1.1 INTRODUCTION

Industrial development and population growth in the recent decades have introduced dramatic changes in the earth’s atmosphere. The rapidly changing concentration and distribution of trace gas composition in the earth’s atmosphere leads to an increase in atmospheric researches, in particular, a great effort has been directed toward the measurement of trace gases. Trace gases play a great role in atmospheric composition, chemical reaction, radiative interaction, climate change and pollution even if their abundance is very low. Ozone, which is the most important trace gas much talked about ever since it was discovered, plays a key role in the earth’s atmosphere due to its chemical, human health, vegetation and climate influences. During the past few decades, rapid growth of industries in the Indian region has resulted in an unprecedented growth in emissions of some important pollutants like oxides of nitrogen, carbon monoxide, methane and non-methane hydrocarbons in the atmosphere which are acting as ozone precursors. In recent times, one of the major concerns is the photochemical pollution, where surface ozone is identified as one of the prominent and more serious photochemical pollutants. With these ideas at the base, this chapter gives a brief introduction to the earth’s atmosphere, importance of the trace gases in the atmosphere, atmospheric ozone and nitrogen dioxide.

1.2 EARTH'S ATMOSPHERE

The earth’s atmosphere is composed of thin films of fluid under the influence of gravity, earth’s rotation and differential heating by solar radiation. The atmosphere
possessed by the earth is due to gases released from the interior and the reactions of these gases have undergone. For ages, this atmosphere has balanced the extreme events of physical and chemical changes. The gaseous envelope surrounding the earth is unique among the atmospheres of the planets of the solar system. It absorbs most of the harmful very short wavelength radiation from the sun, recycles water and other chemicals, absorbs and redistributes part of the energy radiated by the earth and works with the electrical and magnetic forces to provide a moderate climate for the sustenance of life. In the most recent century, substantial effects of human activities in the global cycles have arisen leading to an unnatural and unhealthy atmosphere.

1.2.1 Composition of the Earth’s atmosphere

The earth’s atmosphere has a unique composition, structure and life sustaining biogeochemical cycles in its lower reaches. It is composed primarily of nitrogen (78%), oxygen (21%) and Argon (0.93%), the concentrations of which have remained remarkably fixed over time. However, there are many other gases, which are in low quantities but play a major role in the earth’s atmospheric chemistry and radiation budget. They are divided in two different levels of concentration, namely minor constituents and trace gases (Table 1.1). In spite of its apparent unchanging nature, the atmosphere is in reality a dynamic system, with its gaseous constituents continuously being exchanged with the vegetations, the oceans, and the biological organisms. Sometimes when their concentration exceeds substantially above the normal level they become air pollutant. The cycles of the atmospheric gases involve a number of physical, chemical and biological processes. The average lifetime of a gas molecule introduced in the atmosphere can range from seconds to millions of years,
depending on the effectiveness of the removal processes. In order to assess the effect of man-made emissions on the atmosphere as a whole, it is essential to understand the atmospheric cycles of the trace gases, including natural and anthropogenic sources as well as predominant removal mechanisms.

**Table 1.1  Minor constituents and trace gases in the earth’s atmosphere**

(Adapted from Lal, 2007)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical Formula</th>
<th>Volume mixing ratio</th>
<th>Major sources / Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Minor Constituent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water vapour</td>
<td>H₂O</td>
<td>10,000 – 2ppmv</td>
<td>Variable</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>360 ppmv</td>
<td>Combustion &amp; Biosphere</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>1.7 ppmv</td>
<td>Biogenic</td>
</tr>
<tr>
<td><strong>Trace Gases</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td>310 ppbv</td>
<td>Biogenic and Anthropogenic</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>10-200 ppbv</td>
<td>Anthropogenic</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>10 ppbv – 10 ppmv</td>
<td>Photochemical</td>
</tr>
<tr>
<td>Non-methane hydrocarbons</td>
<td>NMHCs</td>
<td>5-20 ppbv</td>
<td>Biogenic and Anthropogenic</td>
</tr>
<tr>
<td>Halocarbons</td>
<td></td>
<td>1-600 pptv</td>
<td>Anthropogenic</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>SO₂</td>
<td>10 pptv – 1 ppbv</td>
<td>Photochemical, volcanic and Anthropogenic</td>
</tr>
</tbody>
</table>


