ES 01 -2

Chapter 1
Structure and Composition of the Lower and Middle Atmosphere

1.1 The Evolution of the Earth's Atmosphere

The history of the Earth's atmosphere prior to one billion years ago is not clearly known. Scientists have studied fossils and made chemical analysis of rocks to find out how life on Earth evolved to its present form. Several theories have been suggested. It is hypothesized that life developed in two phases over billions of years.

In the first phase, explosions of dying stars scattered through the galaxy and created swirling clouds of dust particles and hot gases. These extended trillions of kilometers across space. As the cloud cooled, fragmented small particles adhered to each other. Over 4 billion years ago, the cloud had formed into a flattened and slowly rotating disk. The Sun was born in the center of this disk. Away from the disk, Earth and the other planets formed as tiny pieces of matter which were drawn together. Earth started out as a molten mass that did not cool for millions of years. As it cooled it formed a thin, hard crust with no atmosphere or oceans.

Molten rock frequently exploded through the crust. Water vapor was released from the breakdown of rocks during volcanic eruptions. Eventually, the crust cooled enough for this vapor to condense and come down as rain to form the oceans that covered most part of the Earth.

In the second phase, scientists have hypothesized that bubbles floating on the ancient ocean trapped carbon-containing molecules and other chemicals essential for life. These bubbles may have burst and released these chemicals into the atmosphere. Organic compounds formed and dissolved in the early atmosphere, collecting in the shallow waters of the Earth. However, no one is aware how the first living cells developed between 3.6 and 3.8 billion years ago. Eventually, these protocells developed into cells having the properties presently known as life.

These unicellular bacteria multiplied in the warm shallow waters, where they mutated and developed into a variety of protests and fungi. About 600 million years ago plants and animals were formed on the Earth. Life could not develop then on land since there was no ozone layer to shield early life from damaging ultraviolet (UV) radiation. The photosynthetic bacteria which emerged about 2.3–2.5 billion

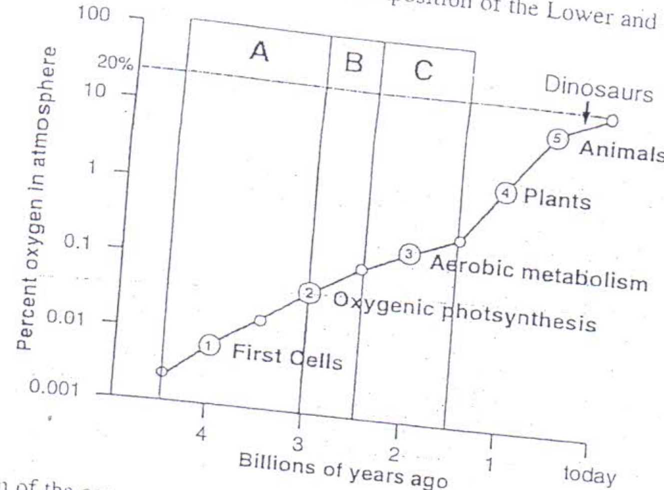


Fig. 1.1 Evolution of the concentration of oxygen in the Earth's atmosphere: (A) No oxygen produced by the biosphere; (B) Oxygen produced but absorbed by Oceans and sea bed rock; and (C) Oxygen absorbed by land surfaces and formation of ozone layer (Courtesy: Tameera, Wikipedia)

years ago, could remove carbon dioxide (CO_2) from the atmosphere and, using sunlight, combine it with water to make carbohydrates. In the process they created oxygen (O_2) and released it into the ocean. Some of the oxygen escaped into the atmosphere.

The evolution of geological and biological events leading to changes of oxygen contents in the Earth's atmosphere since the formation of the planet are shown in Fig. 1.1. Evidence of oxygen in the ocean is noted between 2.5 and 3 billion years ago, by identifying oxidized iron bands in the seabed rock. Ozone layer formation was substantiated from the oxidized iron bands in the land 1.5–2.5 billion years ago. Biological events show that the photosynthetic bacteria started producing oxygen 3 billion years ago and the aerobic metabolism evolved about 2 billion years ago. Evolution of multicellular plants and animals started in the later parts as illustrated in Fig. 1.1.

