii) Polar ice caps, glaciers, rivers, rocks, mountains, soils are the parts of
   (a) Lithosphere
   (b) Hydrosphere
   (c) biosphere
   (d) Geosphere

iii) Most of mass of atmosphere is present in:
(a) Troposphere
(b) Stratosphere
(c) Mesosphere
(d) Thermosphere

iv) Rust is:
(a) Iron (III) oxide
(b) Iron (II) oxide
(c) Hydrated Iron (III) oxide
(d) Hydrated Iron (II) oxide

v) Acid rain is mainly caused in the atmosphere by the emission of:
(a) NO_X and KNO_3
(b) SO_X and charcoal
(c) CO_X and sulphur
(d) SO_X and NO_X

vi) Smog is derived from:
(a) Smoke and water droplet
(b) Fog and water droplet
(c) Fog and smoke
(d) Mist and water droplet

vii) London smog or gray smog is caused by
(a) SO_2 + particulates + moisture of fog
(b) NO_2 + particulates + moisture of fog
(c) CO_2 + particulates + moisture of fog
(d) PAN + particulates + moisture of fog

viii) Brown smog results from the mixing of:
(a) NO_2 + particulates + sun light
(b) NO_2 + VOCS + sun light
(c) CO_2 + VOCS + sun light
(d) PAN + particulates + sun light

ix) Which two gases of the following are the major contributors to global warming:
(a) Carbon dioxide and nitrous oxide
(b) Methane and nitrous oxide
(c) Carbon dioxide and methane
(d) Methane and water vapours

x) The ozone layer lies in which of the following layers of the atmosphere?
(a) Troposphere
(b) Mesosphere
(c) Exosphere
(d) Stratosphere

Short Answer Questions

Q.1. Why Environmental Chemistry is important?
Q.2. Why it is important to protect the environment?
Q.3. Why is the environment important to us?
Q.4. How do human activities affect the environment?
Q.5. What are the effects of pollution in our environment?
Q.6. Earth is called blue planet, why?
Q.7. How does the hydrosphere affect us?
Q.8. What is the importance of the hydrosphere?
Q.9. How atmosphere is important for us?
Q.10. What is the Earth's atmosphere made up of?
Q.11. What are the main pollutants in the air?
Q.12. How much do automobiles contribute to air pollution?
Q.13. What is the role of the catalytic converter?
Q.14. What is the importance of catalytic converter?
Q.15. How is smog caused?
Q.16. How is smog harmful to the environment?
Q.17. What is the main cause of greenhouse gases?
Q.18. How are greenhouse gases produced by humans?
Q.19. How does acid rain affect humans?
Q.20. Why is chlorine added to remaining treated waste water?

Long Answer Questions

Q.1. What is environmental chemistry? Briefly describe the segments of the environment.
Q.2. Explain the chemical reactions of nitrogen oxides and sulphur oxides in the atmosphere.
Q.3. Discuss the chemical reactions of oxygen in atmosphere.
Q.4. How do the chemical reactions of organic compounds carried out in the atmosphere?
Q.5. Define air pollutants. Describe the sources and harmful effects of oxides of carbon, nitrogen and Sulphur.
Q.6. What are the sources of volatile organic compounds in the atmosphere? What are the adverse effects indicated by them?
Q.7. Discuss the characteristic and undesirable effects of ozone and peroxyacetyl nitrate (PAN).

Q.8. What do you know about automobile pollutants? What are the importance and role of catalytic converters?

Q.9. Define smog and explain industrial and photochemical smog.

Q.10. What is the effect of smog on the health of peoples? How to prevent smog?

Q.11. How does car exhaust produce the smog that hangs over our cities?

Q.12. What is greenhouse effect? What are greenhouse gases? Discuss their contribution to global warming? What are the consequences of global warming?

Q.13. What is the acid rain? Discuss briefly. What are bad effects of acid rain on the environment and public health? How can we minimize its bad effects?

Q.14. Define water pollution and water pollutants? What are the different types of water pollutants and how they are produced? What are their effects?

Q.15. Explain the various parameters of water analysis.

Q.16. Define waste water and write an informative note on waste water treatment. What are the steps involved in waste water treatment?