1.2.2 Layers of the atmosphere

Interacting radiative, dynamical and chemical processes determine the structure of the atmosphere. The atmosphere can be divided into several different vertical layers possessing very distinct chemical, physical and dynamical properties (Houghton, 2002). Based on the vertical temperature profile, it is divided into four distinct layers namely troposphere, stratosphere, mesosphere, and thermosphere (Figure 1.1). The top of these layers are called the tropopause, stratopause, mesopause and thermopause respectively. Troposphere is the lower part of the atmosphere which ranges from 7 km at poles to 20 km at tropics. Its thickness depends on the latitude, season and meteorological conditions. The average thickness of the troposphere is around 10 km. In the troposphere, the temperature decreases with the altitude \((0.6^0 - 0.9^0 \text{C/100 m})\). High convective and turbulent processes also characterize the troposphere. Because the pressure decreases exponentially with altitude, \(P(z) = P(0) \exp(-z/H)\), where \(z\) is altitude in km, \(H\) is the scale height given by \((RT/mg)\), it contains about 80% of the total mass (nearly all of the water vapour, clouds, and precipitation) of the atmosphere. This region is rich in myriads of major and minor constituent gases. Almost all of the weather activities occur in troposphere. Most of the photochemical and physical changes of the atmosphere and meteorological phenomena occur within the troposphere. As a result, the troposphere is also called the chemical reservoir of the atmosphere. The portion of the atmosphere between the tropopause and approximately 50 km altitude is the stratosphere. In the stratosphere the temperature increases with altitude. Beyond the stratosphere are the mesosphere and thermosphere (Wallace and Hobbs, 1977; Jacobson, 2002).
The troposphere can be further divided into two sub layers: (i) a rapid turbulent mixing region called the *Planetary Boundary Layer (PBL)* or *Atmospheric Boundary Layer (ABL)* where reactions of short-life elements occur and (ii) a less turbulent region called the *free troposphere* where the reactions of long-life elements occur (Figure 1.2). The PBL is directly influenced by the surface of the earth. The different ways in which the surface interacts with the boundary layer or the boundary layer responds to the surface are called surface and boundary layer processes. Processes such as friction, heat transport, evaporation, and air pollution lead to changes in conditions that occur within an hour in this layer. The thickness of this layer varies between a few hundred meters and about two kilometers (ESPERE, 2006). The height of PBL controls the vertical extent, concentration and transformation of atmospheric pollution and has influence on the concentration of trace gases and ozone in the lower troposphere. Thus, the vertical mixing of the atmospheric pollutants are strongly influenced by the height of the PBL, which acts as an interface between the more polluted regions near the earth’s surface and the relatively cleaner free atmosphere above (Mahalaxmi *et al.*, 2011).

### 1.2.3 Stability of the Atmosphere

A dry air parcel that moves adiabatically upwards in the atmosphere expands and consequently cools down. The cooling is about 1°C per 100 m and is referred to as adiabatic temperature gradient. If the environmental lapse rate corresponds to this adiabatic lapse rate, then an air parcel forced to rise or to fall will always have the same temperature as the surrounding atmosphere and therefore always be in
equilibrium. The atmosphere may be stable or unstable. In a stable atmosphere an air parcel that is forced to rise will always have a temperature inferior to the temperature of the surrounding air and hence return to its former position. The same occurs if the parcel is forced to fall; its temperature will always be superior to the temperature of the surrounding atmosphere and therefore have a tendency to rise to its former level. If the atmosphere is unstable, an air parcel forced to rise will cool down less than the surrounding atmosphere and hence always have a temperature superior to the one of the surrounding air. A parcel forced down has always a temperature inferior to the temperature of the surrounding air and will therefore continue its downward movement.