Earth's atmosphere was formed over a period of 2 billion years. Some of the oxygen was converted into ozone (O_3), which was produced in the lower stratosphere and protected life from harmful UV radiation. This allowed green plants to live closer to the surface of the ocean, making it easier for oxygen to escape into the atmosphere. About 400–500 million years ago the first plants began to exist on land. Over the following millions of years a variety of land plants and animals evolved. As more plants appeared, the levels of oxygen increased significantly, whereas the carbon dioxide levels dropped. At first it combined with various elements, such as iron, but eventually oxygen accumulated in the atmosphere resulting in mass extinctions and further evolution. With the appearance of an ozone layer life-forms were better protected from UV radiation. The present nitrogen-oxygen enriched atmosphere is sometimes referred to as Earth's third atmosphere in order to distinguish the current chemical composition from two notably different previous compositions.

ES01-1

ATMOSPHERE

The Earth's four spheres:

Lithosphere, Hydrosphere, Biosphere, and Atmosphere

Atmosphere:

The gaseous envelope surrounding the earth is called atmosphere. It is an integral part of our planet. It provides us air that we breath and act as a shield to protect the life forms from the sun's intense heat and dangerous radiation. The energy exchanges that continually occur between the atmosphere and the earth's surface and between the atmosphere and the space produce the effect we call weather.

Composition of the atmosphere:

Air consists of two broad parts – (1) Dry air (mixture of gases) and (2) water vapour. Dry air contributes 96% - 99% of the total mass. Total mass of the atmosphere is 5.3×10^{21} gms. Of this total mass 99.9% lies below 80 km level. The atmosphere extends upto a height of 900 km (approx.) from the surface.

The air is a mixture of many discrete gases. The composition of air is not constant, it varies from time to time and from place to place.

Composition of dry air: (By Volume)

Element	Percentage	ppm	ppb
Nitrogen (N_2)	78.08		
Oxygen (O_2)	20.95		
Argon (Ar)	0.93		
Carbon dioxide (CO_2)	0.036		
Neon (Ne)	0.00182	18.2	
Helium (He)	0.000524	5.24	
Methane (CH_4)	0.00015	1.50	
Krypton (Kr)	0.000114	1.14	
Nitrous Oxides (N_2O)	0.00005	0.5	
Hydrogen (H_2)	0.00005	0.5	
Ozone (O_3)			
Stratosphere		10.0	
Troposphere			5 – 500
Carbon monoxide (CO)		0.1	
Xenon (Xe)		0.09	
Ammonia (NH_3)			6
Nitrogen dioxide (NO_2)			1 – 100
Sulpher dioxide (SO_2)			0.2
Hydrogen sulphide (H_2S)			0.2

The amount of **water vapour** varies from 1% (desert and polar regions) to 4% (warm and wet tropics) by volume of the atmosphere depending upon geographic location of an area and climatic condition.

