

# Major Anthropogenic Global Environmental Problems

## SYNOPSIS

*General account, Acid rain, Eutrophication, Greenhouse effect, Smog, Ozone depletion.*

### General Account

The planet (earth) was formed over 4,600 million years ago from hot gases and cosmic dust. Primitive life probably evolved about 3,500 million years ago in the form of a single cell organism and bacteria. 400 million years ago life forms began to colonise the dry land. The human species evolved about 100,000 years ago. It was not until about 10,000 years ago that modern man emerged with the development of village, agriculture and the domestication of animal and plant species. From this perspective the human species may seem to be an insignificant episode in the planet's history. However, the global population is growing by 75-80 million a year and is expected to reach approximately 8 billion by the year 2025. This enormous population requires food, water, clothes, houses, medical care, transport, education, employment and recreation. The world we live in has to provide the raw materials for all these activities. The problem we face today is managing the earth's resources by utilizing man's ingenious technology, to support a huge population while not destroying the planet we live on.

The environmental awareness of the 1990s has enabled us to look at our activities and examine the effect that we are having on the planet earth. We are faced with the following major man-made global environmental problems :

1. Acid rain
2. Greenhouse Effect
3. Smog
4. Ozone depletion
5. Eutrophication.

## 1. ACID RAIN

### Introduction

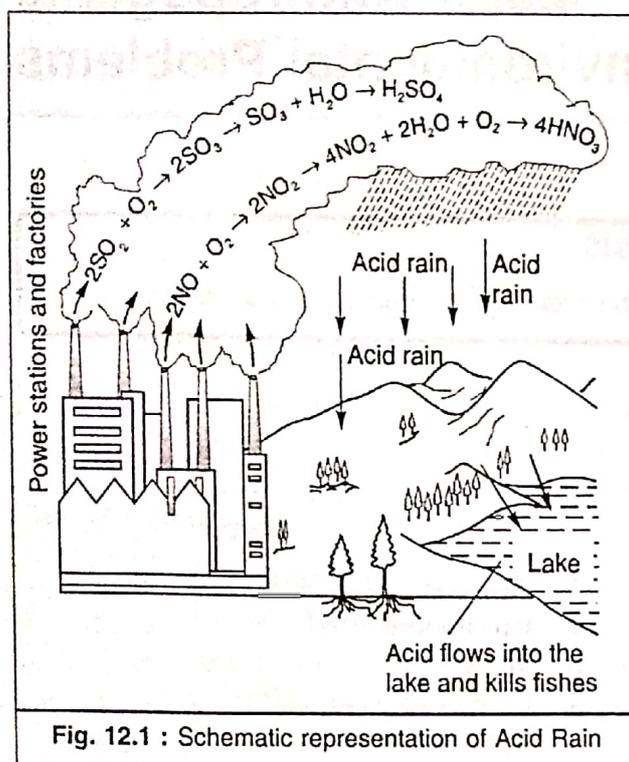
The term "acid rain" was first coined by Robert Angus in 1872. "Literally it means the presence of excessive acids in rain waters". Acid rain is, in fact, a mixture of mainly  $H_2SO_4$  and  $HNO_3$  where the ratio of these two may vary depending upon the relative quantities of oxides of sulphur and nitrogen emitted.  $H_2SO_4$  is the major contributor (60-70%) to acid precipitation,  $HNO_3$  ranks second (30-40%) and HCl third.

Acid formation takes place only at higher relative humidities (>70%).

### Definition

One of the major environmental issues facing human societies at the national and international level is the problem of acid. The rainwater is always slightly acidic as  $CO_2$  in the atmosphere gets dissolved in it. However, during recent years, it has been noted a further lowering of pH of rain water — often as low as 5.0 to 4.0. This lowering of pH is

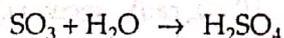
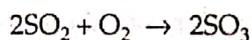
due to the dissolution of acids in the rain water. Precipitation of oxides of sulphur ( $SO_x$ ) and nitrogen ( $NO_x$ ) with rain is termed acid rain.



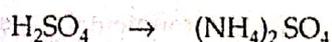
### Causes of Acid Rain

Acid rain (Fig. 12.1) is caused by air pollution. When oxides of sulphur ( $SO_x$ ) and oxides of nitrogen ( $NO_x$ ) dissolve in rain water they form sulphuric and nitric acids, respectively. The rain water falls as acid rain. The chemical reactions for  $H_2SO_4$  and  $HNO_3$  formation are :

#### A. Reactions for sulphuric acid ( $H_2SO_4$ ) formation

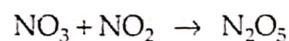
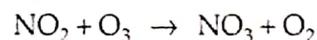
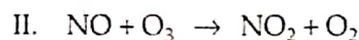
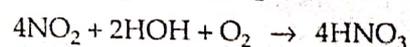
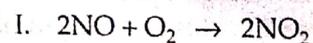


The  $H_2SO_4$  (sulphuric acid) in combination with  $NH_3$  as an environmental pollutant may form aerosols :



#### B. Reactions for Nitric Acid ( $HNO_3$ ) formation

Actually, two processes may be involved in the formation of nitric acid :



From the above reactions it becomes clear that acid rain formation may take place in two phases :

- (i) *Gas phase* — Where sulphuric acid and nitrogen are oxidized, and
- (ii) *Liquid phase* — Where hydroxylation of oxides of S and N — ( $SO_x$ ,  $NO_x$ ) — takes place.

### Sources of $SO_x$ and $NO_x$

The main source of oxides of sulphur and nitrogen is the burning of fossil fuels in power plants based on coal and oil. This contributes more than 60% of all  $SO_x$  and 25-30% of  $NO_x$  in the atmosphere. Other source of oxides of sulphur and nitrogen are smelters.

Automobiles make a substantial contribution in large cities. Ozone is now regarded as a major factor in the formation of acid rain.

### Acid Rain Problem Areas

Acidification of environment is a man-made phenomenon. The problems of acid rain are realized in North American and the Scandinavian countries where the pH of rain water has been recorded in the range of 4.4-4.0. In some regions, pH values as low as 2.8 have been recorded. In Holland, the normal pH of rainfall was anticipated to be only 3.7 in 1985. In India, low pH rain has been recorded in Mumbai (pH 4.8), Hyderabad (pH 5.7), Kolkata (pH 5.8) and Delhi (pH 6.2). Some areas like Mediterranean region and Balkans are noted as secured areas, as the soil is better and able to resist the acidification.

### Role of Wind in Acid Rain

The oxides of sulphur and nitrogen ( $SO_x$  and  $NO_x$ ) are swept up into the atmosphere and can travel thousands of kilometers. The longer they stay in the air, the more likely they are to be oxidized into acids. For example, a given molecule of  $SO_2$  may remain in the atmosphere up to 40 hours, while a sulphate particle remains for three weeks. They have enough long life period and so these molecules may be transported by wind several kilometers away from their point of release.

It has been observed that a molecule of  $\text{SO}_2$  originated in Ohio might be transported to New York. These are also wind blown from USA to Canada, or vice versa. Recently it is estimated that 80% of the sulphate in New York and New Jersey and 92% of it in New England has been carried in by long distant transport from the middle west (Wolff, 1982).

### What is Wet and Dry Acid Rain?

Actually, acid rain is the one phase of acid deposition which can either be wet or dry. Acid rain, snow, dew, fog, frost and mist represent the wet form of deposition, while dust particles containing sulphates and nitrates settled on earth is called dry deposition. The wet rain is much more common.

### Effects of Acid Rain

Acid rain problem is one environmental evil in India and is spreading fast in the developing countries. The most worrying aspect is that the area affected by acid deposition has been increasing day by day.

Some of the acid precipitation effects are

#### Effects of Acid rain on Aquatic Ecosystem

1. Acid rain creates complex problems and their impacts are far reaching in aquatic ecosystem. There are 15,000 fishless lakes in Sweden and about 100 such lakes in the Adirondack region of USA because of increased acidity of the lake. The fishless lakes are now "fish graveyards".
2. Acid rain causes impairment in biological activity of aquatic biota.
3. Acid rain (pH below 6) causes decline in the population of phytoplanktons and zooplanktons.
4. It adversely affects nutrient cycle.
5. It causes decrease in fish food.
6. Fish population declines.
7. pH below 5 makes fish unable to reproduce.
8. It causes osmoregulatory failures in fingerlings.
9. Fecundity in fishes is highly reduced in acidified lakes.
10. Different fish species react differently to acidified lakes. Adult fish can survive in more acidic water having high concentration of aluminium than fry fish.

Brook trout is most acid tolerant while rainbow trout the least. So a few critically affected lakes still have a population of mature fish.

11. Ion exchange across gill membrane in fishes is impaired causing death.
12. Low pH in lake enhances the toxicity of dissolved heavy metal ions in fishes.
13. Low pH of the lake causes damage of the leaves of aquatic plants.
14. The acidic water can also leach aluminium from the soil. So the run-off can carry dissolved aluminium to lakes, rivers and streams. It is highly toxic to aquatic animals and cause death of fishes by clogging its gills and depriving it of oxygen. Besides this, aluminium can also bind with organic particles, which are also toxic for fishes.
15. Many bacteria and blue green algae are killed due to acidification, disrupting the whole ecological balance.
16. Low pH of the aquatic environment, where fishes cannot survive, provides favourable conditions to flourish mosquitoes, black flies and other aquatic worms. Dragon fly larvae and water boatman also flourish in acidified lakes.

To sum up, acid rain causes a number of complications in ponds, rivers and lakes where it accumulates as "acid snow". In summer, rapid snowmelt gives a jolt of acid waters to lakes.

This "acid jolt" is most damaging to young fishes, algae, insects and to the food chain. In Sweden more than 2,500 lakes have their water acidic due to acid rains, and this has resulted in great damage to fish and fisheries in these lakes.

#### Effects of Acid Rain on Forest Ecosystem

1. In 1958, the pH of the rain at Europe was 5.0 and in 1962 the pH of rain at Netherlands was 4.5. This acid rain had damaged leaves of plants and trees and had retarded the growth of *Swedish forest*.
2. Due to acid rain, forests in *Germany, Switzerland, Netherlands and Czechoslovakia* have been damaged.
3. Acid rain causes leaching away of nutrients like calcium, potassium, iron and magnesium from the soil. Hence soil fertility is reduced.

4. Acid rain causes reduced plant growth by decreasing soil respiration and fertility.
5. Acid rain also leaches away the nutrients from the plants.
6. Acid rain reduces the photosynthetic rate of plants.
7. Acid rain decreases activity of symbiotic nitrogen fixing microbes present in the soil.
8. Acid rain also affects the mineralization of nitrogen.
9. Acid rain in Japan has damaged 5,000 sq. kms of cedar trees in Kanto plain, north of Tokyo.
10. Acid rain produces chlorotic spots on the leaves.
11. Acid rain accelerates cuticular erosion of leaves.
12. Acid deposition weakens the trees like pine, spruce, ashes, and birch which can be easily attacked by pathogens and drought.
13. Root systems are damaged by the uptake of aluminium released from the soil.
14. Lichens are adversely affected due to rise in soil sulphate concentration.

#### Effects of Acid Rain on Terrestrial Ecosystem

1. Acid rain causes reduced rate of photosynthesis, growth and increased sensitivity to drought and disease.
2. Acid rain has severely retarded the growth of crops such as pea, beans, radish, potato, spinach, broccoli, carrots etc.
3. The activity of symbiotic nitrogen-fixing bacteria present in the nodules of leguminosae family inhibited, thereby decrease in the fertility of soil takes place.
4. Acidification of soil changes its biology and chemistry. Plants can easily absorb cadmium from acidified soil. High level of cadmium in plants are deleterious for animals and human beings.
5. Due to acid rain, the lichens growing on plant barks lose their hold and, therefore, fail to grow.
6. Death of lichens affects nitrogen cycle.
7. Acid rain causes leaching of aluminium and nitrates from the soil and hence root system is damaged.
8. Trees pull heavy metal ions, like Cd, Cr and Al, into their systems. These ions are

immobile in many soils, but acidic water mobilizes them and causes tree damage.