1.2.4 Thermal inversion

A special case of a stable atmosphere is the formation of an inversion layer. In the troposphere, temperature decreases with increasing altitude. This results in efficient mixing of the troposphere, warm air close to the earth’s surface rises and is replaced by cooler air from higher elevations. However, in certain situations the temperature can increase with altitude. The effect of this “thermal inversion” is an extremely stable layer; warmer air is situated above colder, denser air. This inversion layer permits no mixing with the atmosphere above. For the air quality, the formation of an inversion layer can be extremely important. The pollutants emitted are trapped under the inversion layer. This phenomenon is represented in Figure 1.3. Generally, the formation of an inversion layer is due to the cooling of the earth’s surface during the night. Energy losses in the form of infrared radiation can cool down the earth surface and the adjacent air layers, leading to a thermal inversion.
1.2.5 Mixing layer height

A concept closely related to the stability of the atmosphere is the mixing layer height. As mentioned already, the temperature of the air close to the earth’s surface cools down during the night, leading sometimes to the formation of an inversion layer but leading always to a stable atmosphere at low altitudes. During the morning, when the sun begins to warm up the earth’s surface, the temperature of the adjacent air also rises. The inversion layer disappears and the atmosphere becomes unstable. At first, near the ground and with increasing warming up, the upper limit of the layer with unstable air rises. This layer of unstable air is called mixing layer. In this layer mixing through turbulent diffusion is possible. During the night the mixing layer height is low. Owing to obstacles on the earth’s surface and the induced turbulence, the mixing layer height in urban areas never descends under 40 to 50 m (Bernhard Hohl, 2003). In the morning and during the day the mixing layer height increases. Generally about 16:00 hr the maximum of about 3000 to 4000 m above ground level is reached. Then during the evening mixing layer height descends. Minimum levels are reached in the morning before sunrise. The mixing layer height proves very important for the same reasons as the inversion layer. If mixing layer height is low the pollutants mix only with a small volume of air resulting in high pollutant concentrations.

1.2.6 Radiative forcing of the atmosphere

Basically, all the energy that reaches the earth comes from the sun. The absorption and loss of radiant energy by the earth and the atmosphere are almost totally responsible for the earth’s weather, both on a global and local scale. The average temperature on the earth remains fairly constant, indicating that the earth and
the atmosphere on the whole lose as much energy by re-radiation back into space as is received by radiation from the sun. The accounting for the incoming and outgoing radiant energy constitutes the earth’s energy balance. The atmosphere, although it may appear to be transparent to radiation, plays a very important role in the energy balance of the earth. In fact, the atmosphere controls the amount of solar radiation that actually reaches the surface of the earth and at the same time controls the amount of outgoing terrestrial radiation that escapes into space. An average of 28% of incoming radiation is returned into space by backscattering from clouds (19%), air molecules and particles (6%) and by the surface (3%). Almost 25% is absorbed within the atmosphere, mostly by stratospheric ozone (3%), clouds (5%), and water vapour (17%). The remaining 47% is absorbed by the earth (Graedel, 1993). The solar radiation absorbed at the surface is transformed into latent heat (24%), and sensible heat (5%) whereas only 5% is lost by radiation, the remainder is captured in the atmosphere by the greenhouse gases. Thus greenhouse gases have impact on the energy balance and hence on the climate change.