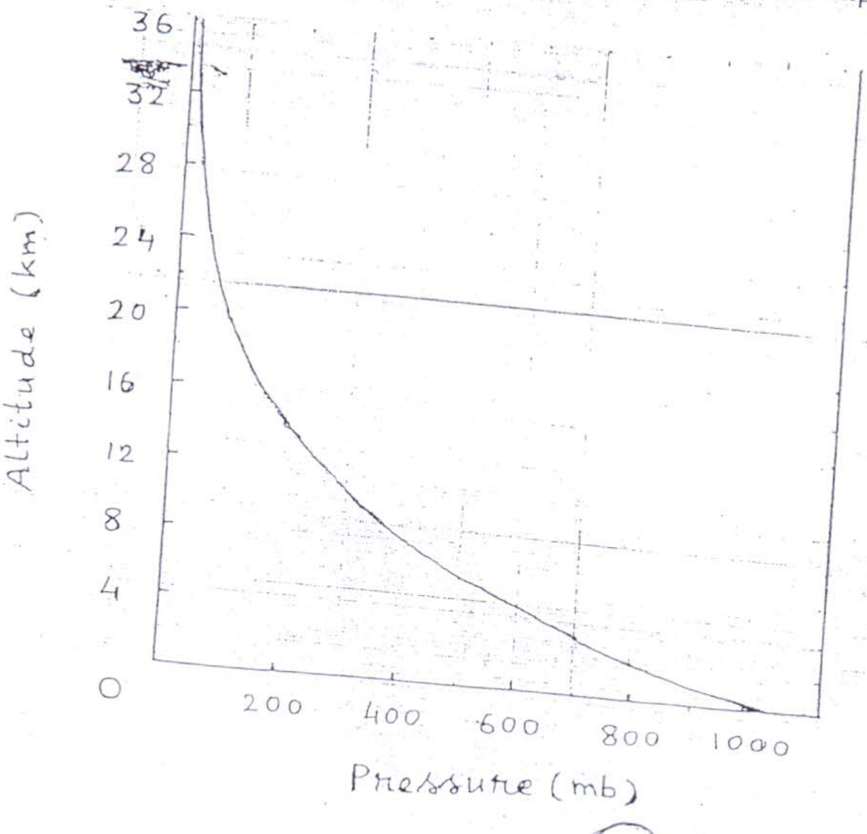
Suspended particles, from visible to microscopic scale, may originate from many sources, both natural and human made. These particles include sea salt, fine soil, smoke and soot from fire, pollen and micro organisms, ash and dust from volcanic eruption, and more. Such particles are most numerous in the lower part of the atmosphere near their primary source. The upper atmosphere is also not free of them.

Vertical variations in composition:
Based on composition, the atmosphere is often divided into two layers, the homosphere and the heterosphere. The **homosphere**, the zone of homogeneous composition, extends upto 80 km above the surface. The atmosphere beyond 80 km height is not uniform, rather has a heterogeneous composition, so the term **heterosphere** is used. This layer consist of four spherical layers: The lowermost layer is dominated by molecular nitrogen; next a layer of atomic oxygen; the third one is dominated by helium atoms; and finally a layer of hydrogen atoms.