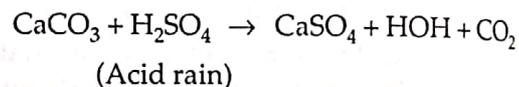
9. Acid rain enhances rise in harmful microbes.
10. Acid rain affects adversely the nitrogen balance of the ecosystem.
11. Germination index of seeds slows down in acidified soils.
12. Barks of trees absorb acid and thus the protective cover of trees becomes weak, which exposes them to other diseases.
13. Acid rain kills small invertebrates of the terrestrial ecosystem.

#### Effects of Acid Rain on Human Beings

Acidification can play havoc with human digestive system, respiratory system and nervous system by making the person an easy prey to neurological diseases. This happens because these acids produce highly toxic compounds, which contaminate the portable water and enter man's body. Acid rains containing air pollutants contribute to a variety of safety hazards, associated with reduced visibility due to smog etc. These contaminants can be nuisance in several aspects and cause adverse health effects.

#### Effect of Acid Rain on Buildings

1. Acid rain causes extensive damage to building and structural components of marble, limestone, slate, mortar, etc. Limestone is attacked rapidly :

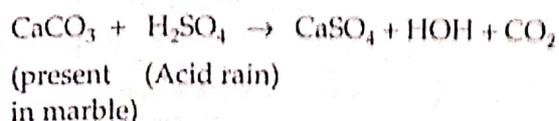


The attack on marble is termed "stone leprosy".

2. In Greece and Italy invaluable stone statues have been partially dissolved by acid rain.
3. British Parliament building also suffered damage due to  $\text{H}_2\text{SO}_4$  rain.
4. Due to acidity, levels of heavy metals as Al, Mn, Pb, Cd, Cr and Cu in water increases beyond the safe limit which indirectly affect the buildings.
5. Acid rains are great threat to British environment. Much of the falling snow in Britain is now highly acidic. If it does not melt it may turn into a "pollution time bomb".

### Episode : Taj Mahal and Acid Rain

The world's attention was drawn seriously to  $\text{SO}_2$  emissions in India, when an oil refinery — a stationary  $\text{SO}_2$  emission source — was planned for construction near Taj Mahal. But this refinery was badly needed by the farmers of the area, for the supply of diesel fuel for tractors and irrigation pumps. This oil refinery, lying only 40 km away from Taj Mahal, emitted about 25-30 tons of  $\text{SO}_2$  daily. The atmospheric concentration of  $\text{SO}_2$  in Agra have been around  $1.75 \text{ mg/m}^3$ . However, if the  $\text{SO}_2$  levels in air increase, the resulting acidic precipitation may react with  $\text{CaCO}_3$  present in the marbles :



It may cause pitting in the wonderful monument that has attracted people from around the world. Thus any increase in  $\text{SO}_2$  pollution levels in the long run may prove dangerous to this structure.

### Control of Acid Rain

No effective control for acid rain has yet been devised. There is an urgent need for proper regular monitoring to provide timely warnings about acidification of our environment. Short-term control of acid deposition problem can be achieved by using lime. New York has been liming the lakes and ponds since 1959. Mr. M. C. Chawala (1989) was the first Indian citizen who filed writ petition in the Supreme Court of India regarding the protection of Taj, a wonderful monument. The Supreme Court of India immediately issued an order for Taj to be secured, especially from acid rain.

## 2. GREENHOUSE EFFECT

### Introduction

Actually, 'greenhouse' effect is a theory which proposes that pollution by common anthropogenic pollutants such as  $\text{CO}_2$ ,  $\text{CH}_4$ , CFCs, ground  $\text{O}_3$  etc. may lead to an increased global temperature. Over the last century, especially  $\text{CO}_2$  concentration have risen and global air temperatures have increased by  $0.4-0.7^\circ\text{C}$ , which supports this theory. The atmosphere formed around the earth insulates the planet from the full effects of heat loss by trapping heat in the atmosphere using greenhouse gases like  $\text{CO}_2$ ,  $\text{CH}_4$ , CFCs, ground  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ , water vapour etc. Doubling of the atmospheric  $\text{CO}_2$  concentration from its present level is predicted to lead to a further warming of around  $3.5^\circ\text{C}$ .

The concentration of  $\text{CO}_2$  in the atmosphere has increased from about 280 ppm in 1750 to about 350 ppm in 1990 and is still rising, with the main reason for the increase being the combustion of fossil fuels. Estimates vary, but it appears likely that the concentration will rise to a mean of about 550 ppm by the year 2050.

**Term Greenhouse effect coined by** — J. Fourier (1827). It is also called "Atmospheric Effect" or "Global Warming".

**Definition of Greenhouse Effect :** According to Botkin and Keller (1982), in a greenhouse, visible light passes through the glass and heats up the soil warming the plants. The warm soil emits radiation in longer wavelengths, particularly the infrared or heat. Because glass is opaque to longer wavelength of infrared radiation, it partly reflects and partly absorbs infrared radiation. This mechanism keeps the greenhouse warmer than the outer atmosphere (Fig. 12.2).

Thus a *greenhouse* is that body which permits the short wavelength incoming solar radiation (light energy) to come in, but does not permit the long wave (heat energy) outgoing terrestrial infrared radiation to escape.

In a similar way, the earth's atmosphere bottles up the energy of the sun and is said to act like a *greenhouse*, where  $\text{CO}_2$  — whose concentration is increasing at the rate of 0.4% per annum — acts like a glass window (Fig. 12.3 A and B). Increasing  $\text{CO}_2$  content along with water vapours in the atmosphere transmits short wave length solar radiation but reflect the longer wave length heat radiation from warmed surface of the earth.  $\text{CO}_2$  molecules are transparent to sunlight but not heat radiation. So they trap and reinforce the solar heat stimulating an effect which is popularly referred to as "Greenhouse Effect" (Fig. 12.4).

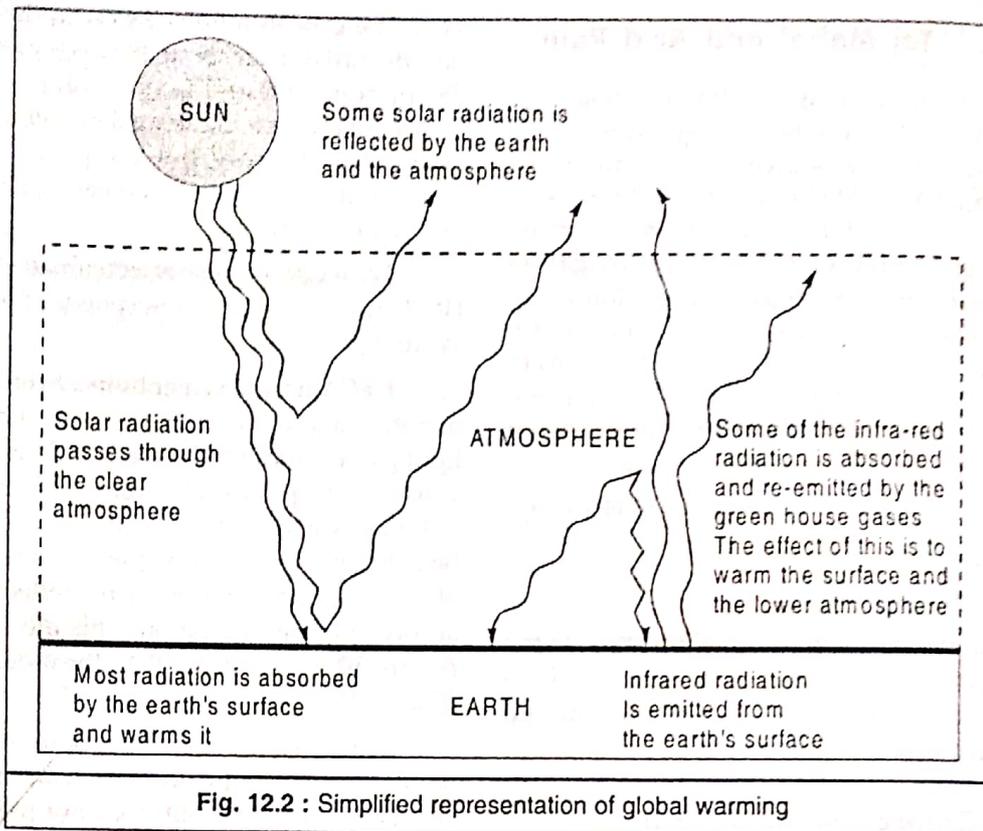
The *Greenhouse Effect* may, therefore, be defined as "the gradual warming or heating up of the earth's surface due to blanketing effect of man-created excess  $\text{CO}_2$  in the atmosphere".

or

*Greenhouse Effect* is "the phenomenon due to which the earth retains heat."

or

*Greenhouse Effect* means the excessive presence of gases like  $\text{CO}_2$ ,  $\text{CH}_4$ , CFCs etc. blocked in the infrared radiation from the earth's surface to the atmosphere leading to an increase in temperature, which, in turn, would make life difficult on earth in the coming future. This phenomenon is popularly known as "Global Warming".



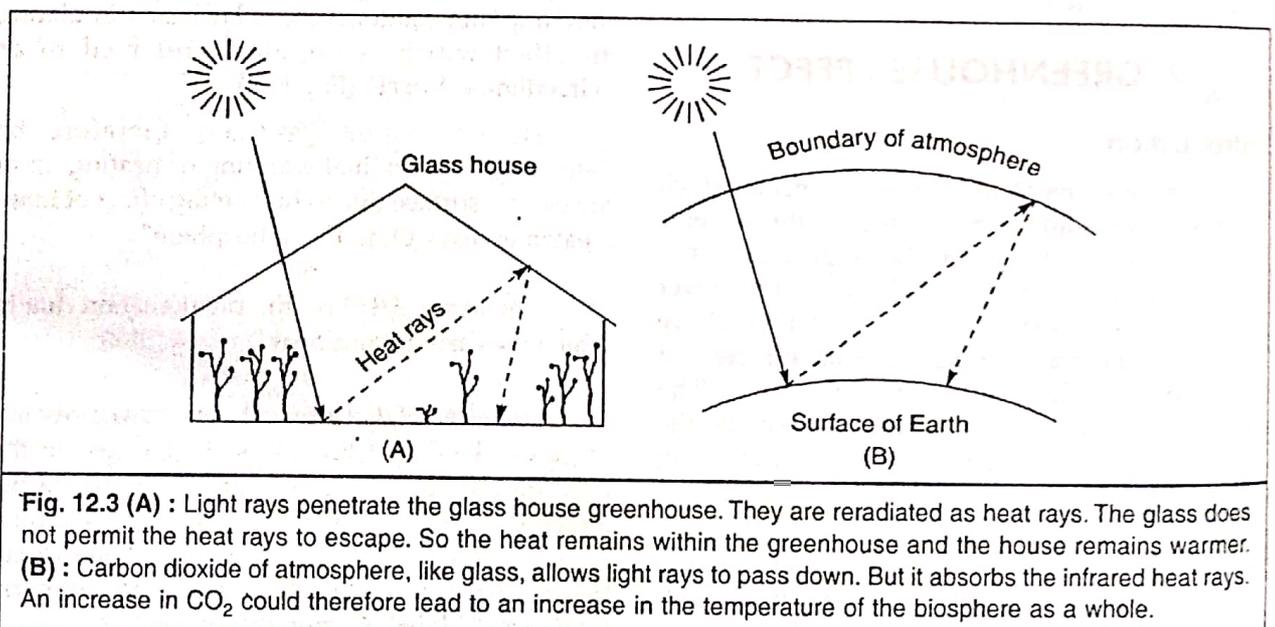
## Greenhouse Gases

The principal gases responsible for Greenhouse Effect are

1. Carbon dioxide ( $\text{CO}_2$ )
2. Methane ( $\text{CH}_4$ )
3. Nitrous oxide ( $\text{N}_2\text{O}$ )
4. Synthetic chlorofluorocarbons (CFCs)
5. Ozone ( $\text{O}_3$ ) at ground