A change in average net radiation at the tropopause, due to a change in the fluxes of either longwave or shortwave radiation, has been defined as a radiative forcing of climate (IPCC, 1990, 1994). A radiative forcing disturbs the balance between incoming and outgoing radiation at the tropopause, but over time a new balance is established as climate responds to the radiative forcing. A positive radiative forcing means that more energy is trapped by the troposphere and this will have a warming effect on the coupled troposphere-surface climate system. A negative radiative forcing will have a cooling effect.
1.3 IMPORTANCE OF TRACE GASES IN THE ATMOSPHERE

Trace gases play a great role in atmospheric composition, chemical reaction, radiative interaction, climate change and pollution even if their abundance is very low. Many of these trace gases are radiatively active or they go through photochemical and other reaction cycles in the atmosphere giving rise to products which play important roles in atmospheric energetics and radiation balance (Subbaraya and Lal, 1998). Absorption of radiation by gases is one of the most important aspects of both global meteorology and atmospheric chemistry. The solar spectrum is radically altered by absorption as the radiation traverses the atmosphere. It is important to note that the molecules that are responsible for the most pronounced absorption of both solar and terrestrial radiation are only the minor constituents of the atmosphere and not the major constituents – N₂ and O₂. The thermal budget and chemistry of the atmosphere depends highly on some of the key trace gases like water vapour, O₃, CO₂, CH₄, N₂O, CFCs and other gases affecting their concentrations directly or indirectly (Lal, 2007). Although representing collectively less than 1% of the atmospheric mass, some of these trace gases have great influence on the climate, photochemical and dynamical processes of earth. In particular, the way these trace gases interact with each other and with the earth’s surface include human activities that characterize the physical and chemical properties of the troposphere. The high-degree variation in time and space of their optical and morphological properties can cause a significant uncertainty to the climatic system and the earth’s energy balance (Pasquale Sellitto, 2009). Knowing the variations in the concentrations of these active trace gases is important to understand and quantify the atmospheric changes, such as
global warming, atmospheric pollution and change in the chemical composition of the troposphere.

1.4 ATMOSPHERIC OZONE

Ozone (O₃) is a chemical compound that has gained considerable attention in the past few years. It is an allotrope of oxygen that is much less stable than the diatomic allotrope O₂. Ozone was proposed as a distinct chemical substance by Christian Friedrich Schönbein in 1840, who named it after the Greek verb ozein ("to smell"), from the peculiar odor in lightning storms (Rubin Mordecai, 2001). The formula for ozone, O₃, was determined by Jacques-Louis Soret and confirmed by Schönbein in 1867.

Ozone plays a vital role in atmospheric chemistry and physics in the tropospheric and stratospheric region and also plays a key role in the temperature structure of the earth’s atmosphere. It occurs naturally in the stratosphere (90%) and a much smaller portion (10%) is also found in troposphere (Crutzen, 1999). Though ozone molecules in the stratosphere and the troposphere are chemically identical, they have quite different consequences for the health of the planet. The radiation properties of this “greenhouse” gas make it a significant contributor to the radiative energy balance of the atmosphere, and an important regulator of the ultraviolet solar radiation received at the earth’s surface.
1.4.1 Altitude and Ozone

The geographical and vertical distributions of ozone in the atmosphere are determined by a complex interaction of atmospheric dynamics and photochemistry. Ozone concentration increases with altitude and its density is the maximum at about 25 km. At this height, the flux of UV light of the solar radiation and the availability of the molecular oxygen for the production of oxygen atom reach its highest value and it forms continuously from reactions promoted by radiation from the sun. The height of maximum production of $O_3$ varies from place to place; depending on solar flux, which varies according to latitude. $O_3$ is highly unstable, reacting with other molecules in the atmosphere, so that its life time is very short.