Vertical structure of the atmosphere

Pressure changes in vertical

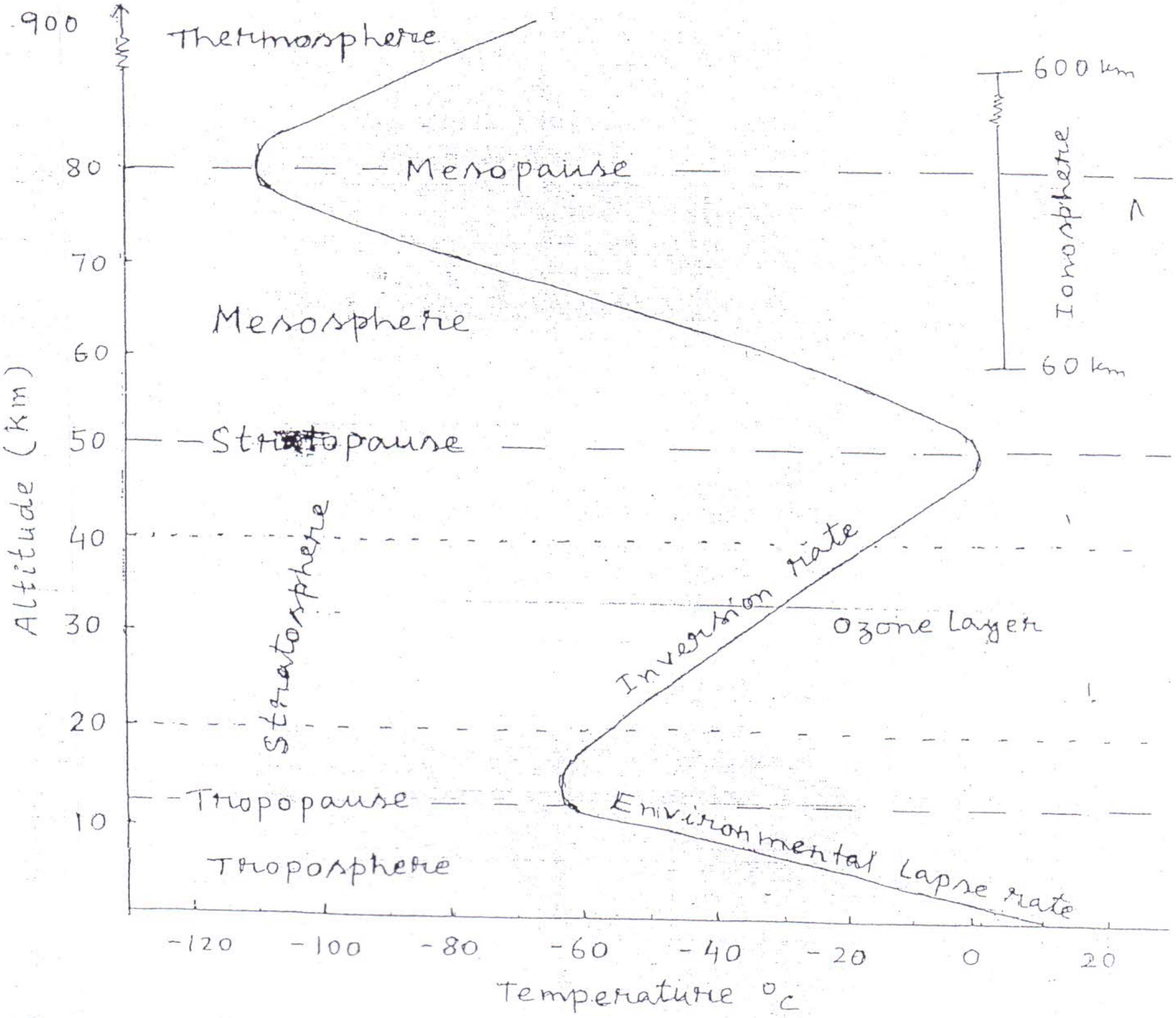
The atmospheric pressure changes with height. The pressure at higher altitudes is less. One half of the atmosphere lies below an altitude of 5.6 km. At about 16 km, 90% of the atmosphere has been traversed, and above 100 km, only 0.00003% of all the gases making up the atmosphere remains. The rate of pressure decrease is not constant, rather pressure decreases at a decreasing rate with an increase in altitude. Data on vertical pressure changes reveal that the vast bulk of the gases making up the atmosphere is very near the earth's surface and that the gases gradually merge with the emptiness of space.



Temperature changes in vertical:

The atmosphere is divided vertically into four layers on the basis of temperature. The bottom layer, where temperature decreases with an increase in altitude, is known as the **troposphere**. This layer is characterized by strong vertical mixing, overturning, turbulence and weather phenomena. The temperature decrease in the troposphere is called the environmental lapse rate. Its average value is $6.5^{0}C$ per km, a figure known as the normal lapse rate. The temperature decreases continues to an average height of 12 km. This layer reaches a maximum height of 16 km in the equatorial region but in the polar regions it extends upto 8 km. Almost all clouds and certainly all precipitation, violent storms are developed in this layer; so the troposphere is often called as **weather sphere**.

Beyond the troposphere lies the **stratosphere**, and the boundary between these two layers is known as the **tropopause**. In this layer the vertical mixing is very week and this layer is stratified in nature. In this layer the temperature increases with increasing height (which is known as inversion rate) upto a height of about 50 km. The high temperature in this layer is due to absorption of UV radiation by O_3 gases concentrated in this layer (between 20 and 40 km).