6. Sulphur dioxide ( $\text{SO}_2$ )
7. Sulphur hexafluoride ( $\text{SF}_6$ )
8. Water vapour.

Among these,  $\text{CO}_2$  is the most common and important greenhouse gas which gets introduced into the atmosphere from fossil fuel burning, furnaces, uncontrolled industrial emissions, destruction of forests, automobile emissions, breathing of organisms etc. It shall not be out of



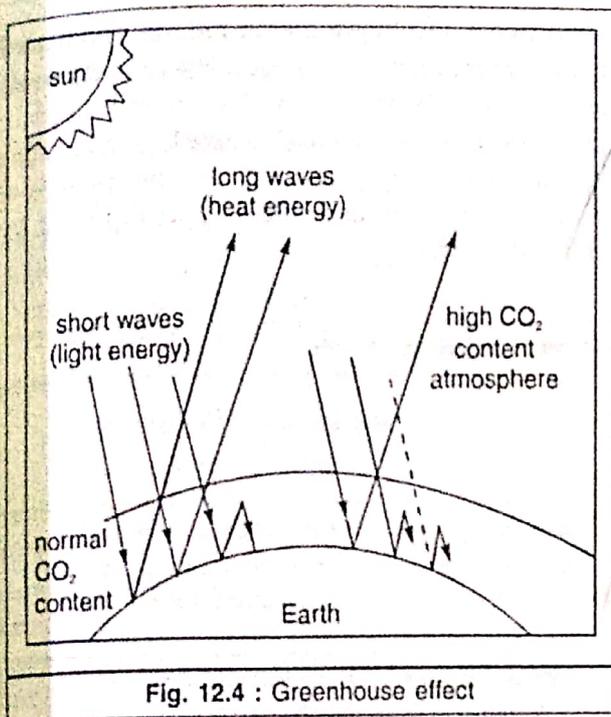


Fig. 12.4 : Greenhouse effect

place to mention here that global background of CO<sub>2</sub> in the atmosphere was around 210 ppm, before the Industrial Revolution (started about 1760). After about 200 years, in 1981-82, CO<sub>2</sub> in the atmosphere was about 340 ppm — which might double up in another 50 years. It may change the climatic conditions, especially by raising the global temperature. This effect caused by CO<sub>2</sub> is chiefly due to the absorption of the long-wave radiation of the sun and retention of the back-radiation from the earth. It is similar to the role of glass panels in a greenhouse (greenhouse is a structure built with glass walls and roof, inside which experimental studies with plants are carried out by scientists (Fig. 12.4), which reduces the convective cooling by the outside air. Similarly, CO<sub>2</sub> accumulating in the atmosphere environment prevents the heat escape and increases the temperature of the earth surface that is within its coverage. Such a phenomenon is called Greenhouse Effect. Such effect would result in the warming up of the earth. Mentioned above O<sub>3</sub> and SO<sub>2</sub> also act as serious pollutants in causing global warming. The Greenhouse gases such as CH<sub>4</sub> and CFCs contribute about 18% and 14%, respectively, to the global warming.

One molecule of CH<sub>4</sub> absorbs 20 times more heat than CO<sub>2</sub> molecule and one molecule of CFC absorbs 10,000 - 20,000 times more heat than CO<sub>2</sub> molecule.

All the greenhouse gases are increasing at a rapid rate. For example, CH<sub>4</sub> has approached at present a level of approximately 1.65 ppm from a pre-industrial value of 0.7 ppm. N<sub>2</sub>O is increasing at the rate of 0.25%, while CFCs at the rate of 5%. It is expected that in a period of about 25 years, i.e. around

the year 2030, the non-CO<sub>2</sub> effects are going to be one and half times longer than those of CO<sub>2</sub> itself!

### Principle of Greenhouse Effect

The principle of the phenomenon of Greenhouse Effect is based upon the principle of infrared absorption characteristics of gases. Higher the concentration of CO<sub>2</sub>, greater would be the absorption of thermal radiation, which means that more infrared radiation (heat energy) are reemitted back to the earth's surface, resulting in 'heat trap' — increasing mean global temperature (Fig. 12.5).

### Illustration of Greenhouse Effect

Greenhouse gases, for example, thick CO<sub>2</sub> layer, acts like a glass panel of greenhouse or the window glass of a closed car, allowing the sun rays to filter through but preventing the heat from being escaping in the outer space; thereby warming the troposphere of the atmosphere. This phenomenon may well be understood when one returns to the car after a while whose window glasses are closed and have trapped the heat inside on a warm day. This is exactly what happens in a greenhouse. Greenhouse gases have no effect on the incoming short wave radiations.

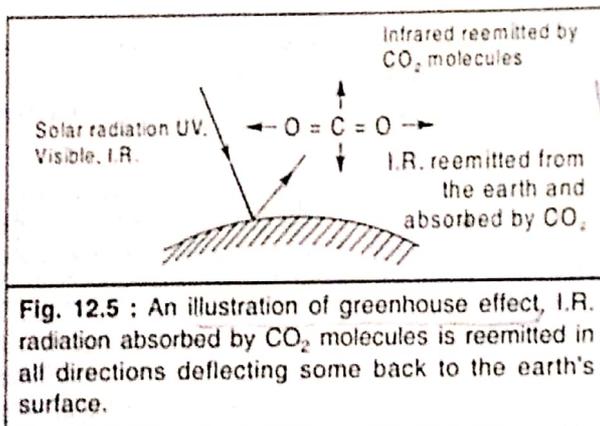


Fig. 12.5 : An illustration of greenhouse effect, I.R. radiation absorbed by CO<sub>2</sub> molecules is reemitted in all directions deflecting some back to the earth's surface.

### Major sources of Greenhouse Gases

W.M.O. (World Meteorological Organization) has suggested that a rise in global air temperature could occur in coming 40 - 50 years and that will exceed any climatic change ever experienced in human history. The earth's temperature has not varied by more than 1 or 2°C during the past 10,000 years : but with the increasing concentration of CO<sub>2</sub> in the atmosphere, the earth may become warmer by about 1.5 - 4.5°C by the year 2025-2050 A.D.

Various industrial as well as agricultural operations generate and emit waste gases into the

atmosphere. For instance, from burning of fossil fuels alone, more than  $2.5 \times 10^{13}$  tons of  $\text{CO}_2$  is being emitted into the atmosphere each year. Growing paddy or live-stock releases  $\text{CH}_4$ . The application of aerosols as coolants in refrigerators and air-conditioning devices or sprays release CFCs into the atmosphere. These gases create a canopy in then

atmosphere and trap the solar radiations reflected back from the earth's surface, leading to atmospheric and climatic changes. Some important sources of greenhouse gases are given in Table 17.1 and relative global warming potential of the principal greenhouse gases in Table 12.2 as reported by O'Riordan (2000).

Table 12.1 : Greenhouse Gases and their Use/release Sources

Sl. No.	Name of Greenhouse gases	Use/Release sources
1.	$\text{CO}_2$	Burning of fossil fuels, factories (through their chimneys), power stations, automobiles, railways, aircraft, burning of firewood, deforestation, reduction in the forest cover, animal and plant respiratory end product, petroleum by-products, cement industry etc. It is the principal greenhouse gas and is responsible for 50% of global warming.
2.	$\text{CH}_4$	Forest fires are the principle sources of $\text{CH}_4$ and emit one unit of $\text{CH}_4$ for every 100 units of $\text{CO}_2$ . Other sources are anerobic decomposition in biological systems, termites, biomass burning, landfills and wetlands. The main sources are paddy rice farming and cattle. Methane is responsible for approximately 18% of global warming.
3.	Man-made CFCs as (i) $\text{CFCl}_3$ (ii) $\text{CF}_2\text{Cl}_2$ (iii) $\text{CF}_3\text{Cl}$ (iv) $\text{CCl}_4$ (v) $\text{CH}_2\text{Cl}_2$ (vi) $\text{CHClF}_2$ (vii) $\text{CF}_2\text{ClBr}$ (viii) $\text{CBrF}_3$	CFCs are released to the atmosphere during the operations and maintenance of appliances and equipments using these molecules as coolants and propellants. CFCs are inert, non-toxic and easily liquefied. CFCs are being frequently used in refrigerators, air-conditioners, in packaging (Styrofoam cups, egg cartons), insulation, in aerosol propellants, and as a solvent for cleaning microchips and electronic circuit boards in computers, automobile air-conditioning etc. About 90-95% of the CFCs emitted are still accumulating in the atmosphere; only 1% of CFCs in the atmosphere is being removed in any one year; annual increases are about 10-11%. Recent global use of CFC 11 and CFC 12 is about 800 million kg. CFCs are considered to be the most potent greenhouse gases. CFC is responsible for approximately 14% of global warming.
4.	$\text{N}_2\text{O}$ (Nitrous oxide)	Deforestation, biomass burning, nitrogenous fertilizers, and combustion of fossil fuels, $\text{N}_2\text{O}$ contributes approximately 6% to global warming
5.	$\text{SO}_2$	Combustion of fossil fuels, industries, transportation etc.
6.	Ozone	At ground level, $\text{O}_3$ is used as a disinfectant for air and water bleaches, textiles and oils. It is produced as a result of chemical manufacturing processes, electrical discharges, occurring with lightning during thunderstorms or with the sparking of electrical appliances. It contributes approximately 12% to global warming.

Table 12.2 : Global warming potential of selected principal greenhouse gases

Greenhouse gas	Chemical Formula	Lifetime (Years)	Global warming potential (years)		
			20	100	500
Carbon dioxide	$\text{CO}_2$	140	1	1	1
Methane	$\text{CH}_4$	12	56	21	6.5
Nitrous oxide	$\text{N}_2\text{O}$	120	280	310	170
HFC group	C-H-F	1.5 - 50	5,000	3,000	500
Sulphur hexafluorides	$\text{SF}_6$	3,200	16,300	24,900	35,900
Perfluorocarbons	C-F	3 - 10,000	6,000	8,000	14,000

## Possible Consequence of Greenhouse Effects

### 1. Temperature changes

If the present rate of CO<sub>2</sub> emission continues unchanged, the temperature of the earth would increase by 22°C (40°F) in another 50 years. Considering the effects of other greenhouse gases (CH<sub>4</sub>, O<sub>3</sub>, N<sub>2</sub>O, CFCs) this effect could be more pronounced.

### 2. Melting of polar ice cap

Scientists feared that an increase in the average global surface temperature by 4.5°F - 10°F could lead to increased melting of the polar ice sheets and glacial ice. The melting glacier may raise the sea level so much that many major coastal cities like New York, Los Angeles, London, Venice and Shanghai will be flooded. Kolkata and Mumbai in India may similarly be affected.