There is a little ozone at very high altitudes, such as the mesosphere, because the formation of ozone requires $O_2$ and other molecule (M), whose densities are low there. A much smaller portion of naturally occurring ozone is found in the low altitudes. The natural concentration of ozone in the low altitudes is very small, usually a few tens of parts per billion (ppb) in mixing ratio (molecules of $O_3$ / molecules of air; 10 ppb = $2.5 \times 10^{11}$ molecules/cm$^3$ at sea level and 298K) compared with more than 10,000 ppb (10 parts per million (ppm)) typically found at peak stratospheric mixing ratios. Since there is little atomic oxygen at low altitudes where solar radiation does not penetrate, the $O_3$ production is not like that of in high altitudes. Also, ozone is removed at low altitudes by reactions with dust particles or by reactions at ground. Therefore, the ozone densities are low in the lower atmosphere as well as at high altitudes. A plot of ozone partial pressure and atmosphere mixing ratio as a function of altitude is shown in Figure 1.4. If the whole atmosphere is
compressed at normal temperature and pressure, the thickness of the column of air would be about 8 km, while that of ozone will only 0.3 cm (Gruijl and Leun, 2000).

1.4.2 Stratospheric Ozone

Ozone concentrations in the stratosphere range from $10^{12}$ molecules/cm$^3$ (0.5 ppmv) at an altitude of 15 km, to $10^{13}$ molecules/cm$^3$ (8 ppmv) at an altitude of 25 km, to $10^{11}$ molecules/cm$^3$ (3 ppmv) at 45 km. In the stratosphere, the ozone concentration is regulated through natural photochemical reactions involving oxygen. If the concentration is viewed from the aspect of actual molecular density or mixing ratio, the highest concentration is at about 25 km and this region of higher ozone concentrations is called ozone layer. Stratospheric ozone layer protects the biosphere from the dangerous UV radiations in the wavelength between 230-320 nm (Kevin Locke Wilson, 2005). Increased emissions of N$_2$O, CH$_4$, CFCs, HCFC, carbon tetrachloride (CCl$_4$), methyl chloride (CH$_3$Cl), methyl chloroform (CH$_3$CCl$_3$) as well as halons and methyl bromide (CH$_3$Br) may increase the loss of stratospheric ozone and it may have an impact on the tropospheric chemistry via changes in the UV fluxes reaching the troposphere (Fuglestvedt et al., 1994).

1.4.3 Tropospheric Ozone

Though most of the atmospheric ozone is located between the altitudes of 20 and 30 km, a significant amount is also found in the troposphere, close to the ground called the tropospheric ozone. It is also known as surface ozone or the ground level ozone (Jacob, 2006; The Royal Society, 2008). It is a secondary pollutant formed by photochemical reaction of primary pollutants known as precursors (nitrogen oxides: NOx, carbon monoxide: CO, volatile organic compounds: VOCs) in the presence of
sunlight (Tshiamala Mbuyi, 2001). Ozone in the troposphere has also relevance to the climate change issue since it is a greenhouse gas as already mentioned (EEA, 1998). The changes in the concentrations of O$_3$ have increased the trapping of terrestrial radiation in the atmosphere and thereby enhanced the greenhouse effect above its natural level (IPCC, 1990, 1994). It plays an important role in global warming because of its strong absorption band, centered at 9.6 µm (Lacis et al., 1990). The ozone concentration in any given area results from a combination of formation, transport, destruction and deposition. Emissions of nitrogen oxides (NOx) are responsible for much of the ozone formation occurring in rural areas (EEA, 1998; Matyssek and Innes, 1999). In addition, the O$_3$ formation is becoming more pronounced by the presence of VOCs.

Observations of ozone in the troposphere are scarcer in time and space, but increases in free tropospheric ozone over the last 30 years are reported by several monitoring stations in the Northern Hemisphere (IPCC, 1994). Observations and model studies together indicate that the amount of tropospheric ozone in the Northern Hemisphere might have doubled since the pre-industrial times. The enhancement is a result of increased emissions of the ozone precursors such as nitrogen oxides (NO + NO$_2$ = NOx), carbon monoxide (CO), methane and non-methane hydrocarbons (NMHC) (IPCC, 1994).