The stratosphere is followed by **mesosphere**, which is separated from the lower layer by a surface known as **stratopause**. In this layer temperature again decreases with height upto a height of 80 km above the surface. The temperature approaches as low as -110^0C. The upper boundary of the mesosphere is called **mesopause**.
Mesosphere is followed by **thermosphere**, where temperature again rises with increasing height. The high temperature is due to the absorption of very short wavelength solar energy by atoms of oxygen and nitrogen. Temperature rises more than 1000^0C.

Ionosphere

An electrically charged layer known as the ionosphere is located in the altitude range between 60 to 600 km. In this layer molecules of nitrogen and atoms of oxygen are readily ionized as they absorb high-energy, short wave solar energy (UV and X-rays). The ionosphere is useful in that it can reflect radio waves. On the basis of ion density, the ionosphere is subdivided into three layers, the D (Dynamo) layer between 60 and 90 km above the earth, the E layer (Heaviside-Kennelly layer) between 90 and 150 km and the F layer (Appleton layer) above 150 km. The concentration of charged particles changes from day to night, particularly in the D and E layers. These layers weaken and disappear at night and reappear during the day. The F layer is present both day and night.

Aurora

The auroras, certainly one of nature's most interesting spectacle, take place in the ionosphere. The aurora borealis in the northern hemisphere and the aurora australis in the southern hemisphere appear in a wide variety of form. The occurrence of auroral displays is correlated in time with solar-flare activity and in geographic locations, with the earth's magnetic poles.

Exosphere

This layer lies beyond the ionosphere. The outermost layer of the earth's atmosphere, in which the density is such that an air molecule moving directly outward has a 50% chance of escaping rather than colliding with another molecule.

Magnetosphere

The space surrounding the earth. It includes the Van Allen radiation belt. Two belts occupied by charged particles (proton electron and α-particles) are trapped within the earth's magnetic field. The inner belt, ranging from 2400 to 5600 km above the earth's surface, is believed to consist of secondary charged particles (meson, photon, positron, high energy electrons) emitted by the earth's atmosphere as a consequence of the impact of cosmic rays. The outer belt lies between 13000 to 19000 km and consist of particles originated from the sun.

Origin (chemical evolution) of the Atmosphere

The atmosphere did not always consist of the same relatively stable mixture of gases that we breath today. The very thin envelope of gases that surrounded the earth at the time of its formation (that is the **primary atmosphere**) was swept away by the solar wind, and the planet generated a new, **secondary atmosphere** by degassing volatile constituents from its interior. The present mixture of gases that makes up our atmosphere is the result of very gradual change, a slow evolutionary process that began soon after the earth came into being 4.5 to 5.0 b.y. ago. The principal components of this "new" atmosphere were probably water vapour, carbon dioxide, and nitrogen.

There was no free oxygen in the primitive atmosphere. Two probable sources are **photodissociation** of water molecule and **photosynthesis.**

Some oxygen was almost certainly generated in the early atmosphere by the breakdown of water molecules into H_2 and O_2 as a result of interaction with UV radiations (photodissociation).

Most of the oxygen currently in the atmosphere originated through photosynthesis. First free oxygen produced by early life forms were combined with substances dissolved in sea water, especially with iron. Then once these mineral oxidation needs were met substantial quantities of free oxygen began to accumulate in the atmosphere. Enough oxygen was created through photosynthesis of eucaryotes or bluegreen algae to permit free oxygen to build up in the atmosphere. With the build up of molecular oxygen came a parallel increase of ozone. Then ozone started to function as a protective screen filtering out harmful UV radiation. This permitted life forms to survive and flourish in shallow water and, eventually, on land.

In this process a oxygen free atmosphere has become a oxygen rich atmosphere through geologic time.

Incoming Solar Radiation (Insolation)

The sun emits all of the forms of radiation but in varying composition. The visible light (0.4 to 0.7 μm) represents over 43% of the total emitted, IR radiation represents 49% and UV radiations 7%. Less than 1% of solar radiation is emitted as X-rays, γ-rays and radio waves. The sun radiates its maximum energy within the visible portion of the electromagnetic spectrum. The cooler earth radiates its maximum energy in the IR portion of the electromagnetic spectrum.