### 3. Climatic changes

An average rise in the global temperature by only 3°C could mean increase of more than 10°C at high latitudes in some seasons (U.N.E.P, 1987). The "Greenhouse Effect" will make winters shorter and wetter, and summer longer and drier in the Northern latitudes. Subtropical regions might become even drier than they are at present and tropical regions would become wetter. This is because the rainfall pattern may also be affected. With increasing temperature and thus evaporation, a corresponding rise (11 - 15%) a year in rainfall has been estimated. This could mean that cropping pattern and regions might be affected as well.

### 4. Crop production and nutrient depletion

The promising effect of climatic change due to greenhouse effect will be on agriculture. A warmer climate is likely to move the areas suitable for growing specific crops such as wheat towards the poles. There will also be widespread changes in natural ecosystem with grasslands and desert areas expanding and forests shrinking and moving polewards.

Because CO<sub>2</sub> is a natural fertilizer, most plants would be high yielding and faster in a high CO<sub>2</sub> world, but would demand more fertilizers since the soil could be improvised faster, as it supports an increased crop cover.

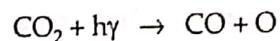
If the CO<sub>2</sub> levels double as expected by 2050 the yields of many crops and weeds could increase by an average of 30%; yields of some crops could even double while that of others change very little. Response actually depends on how a plant photosynthesizes. Plants that produce intermediary chemicals with 3 carbon atoms (C3 plants) would respond well to an increase in the atmosphere levels of CO<sub>2</sub> but those plants that produce metabolic intermediaries with 4 carbon atoms (C4 plants) would do much less so.

Of the world's 20 major food crops, maize, sorghum, millet and sugarcane are C4 plants, whereas the other sixteen crops (e.g., soyabeans, rice, wheat etc.) are C3 plants whose yields would increase in a CO<sub>2</sub> enriched atmosphere. Undoubtedly this would alter the economic viability of farming, agricultural employment, commodity prices and patterns of world trade.

## Miscellaneous Effects

- I. Now due to population explosion, forest destruction have a serious effect on the level of atmospheric CO<sub>2</sub>. If the present trend of deforestation continues, then the amount of CO<sub>2</sub> in the atmosphere might reach up to approximately 0.0355% by volume.

At higher altitudes in the atmosphere, CO<sub>2</sub> undergoes photochemical reactions producing CO, which is drastically dangerous :



- II. Because of increased concentration of CO<sub>2</sub> and due to much warmer tropical oceans, there may occur more cyclones and hurricanes and early snow melt in mountains may cause more floods during monsoon.

According to UNEP, within next 25 years or so, there will be a rise in sea level by 1.5 to 3.5 metres. In Bangladesh alone 15 million people will have to shift or drown.

- III. It is further notable that if CO<sub>2</sub> level continues to increase, it would accumulate and may inhibit the cooling effect of

aerosols and particulate contaminants — consequently temperature of the atmosphere may rise again.

- IV. The cloud cover blanket may rise above 50 - 60%.
- V. Overall equilibrium of the ecosystem will be disbalanced.

### Remedial Measures of Greenhouse Effect

UNEP has chosen the slogan "Global Warming": "Global Warning" to alert the public on World Environment Day, June 5, 1989.

Slight increases in global temperature can adversely affect world food production. Biological productivity also decreases due to warming of surface layer. It is, therefore, absolutely necessary that the forest cover should be maintained at least to one-third of the total land area of the world.

The greenhouse effect can be controlled to certain degree by taking the following important measures :

- (i) Reducing the consumption of fossil fuels such as coal and petroleum. This can be achieved by depending more on non-conventional renewable sources of energy such as wind, solar, nuclear and biogas energies.
- (ii) Disposing of the greenhouse gases as they are formed elsewhere than in the atmosphere.
- (iii) Recovering greenhouse gases present already in the atmosphere and disposing them off elsewhere.
- (iv) Learn to adapt and accept the changing climate.
- (v) International cooperation operating for attempting the reduction of greenhouse gases.
- (vi) Enriching oceans with iron can help in absorbing greenhouse gases such as CO<sub>2</sub>. Actually the theory is that many parts of the ocean lack iron, which stunts the growth of algae. Enriched with enough iron, the algae will bloom luxuriantly, soaking the atmospheric CO<sub>2</sub>, the *principal culprit behind global warming*.
- (vii) Enhancing forestation will certainly reduce the CO<sub>2</sub> level, thereby decreasing the "Greenhouse Effect". As trees are the big

natural 'sink' of CO<sub>2</sub>, they can utilize CO<sub>2</sub> during photosynthesis. According to an estimate, if the forest-cleared lands are reforested in India, Brazil, Indonesia, Africa, Pakistan and Columbia etc., about 50 - 60% of the total released CO<sub>2</sub> may be effectively reduced. Thus there should be a legal ban on deforestation which is increasing alarmingly, particularly in the developing countries.

- (viii) There should be a restriction on the emission of dangerous CO<sub>2</sub> and CFCs from the factories and automobiles.
- (ix) 'No Driving' day once a week should be imposed on all the countries — especially in developed countries like U.S.A.

### 3. SMOG

Term coined by — Voeux, H.A. Des (1905).

#### Introduction

The word smog is derived from an elision of smoke and fog. The oldest smog, a mixture of coal smoke and fog, has plagued human beings since 14<sup>th</sup> century. Urban smog, also known as smoky fog (occurs normally over industrial areas), happened in Dec. 1930 in Meuse Valley of Belgium, which killed about 600 people. A classical example of smog (smoke + fog) is London smog of Dec. 1952, which killed approximately 5,000 people in a single year and thousands became ill. Another example of smog is Donora Pennsylvania Smog (USA) which killed 20 people and made hundreds ill. This smog persisted for 5 days and was preceded by the formation of thick fog due to strong inversion temperature on Dec. 26, 1948.

The other type of predominant smog is called Photochemical or Los Angeles or Killer Smog or Oxidizing Smog. Its first clue appeared in 1944 in Los Angeles and hence the name Los Angeles Smog. It was mainly a mixture of oxidizing pollutants, hence it is known as *oxidizing smog*, while London Smog consisted mainly of a mixture of reducing pollutants and so it has been called *reducing smog*. Photochemical smog problems also occur in several other countries like Tokyo (Japan), Mexico, Sydney, Melbourne etc. This problem is also experienced in some cities of India, such as Mumbai, Chennai, Delhi, Kolkata, Kanpur, Bangalore and Ahmedabad. During 1987, Mumbai experienced heavy smog for about 10 days.

**Components of London Smog or Reducing Smog or Classical Smog**

(i)  $SO_2$ , (ii) Particulates, such as soot,  $(NH_4)_2SO_4$  etc. (iii) humidity or water from fog. It involves no photochemistry and is commonly known as sulphurous smog.

**Components of Photochemical Smog or Los Angeles Smog or Oxidizing Smog**

1. Inorganic gases such as  $O_3$ , nitrogen oxides ( $NO_x$ ),  $H_2O_2$  and CO.
2. Organic peroxides, peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBN), Peroxy propionyl nitrate (PPN), peracetic acid ( $CH_3COOOH$ ), acetylperoxide [ $CH_3(CO)OO(CO)CH_3$ ], ethylhydroperoxide etc.

The components of typical photochemical smog, along with their optimum level, are given in the Table 12.3 :

Sl. No.	Components	Optimum level (ppm)
1.	Carbon monoxide	2.0
2.	Nitric oxide	0.15
3.	Unsaturated hydrocarbons	0.05
4.	Aromatic compounds	0.20
5.	Nitrogen oxide	0.20
6.	Ozone	0.10
7.	Aldehydes	0.20
8.	Organic peroxides	0.03

London Smog was characterized by bronchitis and irritation whereas Los Angeles Smog was characterized by reduced visibility and eye irritation (lacrimation).

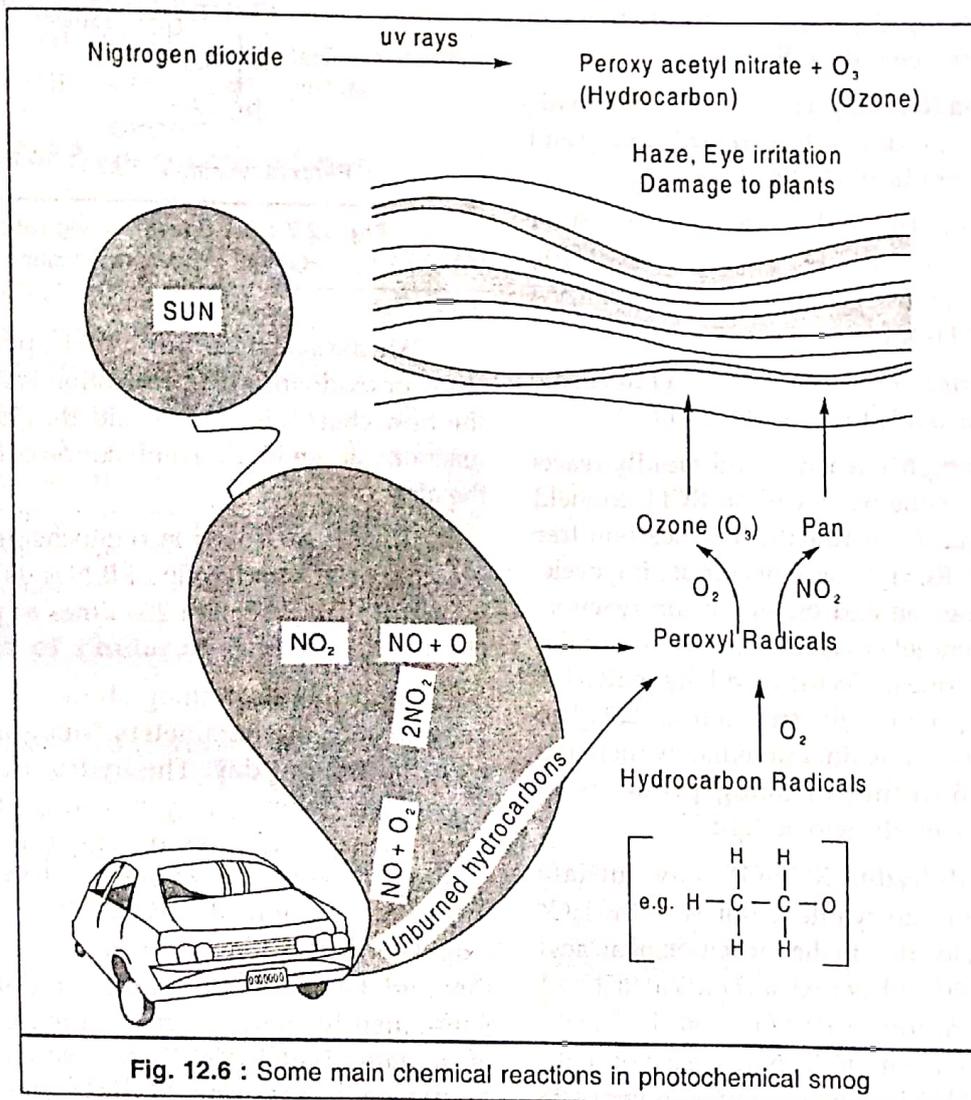


Fig. 12.6 : Some main chemical reactions in photochemical smog

Smog is formed of fog and smoke whereas photochemical smog is formed by a complex series of chemical reactions, when oxides of nitrogen ( $\text{NO}_x$ ) and hydrocarbons of the exhausted gases from factories and engines of automobiles (Fig. 12.6) are exposed to ultraviolet (UV) rays of sunlight.

Photochemical smog is characterized by brown-hazy fumes, which irritate the eyes and lungs, lead to the cracking of rubber and extensive damage to plant life.