The spatial pattern of ozone changes during the two 50-year periods (1950-1980 and 1990-1950) is shown for the surface, a level near the tropopause, and for the total column in Figure 1.5 (Shindell et al., 2006). Both surface and tropopause level ozone, as well as the column, show the largest increases at northern mid latitudes.
There is a very sharp increase in surface level ozone, especially in Asia and in Africa. Given the greater available sunlight at these latitudes compared with northern industrialized regions, photochemical production of ozone from NOx is more efficient (Fuglestvedt et al., 1999), leading to the large tropical ozone increases during the latter half of the 20\textsuperscript{th} century.

1.5 EFFECTS OF OZONE

Ozone is both phytotoxic and cytotoxic. It is an important air quality issue and causes serious health problems and damage to materials and ecosystems (De Leeuw et al., 1999; De Leeuw, 2000). It is considered as a criteria pollutant by the Environmental Protection Agency (EPA) and World Health Organization (WHO).

1.5.1 Health Effects

Ozone is a powerful oxidant, and, as such, it can react with a wide range of cellular components and biological materials. Epidemiological and toxicological studies indicate that higher concentration of ozone in the boundary layer is harmful to biological health (Avol et al., 1998) and so far, several types of ozone related short-term health effects have been detected. Even at very low levels, ozone can:

- irritate the respiratory system and cause acute respiratory problems;
- reduce lung function and temporarily decreasing lung capacity approximately 15 to 20 percent in healthy adults;
- aggravate asthma
- inflame and temporarily damage lung tissue;
• may aggravate chronic lung diseases, such as emphysema, bronchitis, and pneumonia;
• impair the body's immune system defenses, making people more susceptible to respiratory illnesses, including emphysema, bronchitis, and pneumonia;

(Seltzer et al., 1986; McDonnell, 1991; Hiltermann et al., 1995).

The biological effects are probably caused by intermediates such as free radicals, lipid hydroperoxides, aldehydes, hydrogen peroxide, etc. (Leikauf et al., 1993). Hatch (1994) has shown that O from O₃ accumulates in the airway lining layers, suggesting that ozone reacts with components of these layers. Several factors influence these health impacts, including the concentrations of ground-level ozone in the atmosphere, the duration of exposure, average volume of air breathed per minute (ventilation rate), and the length of intervals between short-term exposures.

1.5.2. Effects on plants and crop yield

Ozone exposure of ecosystems and agricultural crops result in invisible foliar injury and in reductions in crop yield and seed production, and loss in forest productivity (Matyssek and Innes, 1999; Jackson et al., 2000; Mills et al., 2007; Debaje et al., 2010). A number of recent studies from selected sites across South Asia have specifically addressed the sensitivity of locally-grown crops to the ozone levels (Agrawal, 2005; Wahid, 2003). Although, plants have evolved protective mechanisms to prevent ozone damage, there is a threshold ozone concentration above which the plant’s detoxification processes can no longer cope with (Karenlampi and Skarby, 1996).
The uptake of ozone into the leaf mesophyll occurs mainly through the stomata during photosynthetic gas exchange (Fiscus et al., 2005). Once inside the leaf, it rapidly reacts with the moisture on the surfaces of the underlying cells. The resulting oxygen species are highly reactive and may overload the naturally occurring protective mechanisms of the plant. The effects that occur include reductions in crop yield and quality, growth reductions, changes in morphology and physiology, visible injury, and early senescence (Finnan et al., 1996; Gimeno et al., 2004). In addition to physiological damages, surface ozone may cause reduced resistance to fungi, bacteria, viruses, and insects and inhibiting reproduction. These impacts on sensitive species may result in deterioration in agricultural crop quality and the reduction of biodiversity in natural ecosystems (Morgan et al., 2006; Mills et al., 2007).