λ_{max} (sun) = 0.483 μm $\qquad$ λ_{max} (earth) = 9.66 μm

The heating of the earth's atmosphere involves the processes of conduction, convection, and radiation all of which occur simultaneously.

Although the atmosphere is largely transparent to incoming solar radiation, only about 25% penetrates directly to the earth's surface without some sort of interference on the part of the atmosphere. The remainder is either absorbed by the atmosphere, scattered about until it reaches the earth's surface or returns to space, or is reflected back to space.

Average distribution of Insolation:

Incoming radiation – 100%

(1) Scattered to space by the atmosphere (back scatter) – 6%

(2) Reflected from clouds – 20%

(3) Reflected from earth's land-sea surface – 4%

[Total 30% loss to space by reflection and scattering.]
(4) Radiation absorbed by the atmosphere and by clouds – 19%
(5) Direct solar radiation to surface – 25%
(6) Diffused radiation to the surface (scattered) – 26%
[Total 51% solar radiation absorbed at the surface.]

Absorption within the atmosphere

Gases are selective absorbers, which means they absorb strongly in some wavelengths, moderately in others, and only slightly in still others. Nitrogen is a poor absorber of insolation. Oxygen removes most of the shorter UV radiation high in the atmosphere, and ozone absorbs larger wavelength UV rays in the stratosphere. The most significant absorber of insolation is water vapour.

Terrestrial radiation

On an average 51% of the total insolation reaching the earth's surface and is absorbed, and is then reradiated skyward. The bulk of terrestrial radiation has wavelengths between 1 and 30μm, placing it well within the IR range. Water vapour and CO_2 are the principal absorbing gases in that range. Water vapour absorbs roughly five times more terrestrial radiation than do all other gases combined. Clouds are also good absorbers of terrestrial radiation (IR).

Global warming and Greenhouse effect

When gases in the atmosphere absorb terrestrial radiation, they warm, but eventually they radiate this energy away. Some travels upward and some downward which is again absorbed by the earth. Thus, the earth's surface is being continually supplied with heat from the sun as well as from the atmosphere. This energy will again be emitted by the earth's surface, and some will be returned to the atmosphere, which will, in turn, radiated some earthward, and so forth.
This extremely important phenomenon has been called the greenhouse effect because it was once thought that greenhouses were heated in a similar manner.

Greenhouse gases

Atmospheric gases are efficient absorbers of IR radiation and are referred as radiatively active gases and are commonly known as greenhouse gases. Water vapour is the most important greenhouse gases accounting for about 80% of natural greenhouse warming. The remaining 20% is due to other gases such as CO_2, CH_4, N_2O, and O_3 and chemically manufactured CFCs.

CO_2

It is an important heat absorber, and any change in the air's CO_2 content could alter temperature in the lower atmosphere~~. Since 1880, the mean global~~ temperature has risen approximately 0.5%. At the present rate of increase the atmosphere's CO_2 content will reach about 600 ppm by sometime in the second half of this century.

Methane

It absorbs IR radiation 20 to 30 times more effectively than CO_2 , making it an important greenhouse gas despite its relatively low concentration.

O_3

Tropospheric O_3 contributes to the greenhouse effect as well as to the production of photochemical smog.

Nitrous Oxide (N_2O)

It may make a contribution to greenhouse warming that approaches half that of methane.

CFCs

These are very effective greenhouse gases. CFC- 12 has 20000 times the capacity of CO_2 to trap IR radiation where as CFC-11 has 17500 times more capacity.

Although, individually the impact of the trace gases is modest, taken together the effect of these gases may be as great as CO_2 in warming the earth.
The warming of the lower atmosphere triggered by CO_2 and other trace gases will not be same everywhere. In the polar regions it could be as much as two to three times greater than the global average.