### Mechanism of Photochemical Smog (Oxidizing Smog) Formation

The most probable mechanism of photochemical smog forming reactions are :

1. Reactive hydrocarbons (C=C group) from automobile exhaust interact with  $\text{O}_3$  to form a hydrocarbon-free radical  $\text{RCH}_2^*$ .
2.  $\text{RCH}_2^*$  rapidly reacts with  $\text{O}_2$  to form another free radical  $\text{RCH}_2\text{O}_2^*$ .
3. Formed  $\text{RCH}_2\text{O}_2^*$  reacts with nitric oxide (NO) to produce nitrogen oxide ( $\text{NO}_2$ ) and the free radical  $\text{RCH}_2\text{O}_2^*$ .
4. This new free radical ( $\text{RCH}_2\text{O}_2^*$ ) further interacts with  $\text{O}_2$  to yield a stable aldehyde, (RCHO), and hydroxyperoxyl radical  $\text{HO}_2^*$ .
5.  $\text{HO}_2^*$  further reacts with another molecule of nitric oxide to give  $\text{NO}_2$  and  $\text{HO}^*$ .
6.  $\text{HO}^*$  is highly reactive and rapidly reacts with a stable hydrocarbon  $\text{RCH}_3$  to yield  $\text{H}_2\text{O}$  and regenerate the hydrocarbon-free radical,  $\text{RCH}_2^*$ , thereby completing cycle. This goes on and on as a chain reaction. One complete cycle yields two molecules of  $\text{NO}_2$ , one molecule of aldehyde RCHO, and regenerates the free radical  $\text{RCH}_2^*$  to start all over again. Immediately there is a rapid building of smog products in presence of ultraviolet light.
7. The aldehyde (RCHO) may initiate another route by interaction with the  $\text{HO}^*$  radical, leading to the formation of an acyl radical  $\text{RC}=\text{O}$ , peroxyacyl radical  $\text{RCOO}_2^*$  (by reaction with  $\text{O}_2$ ), and finally peroxyacyl nitrate PAN (by reaction with  $\text{NO}_2$ ). PAN is one of the most potent eye irritants found in smog.

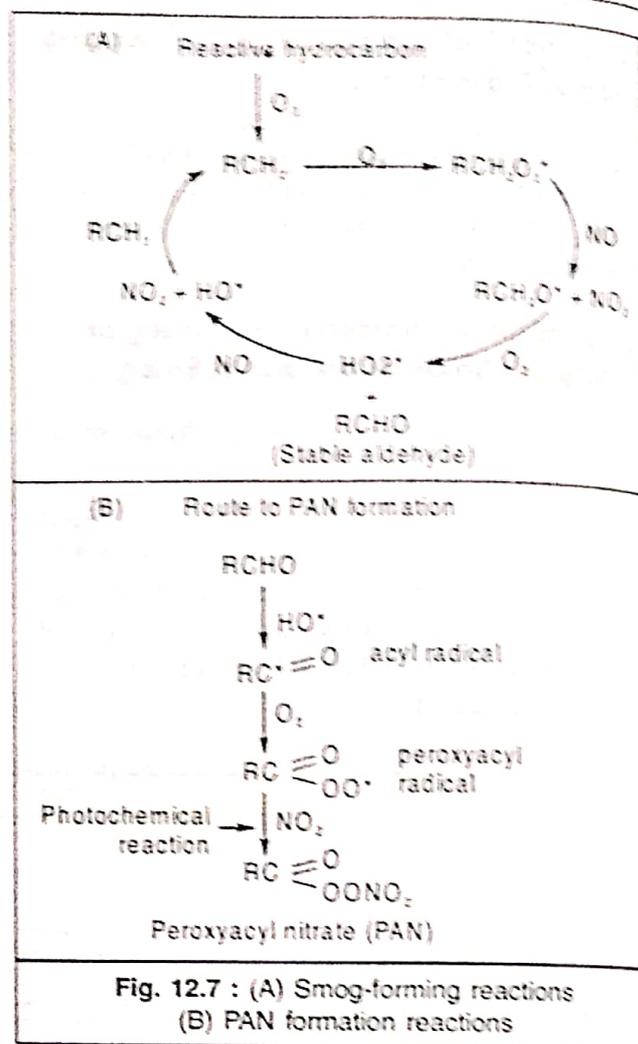


Fig. 12.7 : (A) Smog-forming reactions  
(B) PAN formation reactions

All the reactions from 1-7 in photochemical smog or oxidizing smog formation is illustrated in the flow chart (Fig. 12.7 A and B). Photochemical reactions start with the combination of  $\text{N}_2$  and  $\text{O}_2$  in the air.

$\text{PB}_2\text{N}$  is produced in photochemical smog in presence of  $\text{NO}_2$  and olefins.  $\text{PB}_2\text{N}$  is 100 times more powerful than PAN and 200 times as powerful as HCHO.

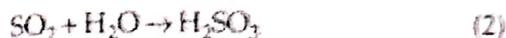
Photochemical smog shows characteristic variations of the parameters (smog ingredients) with the time of day. The hydrocarbon level is maximum during early morning traffic rush hours, then decreases during the remaining daylight hours as it is consumed in the smog-formation reactions described above. NO (nitric oxide) concentration has a peak value at the same time and then falls as  $\text{NO}_2$  concentration increases. Subsequently, there is a rise in the concentration of oxidants (aldehyde, PAN), which are active oxidizing agents and contain the irritating ingredients of smog.

### Mechanism of London or Sulphurous Smog (Reducing Smog) Formation

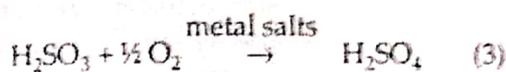
As mentioned above, "smog" means an odd combination of smoke and fog, which in Dec. 1952 was prevalent in London. This is, however, chemically reducing with high level of  $\text{SO}_2$  and is called reducing smog. It is also called *Sulphurous Smog*. The steps in the formation of London smog or sulphurous smog or reducing smog are shown in the form of following reactions :



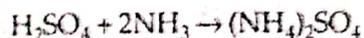
$\text{SO}_2$  combines with moisture from fog to form sulphurous acid ( $\text{H}_2\text{SO}_3$ ).



The oxidation of sulphurous acid ( $\text{H}_2\text{SO}_3$ ) is quite rapid, more so in the presence of metal salts :



It is also notable here that  $\text{H}_2\text{SO}_4$  may combine with  $\text{NH}_3$  in moist air forming  $(\text{NH}_4)_2\text{SO}_4$  :



### Conditions For Photochemical Smog Formation

Automobile exhaust in the presence of  $\text{NO}_2$  and UV radiation produce photochemical smog. Also, when organic substances like alcohol, olefins, paraffins, and carbonyl compounds are irradiated by UV radiation in the presence of  $\text{NO}_2$ , the photochemical smog may be formed. Hot climate ( $>24^\circ\text{C}$ ) with low humidity is favourable for the formation of photochemical smog. It does not rise high above in the air, instead, it circulates in the lower atmosphere of the earth.

### Effects of Photochemical Oxidants on Humans

1.  $\text{O}_3$  and PAN (peroxy acyl nitrate) chiefly cause irritation of the eyes creating lacrimation and affect severely the respiratory tract of human beings.

Lower concentration of  $\text{O}_3$  irritates the throat and nose while its higher concentration causes cough, headache, throat dryness, chest pain, and impairment in breathing. Exposure to 1.0 - 3.0 ppm of ozone produces fatigue and lack of coordination in central nervous system.

2. Exposure to 50 ppm of ozone for several hours may lead to mortality due to pulmonary edema i.e., storage of blood in the lungs.
3.  $\text{NO}_2$  produces nose and eye irritation and also pulmonary discomfort.
4.  $\text{NO}_x$  also cause several chronic diseases of heart, lungs and eyes.
5. PBN (peroxy benzoyl nitrate), a secondary photochemical pollutant, occurs in polluted atmosphere involving aromatic hydrocarbons,  $\text{NO}_x$  and  $\text{O}_3$ . It acts as a powerful eye irritant and lachrymator.

### Effects of Photochemical Oxidants on Plants

1. Smog having  $\text{O}_3$ , PAN and other photochemical oxidants is regarded to produce early maturity or senescence.
2. PAN causes injury in beets, spinach, lettuce, alfalfa, and coniferous trees. It also causes silvering of leaves.
3.  $\text{NO}_x$  and PAN cause death of forest trees.
4. PAN inhibits "hill reaction" of photosynthesis.
5.  $\text{O}_3$  promotes excessive transpiration from the leaves of plants causing dehydration.
6.  $\text{O}_3$  is also harmful for vegetables like radish, carrot and tobacco. It alone causes 50% crop loss.
7.  $\text{O}_3$ , together with PAN, form small drops in air forming smog, thus blanketing the sunshine, which indirectly inhibits the rate of photosynthesis in plants.
8. Photochemical oxidants (products) like  $\text{O}_3$ , PAN (peroxy acetyl nitrate), PBzN (peroxy benzoyl nitrate) are phytotoxic and kill microflora and fauna of soil and water.
9.  $\text{O}_3$  causes leave tip burn, a disease of white pines.
10. Some sulphates and nitrates which are formed during smog formation due to the oxidation of sulphur-containing components ( $\text{SO}_2$  and  $\text{H}_2\text{S}$ ) and  $\text{NO}_x$  ( $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$ ), nitric acid and some nitrates are important toxicants of smog. They adversely affect plant growth and damage crops.

## Ecological Effects of Photochemical Smog

Photochemical smog produces regional ecological effects such as

1. Disturbs thermal equilibrium
2. Reduces soil fertility
3. Affects freshwater lake and pond ecosystem.

## Effects of Photochemical Oxidants on Materials

Scientists now believe that degradation of materials commonly attributed to "weathering" is actually the result of attack by photochemical pollutants. The smoke containing fog, dust, mist, soot etc. in the smog causes corrosion of metals, stones, building materials, textile, paper, rubber, leather and painted surface.

Organic polymers including rubbers, natural and synthetic textiles are subjected to chemical alteration upon exposure to varying quantities of ozone.

Long exposure of ozone to rubber in a relaxed state brings about no characteristic crack. However, exposure to a concentration of 0.01 - 0.02 ppm ozone causes cracks in rubber.

Secondary photochemical pollutants also attack cellulose in textile fabrics. The harmful effects of ozone exposure on textiles increase in the order for fabrics made of cotton, nylon, terrycot and polyester.

## Control of Photochemical pollutants

The control of primary precursors such as hydrocarbons and  $\text{NO}_x$  may ultimately control  $\text{O}_3$  and PAN formation, which are secondary pollutants. In present days some techniques have been devised to control hydrocarbon emissions from stationary sources. Important techniques are :

1. Incineration method
2. Adsorption method

3. Absorption method, and
4. Condensation method.

### 1. Incineration method

This method is based on the fact that hydrocarbon removal efficiencies are greater in flame after burner in which flame is applied to complete the oxidation of hydrocarbon into  $\text{CO}_2$  and  $\text{HOH}$ .

### 2. Adsorption method

In this method, exhaust gases are released through a bed of granulated adsorber, which consists of activated carbon. Hydrocarbon vapours are adsorbed over the surface of activated carbon, which remain there until they are periodically removed by passing steam through the system. The hydrocarbons are then condensed to liquids and can be used for further purpose.

### 3. Absorption method

Liquid containing hydrocarbons is brought to intimate contact of exhaust gases. The scrubbed exhaust then passes on, leaving the hydrocarbons trapped in the scrubbing liquid. The contact between absorbing liquid and exhaust gases is generally carried in tall scrubbing towers.

### 4. Condensation method

Condensation of hydrocarbons requires low temperature. It causes gaseous hydrocarbon, i.e., smog forming pollutants, to condense to liquids, which are collected and reused. However, the control of hydrocarbon emission from automobiles is more complicated. For this, application of oxidizing catalyst may convert hydrocarbons and  $\text{CO}$  to  $\text{CO}_2$  and  $\text{HOH}$ :

1. Hydrocarbons  $\xrightarrow{\text{combustion}}$   $\text{CO}_2 + \text{H}_2\text{O}$
2.  $\text{CO} \xrightarrow{\text{combustion}} \text{CO}_2$

Researches are being conducted to utilize smog-forming gases and hydrocarbons.

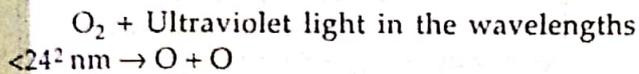
Table 12.4 : Characteristics of "Classical" and "Photochemical" Smog

Sl. No.	Characteristics	"Classical"	"Photochemical"
1.	First occurrence noted	London (U.K.)	Los Angeles (U.S.A.)
2.	Principal pollutants	Sulphur oxides, particulate matters	Ozone, nitrogen oxides, hydrocarbons, carbon monoxide, free radicals
3.	Principal sources	Industrial and household fuel combustion (coal, petroleum)	Motor vehicle fuel combustion (petroleum)
4.	Effects on human	Lung and throat irritation	Eye irritation
5.	Effects on compounds	Reducing	Oxidizing
6.	Time of occurrence	Winter months (especially in morning)	Around midday of summer months
7.	Popular worst episodes	London Smog	Los Angeles Smog

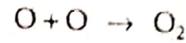
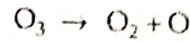
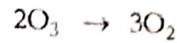
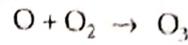
### 4. OZONE DEPLETION

#### Introduction

Ozone (O<sub>3</sub>), a natural constituent of the atmosphere, is composed of three oxygen atoms held together in their configuration by electrical attraction. This electrovalent bond is much weaker than the covalent bond that holds oxygen (O<sub>2</sub>), so the molecule is always susceptible to having one of its oxygen atoms stripped by an 'oxygen-seeking' molecule. The reactivity of the chemical is in large part determined by the strength of the bonds between atoms. The weak bonds in the ozone molecule make it an even more highly reactive gas than oxygen. The word 'ozone' (in Greek, *ozein* means 'to smell') was first introduced by Shoenbein in 1840 to characterize a chemical species which had a pronounced odour. This pale-blue, stinky and explosive gas is formed when an oxygen molecule (O<sub>2</sub>) dissociates thermally. Each atomic oxygen (O) combines with a molecule of oxygen (O<sub>2</sub>) to form an ozone molecule (O<sub>3</sub>). Ozone is unstable and destroyed mainly in upper stratosphere through photochemical reactions with UV waves. However, nature maintains equilibrium as shown below :



The free oxygen then joins an O<sub>2</sub> molecule to form ozone :



Ozone is highly unstable relative to oxygen. Normally, about 90% of the ozone is present in the upper part of the stratosphere extending from 18 to 40 km average height (22 - 33 km) from the sea level. This upper layer of the atmosphere enveloped by ozone is commonly known as *ozonosphere* or *ozone layer*, or *stratospheric ozone layer* or *protective layer* or *ozone umbrella*. The major subdivisions of the atmosphere and the location of the ozone layer are shown in Fig. 12.8.

Actually, composition of air in the stratosphere remains fairly uniform throughout the region. However, O<sub>3</sub> concentration varies by about 10 ppm in the stratosphere compared to 0.02 ppm in winter to 0.05 ppm in summer in the troposphere. Normally, it has been present in the atmosphere at about 0.75 ppm at sea level. The presence of ozone layer in the stratosphere is of vital significance for

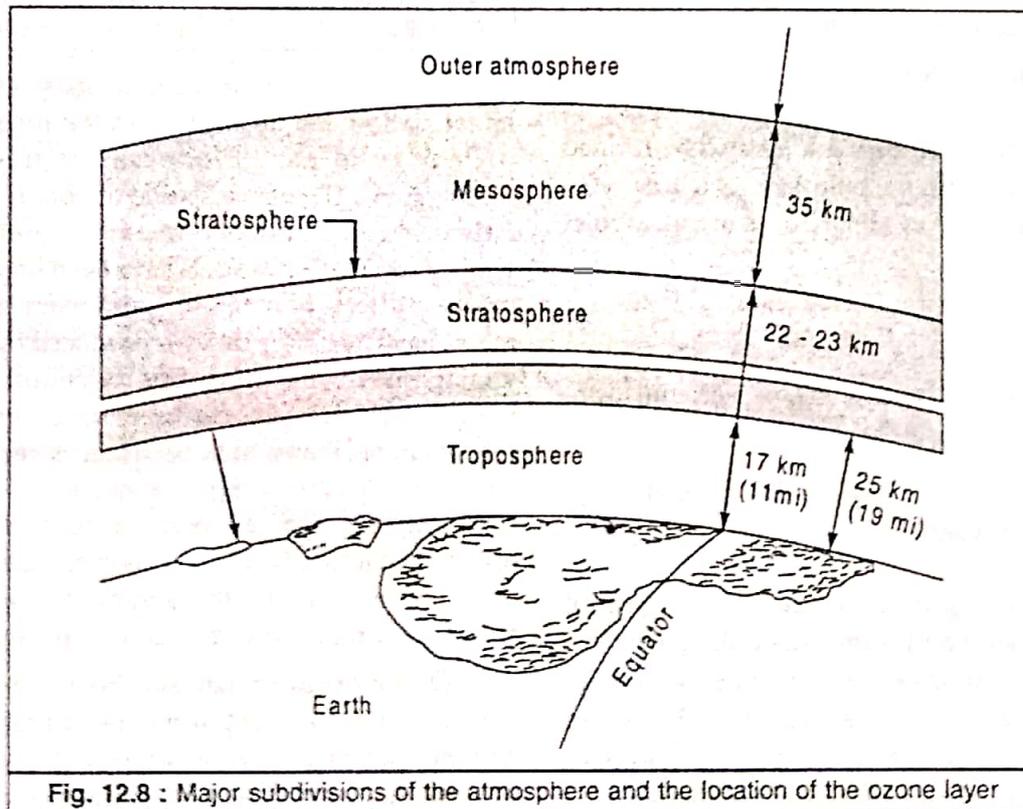
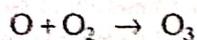
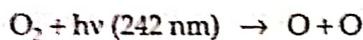


Fig. 12.8 : Major subdivisions of the atmosphere and the location of the ozone layer

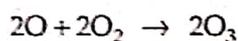
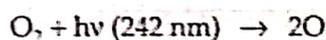
all biota, because the harmful solar radiation (220-230 nm), such as ultraviolet rays, which are lethal to life on the earth are not allowed to enter the earth's atmosphere by ozone layer or ozone umbrella. In absence of this layer, all the ultraviolet rays of the sun will reach the earth's surface and, consequently, the temperature of the lower atmosphere (troposphere) may rise to such an extent that the "biological furnace" of the biosphere may turn into a "blast furnace". It functions as a mechanical barrier for not permitting short wave ionising ultraviolet rays and, therefore, protects the life on earth from severe radiation damage. It shall not be out of place to mention that low-altitude (tropospheric) ozone is toxic, and is produced by photochemical smog resulting from fossil fuel emissions.

### Formation of Ozone

Natural process of formation of ozone is from oxygen in the stratosphere. In the lower mesosphere, the atmospheric oxygen absorbs UV radiation < 242 nm and photo-dissociates into two oxygen atoms. These atoms subsequently combine with molecular oxygen of upper stratosphere producing ozone :

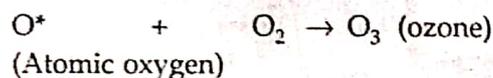
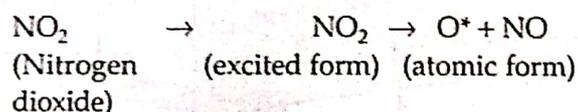


Or



At ground level, ozone may also be formed from oxygen containing pollutants such as  $\text{NO}_2$ ,  $\text{SO}_2$  and aldehyde on absorption of ultraviolet radiation :

absorption of solar UV radiation



Ozone at ground surface acts as a harmful pollutant for plants and animals including man. It is also responsible for the formation of the potentially more hazardous pollutant smog, through a series of photochemical reactions involving oxides of nitrogen, hydrocarbons and other pollutants.

### Sources of Ozone at Ground Level

Exposure to ozone at ground levels (tropospheric) is because of its use as a disinfectant for air and water bleaches in textiles, oil wax and inorganic synthetic industries. Ozone is a key component of oxidant smog and is produced as a result of electrical discharges, occurring with lightning during thunderstorms or with the sparking of electrical appliances. Other sources of ozone in the environment are gamma radiation used in food preservation, commercial UV lamps used for sterilization, high voltage electric equipment, and dermatological phototherapy equipments and even in photocopying machines.

### Toxicity of tropospheric ozone

Tropospheric ozone is an extremely reactive molecule. When ozone occurs in concentration above normal, it creates pollution and may damage human health as shown in Table 12.5.

Sl. No.	O <sub>3</sub> Level (ppm)	Observed effects
1.	0.2	No ill-effect
2.	0.3	Nose and throat irritation
3.	0.8 (long exposure)	Genetic alteration in the lung within 5 days
4.	1.0-3.0	Extreme fatigue after two hours
5.	9.0	Severe pulmonary edema

The toxic effects of ozone are manifested upon its inhalation and absorption in the lungs. Ozone toxicity is, in part, produced via free radical mechanisms. The per oxidation of polyunsaturated fatty acids and oxidation of amines and proteins which produce free radicals have been implicated in ozone-induced damage in pulmonary and extra pulmonary sites. Free radicals produced by oxidants damage DNA and thus modify cellular genetic integrity, which lead to carcinogenic events. But the role of ozone, if any, in lung cancer is very rare.

Emphysema, a destructive and chronic obstructive lung disease such as chronic bronchitis, and development of asthma might be the ultimate results of chronic ambient ozone exposure.

Ozone exposure has also been implicated in dizziness and visual impairment — a sign of central nervous system damage, enlargement of spleen and thymus, and impairment of immune system.

Photochemical smog is the major cause of ozone exposure causing urban air pollution posing a threat to human health.

### Toxic Effects of tropospheric O<sub>3</sub> on Human Beings

As mentioned in above section.

### Toxic effects of tropospheric O<sub>3</sub> on Biotic Community

1. Ozone has been known to be highly toxic to fishes in the concentration ranging from 0.1 to 1.0 ppm.
2. Directly or indirectly, ozone increases the mortality rate of larvae of zooplanktons.

### Toxic effects of tropospheric O<sub>3</sub> on plants

1. Exposure to air having O<sub>3</sub> results in the lesions to plants usually confined to the upper surface of leaves. The uniformly distributed white or brown flecks characterize their lesions and stippled(dots) in irregularly distributed blotches.
2. Ozone flecking is especially observed with the plants of grape, citrus and tobacco.
3. In pine seedlings, ozone causes tip burns.
4. 0.02 ppm of ozone has been observed to damage pea, pine, tomato and other plants.
5. In plants, ozone enters through stomata. It causes visible damage to leaves, thereby reducing their photosynthetic rate and consequently decrease in the yield of certain food crops.
6. Ozone is now known to be the most toxic photochemical product causing injury to plants.
7. Tobacco plants, when exposed for 5.5 hours at 0.10 ppm concentration of O<sub>3</sub>, showed 50% reduction in pollen germination and pollen tube growth.
8. In caliform fruits and vegetables, yields have been reduced due to ozone pollution. Grapes are no longer produced at places chiefly because of ozone pollution.
9. Ozone, along with other environmental pollutants like SO<sub>2</sub> and NO<sub>x</sub>, is affecting crop losses of over 50% in European countries. In Denmark, ozone affects spinach, potato, clover, alfalfa etc.
10. In Netherlands, ozone level was high enough to reduce yields of beans, potato

and poplars. In UK alone, ozone concentration exceeded 400 µg/m<sup>3</sup> in 1976 due to industrial pollution.