Environmental effects of Global warming

The effects of global warming are discussed below:

(1) Global precipitation change: A warmer atmosphere will lead to increased evaporation from ocean, lakes, and streams and lead to more precipitation.
(2) Changes in vegetation: Shifts in pattern of rainfall are likely to upset ecosystems. Eventually it may shift the boundaries of forest and agricultural regions.
(3) Increased storminess: The frequency and/or intensity of violent storms may be increased because of warm ocean water which could feed more energy into high magnitude storms.
(4) Melting/growing of glaciers: Low and middle latitude glaciers are likely to reduce because of warm climate. On the other hand more rainfall will fall over high latitude continental ice sheet and may cause them to grow larger.
(5) Reduction of sea ice: As the climate warm, total sea ice is expected to be reduced.
(6) Thawing of frozen ground: Rising summer air temperature will begin to thaw vast regions of perenially frozen ground at high latitudes.
(7) Global rise in sea level: ~~The sea level will rise because of global~~ warming. Two probable reasons for sea level rise are thermal expansion of warming ocean water and melting of glaciers and polar ice. The various models predict that the rise may be anywhere from 20 cm to 2 m at the end of this century. The rising sea will inundate coastal regions and make tropical regions even more vulnerable to larger and more frequent cyclonic storms.
(8) Changes in the Hydrologic cycle: Significant local and regional changes in streams runoff and ground water levels.

(9) Decomposition of organic matter in soil: As temperature increases, the rate of decomposition of organic matter in soil increase. Soil decomposition releases CO_2 to the atmosphere, thereby further enhancing the greenhouse effect.

(10) Breakdown of gas hydrates: Because of global warming gas hydrates break down and releases methane to the atmosphere, thus further enhance the greenhouse effect.

Depletion of Ozone layer (stratospheric)

The ozone layer actually is not a layer but a zone in the stratosphere where O_3 occurs in higher concentrations than elsewhere in the atmosphere.

Chemistry of the ozone layer:
Ozone is created naturally in the upper atmosphere when high energy UV radiation strikes an oxygen molecule and breaks it down into two highly reactive oxygen atoms. One of the freed oxygen atoms combines with an intact oxygen molecule to form ozone :

$$O_2 \rightarrow O + O \quad ; \quad O + O_2 \rightarrow O_3$$

Ozone can also be broken down by interaction with solar radiation, as well as by interaction with various chemicals such as oxides of hydrogen and nitrogen in the stratosphere.

Anthropogenic causes of ozone depletion
Exhaust gases from jet aircrafts and artificial satellites discharge oxides of nitrogen which immediately react with ozone.

$$O_3 + NO \rightarrow O_2 + NO_2$$
$$O_3 + NO_2 \rightarrow O_2 + NO_3$$

Anthropogenic chlorine in the atmosphere is derived mainly from a group of chemicals known as chlorofluorocarbon (CFC). Because CFCs are practically inert in the lower atmosphere, a portion of these gases gradually makes it way to the ozone layer, where sunlight separates the chemicals into their constituent atoms. The chlorine atoms released this way have the net effect of removing some of the ozone.

$$\text{CFC } (CFCl_2) \xrightarrow[\text{radiation}]{\text{UV}} CFCl_2 + Cl$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

The free Cl radical is regenerated and continues the chain reaction. One atom of Cl may be able to breakdown as many as 100000 ozone molecules. The damage by CFC continues for 100 years because of their long residential time in the atmosphere.

The ozone hole

The phenomenon of ozone depletion centred over the polar regions is known as the ozone hole. The most prominent ozone hole occurs over the Antarctica during the southern hemesphere spring (September to November). Later, during late November and December, the ozone concentration recovers to more normal levels. The hole is caused in part by the relatively abundant ice particles in the south polar stratosphere. The ice boosts the effectiveness of CFCs in destroying ozone, thus causing a greater decline than would otherwise occur. The zone of maximum depletion is confined to the Antarctic region by a swirling upper level wind pattern. When this vortex weakens during the late spring, the ozone-depleted air is no longer restricted and mixes freely with air from other latitudes where ozone levels are higher.