Bombawale (1986) presented evidence that a serious leaf spot disease of potato, which appeared in India during each year since 1978, was primarily due to ozone.

From the above discussion it may be concluded that ozone in the stratosphere protects us but it proves to be lethal when it comes in direct contact with us and plants at earth's surface.

### Unit of Ozone Thickness

The thickness of ozone layer is measured in Dobson Unit (DU), where 1 DU = 0.01 mm of the compressed gas at 0°C and 760 mm Hg pressure.

### Depletion of Stratospheric Ozone Layer (Earth's Protective Umbrella)

Whereas an increase in the concentration of ozone at the ground level is undesirable because it could induce toxicity, a decrease in the stratospheric ozone is also dangerous to human beings, their lives and ecosystem. This is because the stratospheric ozone acts as a protective layer or sheath, which absorbs UV radiations from the sun.

Ultraviolet light arriving in the atmosphere may be divided into three categories according to wavelength. UV-A has the longest wavelength, and UV-C the shortest. Ozone absorbs more than 99% of the UV-C wavelengths, about half of the lower energy UV-B and little of the relatively harmless UV-A. If the equilibrium of the reactions that absorb UV radiation is perturbed, a change in the influx of UV radiation to the surface of earth will occur.

In simple words, an umbrella of ozone in the stratosphere (about 25 km above the surface of the earth) is able to protect us from the harmful solar radiations. In spite of being in a small proportion, it plays a vital role in the climatology and biology of the earth. It filters out all solar radiations below 320 nm, which are biologically harmful, and thereby controlling the thermal budget of the earth. The amount of ozone, therefore, must have been intimately connected with the life-sustaining process. Any large-scale depletion of ozone content, therefore, will exert catastrophic influence on biotic systems including plants.

In the last years of 20<sup>th</sup> century, there has been much hue and cry about the destruction of

stratospheric ozone and the issue has now assumed *global* dimensions. The problem of ozone depletion and its adverse consequences have threatened the existence of life on the planet. IOIP (International Ozone Trend Panel) concluded that the depletion of ozone layer is a global affair and not a seasonal phenomenon confined only to the atmosphere lying over Antarctica.

## World Ozone Day — September 16

### Causes of Stratospheric Ozone Depletion

Two principal causes may be attributed for ozone depletion — (1) The Natural processes, and (2) The Anthropogenic (man-made) processes.

#### 1. The Natural Processes

The mechanism of ozone depletion by natural processes is not well-understood. However, it is believed that ozone is depleted by reactions with atomic oxygen, reactive hydroxyl radicals and mainly by NO as shown in reaction numbers 1, 2 and 3, respectively :

##### Reaction 1



##### Reaction 2

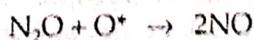


\*Indicates the excited atom.

##### Reaction 3



It may be noted that nitric oxide (NO) is produced in the stratosphere below 30 km by the reaction of N<sub>2</sub>O (nitrous oxide) with excited oxygen atoms, and above 30 km by ionising radiation on nitrogen :



It may further be noted here that NO<sub>x</sub> is also anthropogenic.

#### 2. The Anthropogenic Processes

Anthropogenic processes have been known to cause 50-70% damage to stratospheric ozone. The important anthropogenic processes include the CFCs and NO<sub>x</sub> release.

### Role of Chlorofluorocarbons (CFCs) in O<sub>3</sub> Depletion

Since 1950 it has become evident that the ozone concentration of the stratosphere is gradually decreasing largely due to increasing use of a group of chemicals called chlorofluorocarbons (CFCs) and halons (Table 12.6) :

Table 12.6 : O<sub>3</sub>-Depleting Chemicals (Anthropogenic)

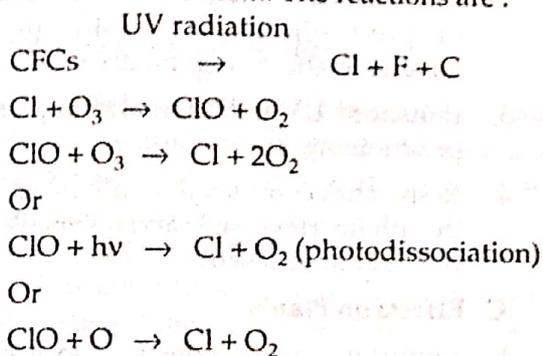
Sl. No.	Compounds	Chemical Compositions	Chemical names
1.	CFC-11	CFCl <sub>3</sub>	Trichloro fluoro methane
2.	CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	Dichloro difluoro methane
3.	CFC-13	CF <sub>3</sub> Cl <sub>3</sub> CCl <sub>4</sub> CH <sub>2</sub> Cl <sub>3</sub>	Trichloro trifluoro methane Carbon tetrachloride Methyl chloroform
4.	CFC-22	CHClF <sub>2</sub>	Dichloro fluoro methane
5.	Halon-1211	CF <sub>2</sub> Cl Br	Di fluoro chloro bromo methane
6.	Halon-1301	CFBr <sub>3</sub>	Tri fluoro bromomethane

CFCs also include chlorofluoromethane (CFM) or freon are the result of a deliberate search for an ammonia substitute for refrigeration uses. These are chemicals that are inert, non-toxic and easily liquefied. The CFCs and halons are entirely man-made being widely used in air-conditioners, refrigerators, electric and metal cleaning, foam blowing, aerosol propellants and as a solvent for cleaning microchips and electronic circuit boards in computers.

The major use of CFC-11 is in foam blowing and CFC-12 is in automobile air conditioning, almost all of CFC-113 is used as a solvent. About 90-95% of the CFCs emitted are still accumulating in the atmosphere; only 1% of CFCs in the atmosphere is being removed in any one year; annual increases are approximately 3-5%. To date, about 15-20 billion kg of CFCs have been produced and used up, these are seriously depleting the earth's protective shield. Earlier models predicted a 6.5% ozone depletion by the year 2030, but it could well be as much as 16%.

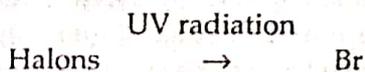
Unlike other compounds, CFCs are neither destroyed nor removed in the lower atmosphere by precipitation; sun rays, however — where their chlorine atoms are released into the atmosphere under the effects of UV radiation — encounter and destroy ozone. Also CFCs and halons have 10,000 times more heat absorption power than O<sub>2</sub>. At current emission rates the heating potential of CFCs may rise from 15% to the equivalent of CO<sub>2</sub> by the year 2025. CFCs and halons remain inactive in the

troposphere and it takes about 20-40 years for these chemicals to travel to reach the stratosphere, but after that their intermediate product (chlorine atom) remains active for 75-110 years. Once these CFCs and halons reach to stratosphere, the chlorine and bromine atoms present in these chemicals are released as a result of interaction with UV radiations in the stratosphere. The ultraviolet light splits up the tight chemical bonds of CFCs and halons and chlorine or bromine atom is set free. These chlorine or bromine atoms act as catalyst in splitting up (breaking down) ozone into oxygen molecule and chlorine monoxide (ClO). The chlorine monoxide molecule is evenly split up by interaction with another ozone molecule to give up two oxygen molecules and a freed chlorine atom. The reactions are :



This chlorine atom again repeats the cycle of destruction of ozone in the stratosphere.

Similar pattern of reaction takes place for halons :



The chlorine or bromine atoms remain active for 75-110 years and are capable of breaking thousands of ozone molecules before the released chlorine gets converted into dilute HCl and come down in the form of acid rain. It is important to note that each atom of chlorine chain reacts with more than 100,000 molecules of ozone converting ozone into oxygen.

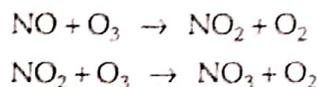
Wide range of CFCs are known as shown in Table 12.6, but widely used are CFC-11, CFC-12 and CFC-13. Almost all the CFC-13 is used as solvent. The developed countries release more CFCs into the air than the developing ones. USA, having 5% of global population, releases 70% of CFCs whereas India and China (having 17% and 20% of world population, respectively) release only 1.8% of CFCs.

### Role of NO<sub>x</sub> in ozone depletion

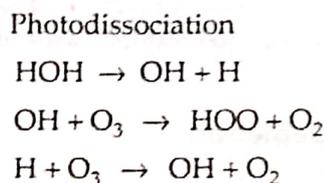
The rate of destruction of ozone is further enhanced by the oxides of nitrogen (NO<sub>x</sub>) released

from the exhaust of large fleet of supersonic aircraft and also from fertilizers. The nuclear explosions directly inject superheated NO<sub>x</sub> into the stratosphere. The SS aircraft generally fly at ozonospheric level and their exhaust gases directly provide water vapours and NO<sub>x</sub> into the stratosphere.

Curtsey (1971) and his collaborators pointed out that SS aircraft fleet could add significant quantities of NO<sub>x</sub> leading to about 40% reduction in the O<sub>3</sub> concentration. Following reactions between O<sub>3</sub> and NO<sub>x</sub> are known to exist :



Further, OH species have been known to cause ozone depletion in the stratosphere :



Also, the process of decomposition of ozone may be enhanced in the presence of some greenhouse gases such as CO<sub>2</sub> and CH<sub>4</sub>.

It is due to continuous breakdown of ozone molecules that ozone layer in stratosphere is getting depleted and at certain locations holes have been created in the ozone layer.

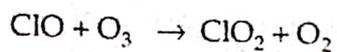
### Ozone Hole

Hole actually represents depletion of ozone concentration in the stratosphere, not an empty space. Besides CFCs, NO<sub>x</sub>, OH species etc., methyl bromide and hydrochlorofluorocarbons also deplete ozone layer. Depletion of ozone concentration at Antarctica (South Pole) is more than Arctic (North Pole).

There has been gradual decrease in the ozone concentration since 1970 to 1993 :

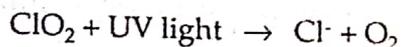
1970	306 DU
1971	245 DU
1993 (October)	240 DU

Ozone hole was first noticed in 1979 in Antarctica. If hole develops in Arctic (North Pole), then consequences would be more dangerous. However, at Arctic, a layer of ClO cover over the ozone has been noticed in 1987. Chlorine monoxide (ClO) is highly active and encounters ozone molecule.



(chlorine monoxide) (chlorine dioxide)

The  $\text{ClO}_2$  is soon broken down by UV light to leave a free chlorine atom and an oxygen molecule :



It is estimated that a single chlorine atom can break down 100,000 ozone molecules.

WMO (World Meteorological Organization) in 1995 reported record increase in the size of the ozone hole at South Pole, which was 20 million  $\text{km}^2$ , twice the size of Europe. At present the ozone hole covers the entire Antarctica. Globally, it appears that about 4-5% of the earth's ozone has been degraded since the early 1980s. If the trend of ozone loss continues, it is predicted that the ozone shield will be depleted by a further 10% by 2050. It is conjectured that this may lead to an additional 300 million cases of skin cancer in human.

### Effects of Ozone Depletion

It is universal fact that ozone layer in the stratosphere protects humans from the deleterious UV radiations coming from the sun. Though ozone accounts for only 3 parts in ten million of the earth's atmosphere, it plays various crucial roles in the radiation balance of the planet. The depletion of ozone-layer by chemical pollution created by man's activities have imparted serious implications by letting "ozone-eaters". The following would be the consequences of ozone - depletion :

The consequences of ozone-depletion :

#### A. Effect on Human beings

1. Eye damages including tumors of the conjunctiva and cornea, cataracts and retinal damage may be enhanced.
2. Three kinds of skin cancer — *Basal cell carcinoma*, *Squamous cell carcinoma* and *Melanoma* — are rapidly climbing the list of human diseases caused by UV rays.
3. Suppression of certain immune responses in human occurs due to UV rays.
4. UV radiations cause blood vessels near the skin's surface to carry more blood, making the skin hot, swollen or red causing *sunburns*.
5. Long exposure to UV radiations caused by  $\text{O}_3$  depletion may cause leukemia and breast cancer.

Studies reveal that a 10% decrease in stratosphere ozone may lead to 20-30% increase in cancer. Nearly 7,000 people die of such diseases in USA each year. Such cases have increased by 10% in Australia and New Zealand.

6. Photochemical changes occurring in such biological molecules as nucleic acids, proteins, lipids, steroids and melanins may cause damage to the cell nucleus, cytoplasm, organelles and membranes.

#### B. Effects on Biotic Community

1. UV solar radiation causes heavy mortality in phytoplanktons.
2. The marked reduction in the productivity of phytoplanktons would, in turn, adversely affect zooplanktons.
3. Enhanced UV radiation also impairs fish productivity.
4. Researches conducted on microbes reveal that photo irreversible and reversible types of injury are caused.

#### C. Effects on Plants

1. Important crops (wheat, corn, rice and soyabean) are sensitive to UV-B rays. Exposure to UV-B radiation may cause reduction in the crop yield.
2. UV-B radiation reaching the earth through the depleted ozone layer in the stratosphere also reduces the effectiveness of photosynthesis and multiplication of phytoplanktons.
3. Due to ozone reduction, intense UV radiation causes greater evaporation of surface water through the stomata of the leaves and decreases the soil moisture content.

#### D. Climatic effects of Ozone Depletion

Ozone depletion changes spectral composition of solar electromagnetic radiation. The increased solar UV radiation causes greenhouse effect changing the global energy and radiation balance. Needless to mention that every molecule of either of two common CFCs —  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  — has the same global warming effect as 10,000  $\text{CO}_2$  molecules.

#### E. Ecological Disturbances due to $\text{O}_3$ Depletion

Scientists are of opinion that the depletion of ozone, if not controlled, would enormously affect

the ecosystem productivity, ecological stability and overall environmental equilibrium. It would also trigger several changes in the biospheric ecosystem.

The resultant climatic alterations would cause certain physiological changes in man and animals. Change in energy balance and radiation would affect the survival and stability of living biota. It appears important to mention here that UV radiation disrupts DNA replication to the point of reproductive failure or death.

The changes in thermal conditions of biosphere would affect type, density and stability of vegetation, which, in turn, would affect several biogeochemical cycles occurring in nature.

### Control of Ozone Depletion

Since CFCs cause maximum damage to ozone layer, hence its application should be completely banned. No safe substitute of CFCs has yet been searched out. In cooling system, natural products should be used but not the CFCs. Indonesia is using a natural product (Kapok fibre) in foam mats in cooling system. Much is yet needed to be done to stop further ozone depletion.

Several of the EEC (European Economic Community) nations have banned CFC production altogether, a protocol for the protection of the ozone layer was adopted in Vienna in March 1985 by 21 countries and the EEC. The convention pledged to protect human health and the environment from the effects of ozone-depletion.

## V. EUTROPHICATION

"Eutrophication" is a natural process, derived from the Greek word '*eutrophos*' meaning well-nourished or enriched. It means eutrophication is a natural process by which lakes are enriched naturally or, more usually, by human activity. As a result, an *oligotrophic lake* ("underfed" or "nutrient poor") may become *eutrophic* ("well-fed" or "nutrient rich") in due course of time. The key nutrients responsible for eutrophication are *nitrogen*, *phosphorus* and *calcium*. The enrichment leads to other slow processes referred to as "*natural ageing of lakes*".

**Sources of Nutrients:** Eutrophication escalates rapidly, however, when abnormally high amounts of nutrients from fertilizers, industrial and domestic wastes, urban drainage, animal wastes, detergents and sediments enter water streams.

### Types of Eutrophication

Eutrophication is chiefly of two types — (1) Natural eutrophication, and (2) Cultural eutrophication.

#### 1. Natural Eutrophication

The process of lake-aging characterized by nutrient enrichment is called *natural* eutrophication. This process gradually converts oligotrophic lake into a eutrophic lake. Due to increase in natural fertility, it pursues the production of phytoplanktons, algal blooms and aquatic vegetations including water hyacinth, water fern, water lettuce and aquatic weeds which, in turn, provide ample food for zooplanktons, herbivores, and fishes.

#### 2. Cultural Eutrophication

When the process of eutrophication is speeded up by human activities, it is called *cultural* eutrophication. Approximately 80% of the nitrogen and 75% of the phosphorus added to lakes and streams in developing and developed countries has its source through human activities. *Lake Mendota* and *Lake Washington* have undergone rapid eutrophication due to human activities. In India, recreational value of Kashmir lakes is diminished while Nainital Lake is undergoing a rapid eutrophication as a result of sewage, domestic waste and detergent addition.

When the average concentration of soluble inorganic nitrogen exceeds 0.30 ppm and the soluble inorganic phosphorus content exceeds 0.01 ppm, algal blooms may appear in any oligotrophic lake.

#### Effects of Eutrophication

Eutrophication causes several physical, chemical and biological changes, which considerably deteriorate the water quality. Eutrophication may otherwise be called "*nutrient pollution*" of lake etc. Their adverse effects are :

1. Eutrophication reduces the recreational values of a lake.
2. During eutrophication, algal blooms release deleterious (toxic) chemicals which kill fishes, birds, and other aquatic fauna — causing water to stink.
3. The algal blooms impair water quality by giving it a bad taste and odours. If the lake is a source of drinking water, considerable expense may be involved in improving its quality.

4. Decomposition of algal bloom leads to  $O_2$  depletion in water. Thus, with a high  $CO_2$  level and poor  $O_2$  supply, aquatic biota begin to die and the clean water turns into a stinking drain.
5. Toxic gas ( $H_2S$ ) that emanates (originates) from rotting algae has foul smell. It indirectly impairs the physiology, metabolism and behaviour of aquatic biota.
6. Dense algal blooms at the lake surface reduce penetration of sunlight to the lake bottom. As a result, the deeper waters contain less amount of DO (dissolved oxygen), which is further reduced by decomposing algae and organic matter accumulated at lake bottom. The  $O_2$  depletion is often responsible to the *winterkill* of fishes in northern lakes of India.
7. Many pathogenic microbes, protozoa, bacteria, viruses etc. grow on sewage products under anaerobic conditions. It results into spread of fatal water-borne diseases such as polio, dysentery, diarrhea, typhoid and viral hepatitis.
8. Macrophytes, particularly *Hydrilla*, *Potamogeton*, *Ceratophyllum* and *Myriophyllum*, assume high population densities making near-shore and shallow regions unsuited for any purpose.
9. The lake undergoing eutrophication may become  $O_2$  - deficient, destroying fish habitats, leading to the elimination of several desirable aquatic species in water.
10. Prolonged eutrophic conditions lead to "dystrophic state". The lake receiving huge amounts of organic matter from allochthonous sources are called dystrophic. These lakes contain bog flora and high amounts of humic acid while planktonic productivity is very low.
11. The rooted weeds gradually reduce the lake size and also interfere with fishing, navigation, irrigation, and the production of hydroelectric power.
12. As a result of sediment pollution, the lake basin is gradually filled in, rendering the lake shallow, and, in due course of time, the lake becomes "extinct" as a result of eutrophication.

## Control of Eutrophication

The role of various nutrients, especially nitrogen and phosphorus, in eutrophication is so overwhelming that an international resolution was ratified at the 9<sup>th</sup> International Congress of Theoretical and Applied Limnology in 1974. Several technical devices along with prevention of further inflow of effluents have been used to control eutrophication. For example :

1. The waste water must be treated before its discharge into water streams to limit the nutrient value.
2. Recycling of nutrients can be checked through harvest.
3. Eutrophication can be reduced by removing nitrogen and phosphorus at the source and by dilution.
4. Algal blooms should be removed upon their death and decomposition.
5. Algal foodweb should be disrupted to stimulate bacterial multiplication.
6. Algal growth can be controlled by limiting the dissolved nutrients. The most suitable, feasible and effective method involves the use of chemicals to precipitate additional phosphorus. Such precipitants include alum, lime, iron and sodium aluminate.
7. Physicochemical procedures can be applied to remove dissolved nutrients. For example, phosphorus can be removed by precipitation and nitrogen by nitrification or denitrification, electro dialysis, reverse osmosis and ion exchange methods.
8. To minimize algal population, copper sulphate may be applied.

## Ecological Classification of Fresh water (Lentic) Biota

**A. Pond Flora :** The floral community of the pond constitutes the producers (autotrophs).

Pond flora are of four types :

1. **Phytoplanktons :** These are plant plankton having chlorophyll. They are capable of synthesizing their own food by the process of photosynthesis and, hence, are called producers.

Important phytoplanktons of pond (lentic habitat) are :

*Volvox, Euglena, Anabaena, Chlamydomonas, Ceratium, Fragilaria, Microcystis, Eudorina, Closterium, Navicula, Asterionella, Richterella* etc.

- Floating Plants**: These includes plants which float freely on the water surface and also rooted plants with floating leaves. Examples — *Wolffia, Lemna, Nymphaea, Pistia* etc.
- Submerged Plants**: This comprises plants which remain submerged in water. Examples — *Hydrilla, Vallisneria, Ceratophyllum, Utricularia* etc.
- Emergent Plants**: This comprises rooted but emergent plants. Examples — *Sagittaria, Typha, Nymphaea, Marsilea, Nelumbo* etc. Few important (emergent plants) flora of a pond have been shown in Fig. 11.4

**B. Pond Fauna**: The fauna of the pond (lenticitat) constitute the consumers and decomers. The consumers are divided into five apical groups: (1) Benthos, (2) Periphyton, Zooplankton, (4) Nekton, and (5) Neuston.

- Benthos**: Animals which live on the bottom are called benthos. Examples — *Pila, Lamellidens, Earthworms, Turtles* etc.
- Periphytons**: Animals attached or clinging to aquatic plants are called periphyton. These are also called Aufwuchs. Examples — *Hydra, Planaria*.

## Revision Questions

### A. Long-Answer Questions

- Name the major environmental effects. Describe any one of them well-studied by you.
- Define "acid rain" and its causes. Give effects of acid rain on:
  - Aquatic ecosystem
  - Forest ecosystem
  - Terrestrial ecosystem

- Human beings
- Buildings.

- Write an essay on Eutrophication.
- Define Greenhouse effect. Name the greenhouse gases and their release sources.
- Describe the principle and consequences of greenhouse effect.
- Write an essay on London and Los Angeles Smog.
- Give the causes of ozone depletion and its mechanism.
- Justify the statement "Ozone is a protector of human on one hand and killer on the other."

### B. Short-Answer Questions

- Briefly describe*:
  - Wet and dry acid rain
  - Role of wind in acid rain
  - Taj Mahal and acid rain.
- Write short notes on*:
  - Principle of greenhouse effect
  - Possible consequences of greenhouse effect
  - Remedial measures of greenhouse effect.
- Briefly describe*:
  - Photochemical Smog
  - Conditions for Photochemical Smog formation
  - Mechanism of Photochemical Smog (Los Angeles Smog) formation
  - Mechanism of London Smog formation
  - Control of photochemical pollutants.
- Write short notes on*:
  - Formation of ozone
  - Toxicity of ozone
  - Depletion of ozone layer
  - Effects of ozone depletion
  - Eutrophication.