A similar but much smaller ozone thinning is detected in the vicinity of the north pole during spring and early summer.

Effects of Ozone depletion

Ozone depletion has a number of serious potential environmental effects, including the damage to the earth's foodchains both on land and in the seas and on human health.

Exposure to UV radiation will increase more cases of skin cancer, especially among fair-skinned people. UV radiation has a negative impact on human immune system as well as damage eyesight promoting cataracts.

Crop yields and quality will be adversely affected by more UV radiations.

Increased UV radiation in the Antarctic region will penetrate the water surrounding the continent and impair or destroy phytoplankton which represent the base of the foodchains.

Even some inanimate materials, such as rubber, paints and plastics, are more susceptible to deterioration when they are exposed to increased levels of UV radiation.

Circulation of the atmosphere (wind)

As long as the earth's surface is heated unequally, air will move to balance the inequallity. Hadley (1735) suggested that on a non-rotating earth, the air movement would take the form of one large convection cell in each hemisphere. The warm, lighter air near the equator rise upward , at the top of the troposphere spreads outward and travel polewards. After reaching the polar regions, the cooler and heavier air sinks down to the surface and goes back to the equator as surface air.

In 1920s, a three-cell circulation model (for each hemisphere) was proposed to explain the wind circulation. In the atmosphere, the coriolis effect breaks up the flow of air between the equator and the poles into belts.

In the zone between equator and 30^0 latitude (for each hemisphere), the surface air flow is known as trade wind. In the northern hemisphere, the trades are northeasterly, whereas in the southern hemisphere they are southeasterly. ~~The upper-air-flow~~ in this cell is poleward and subsides near 30^0 latitude.

In the second cell between 30 and 60^0 latitudes, the net surface flow is poleward and because of coriolis effect, the winds have a strongly westerly component. These winds are known as westerlies.

A third set of circulating air cells (polar cells) lies over the polar region, between pole and 60^0 latitude. In each polar cell, cold, dry upper air descends near the pole and moves toward the equator in a wind system called the polar easterlies.

Observed distribution of surface pressure and wind

If the earth's surface were uniform (all sea or all smooth land), then four longitudinally oriented belts of high and low pressure would be expected to exist.
Near the equator the pressure zone is known as the equatorial low (also referred as intertropical convergence zone/ ITC). The belts around 30^0 latitude on either side of the equator are known as subtropical high pressure zones. Trade winds and westerlies originate from this zone. Another low pressure zone around 60^0 latitude in each hemisphere is known as subpolar low, where easterlies and westerlies meet. The zones around poles are known as polar highs from which polar easterlies originate.
Because of varied land/sea surface, the surface pressure systems are not continuous belts around the earth rather these zones are semipermanent cells of high and low pressure. The only true zonal distribution of pressure exists along the subpolar low in the southern hemisphere, where ocean is continuous.

Cyclones and anticyclones

A moving low pressure area where rotary air motion is prevalent, is defind as a cyclone. Similarly a moving high pressure area is defined as an anticyclone. The surface air that feeds a cyclone generally originates as air flowing out of an anticyclone. Cyclones and anticyclones are typically found adjacent to each other.
For a middle latitude cyclone to form, two important conditions must be met:
(i) Cyclonic flow must be established. In the northern hemisphere, cyclonic circulation has a counterclockwise rotation and airflow is directed toward the centre of low pressure.
(ii) Of equal importance, the inward flow of air near the surface must be supported by outflow aloft. It is upper-level divergence in the vicinity of the jet stream that is most important in cyclone development. Upper-air divergence creates an environment analogous to a partial vacuum, which initiates upward flow. The fall in the surface pressure that accompanies the outflow aloft induces inward flow at the surface.
In the anticyclone, divergence at the surface is balanced by convergence aloft and general subsidence of the air column.