Based on the large-scale experimental studies of the National Crop Loss Assessment Network (NCLAN) conducted in the United States in the 1980s (Heagle, 1989; Heck, 1989), the U.S. Environmental Protection Agency (EPA) estimated that the yields of about one third of U.S. crops were reduced by 10% due to ambient O\textsubscript{3} concentrations during this time (EPA, 1996). Results from the European Open Top Chamber Programme (EOTC) in the 1990s (Krupa et al., 1998) similarly suggests that the European Union (EU) may be losing more than 5% of their wheat yield due to O\textsubscript{3} exposure (Mauzerall and Wang, 2001). Significant losses of agricultural production often occur at ozone exposures above 40 ppb, a level already reached in many Northern hemisphere countries including India (The Royal Society, 2008). Although comparable large-scale studies have not been conducted in developing countries, the potential risk of ambient O\textsubscript{3} exposure to agricultural production has been documented
through both small-scale field studies and modeling efforts in East Asia (Chameides et al., 1999, Aunan et al., 2000; Wang and Mauzerall, 2004; Huixiang et al., 2005), the Indian subcontinent (Wahid, 2003; Agrawal, 2005; Emberson et al., 2009; Debaje et al., 2010), Egypt (Abdel-Latif, 2003), and South Africa (van Tienhoven and Scholes, 2003).

The results of the study conducted by Deb et al., (2009) clearly indicate that presently the enhanced concentrations of ozone can have a potential impact on crop yield and forest over a large area of India. Avnery et al., (2011) studied that the total Crop Production Loss (CPL) due to surface ozone is the greatest in the U.S (21-29 Mt), followed by China (18-27 Mt) and India (8-25 Mt) and the greatest economic losses occur in the U.S ($3.1 billion USD), followed by China ($3.0 billion) and India ($2.5 billion). These three countries account for 59% of the global economic damage (21, 21, and 17%, respectively).

The presence of O₃ and its effects on crops are often not visible in contrast with other yield-reducing factors such as insects or diseases. Besides, surface ozone affects the ability of plants in absorbing carbon dioxide from the atmosphere, accelerating global warming. Therefore, without proper monitoring of O₃ concentrations in rural areas, as is the case in most developing countries, the problem remains unnoticed and lower yields unexplained (Teixeira et al., 2010).

1.5.3 Effects on Materials

Ozone damages many different types of materials, both functionally and aesthetically, alone and in combination with other pollutants and environmental factors. Impacts of ozone alone are more significant in organic materials. Ozone is
known to damage textiles and some polymeric materials such as paints, plastics and rubber. The limited available data indicates significant damage to rubber products and surface coatings (Lee et al., 1996). Ozone may accelerate paint corrosion by attacking inorganic components specifically zinc (Stevenson and Johansson, 1993; OSAD, 1999). In combination with sulphur dioxide, ozone accelerates the corrosive action of sulphur dioxide on metals such as copper, zinc, silver, aluminum, nickel and iron (Health Canada, 2007).

1.5.4 Effects on Climate

Ozone plays an important role in the energy budget of the atmosphere, since it absorbs both solar and infrared radiation (Brasseur et al., 2001). Being a main atmospheric oxidizing component and an optically active constituent, it plays an important role in the climate system of the earth (Park et al., 2001). A decrease in ozone in the lower stratosphere cause decreases in surface temperature, while increase in tropospheric ozone causes increase in surface temperature. Because ozone is a triatomic molecule with a structure similar to water vapor, it has three radiatively active vibrational bands which fall at 9, 9.6, and 14.4 micrometers (Petty, 2006). The 14.4 micrometer band coincides with the strong absorption band of carbon dioxide and therefore has very little climate impact. On the other hand, the 9 and 9.6 micrometer bands fall in the atmospheric window, where the Earth’s atmosphere is otherwise transparent to outgoing radiation and the Plank function corresponding to the Earth’s surface temperature is near its maximum; these absorption bands have a large climatic impact. Hence, the resultant effect on surface temperature and consequently climate of the earth critically dependent on the vertical distribution of the trend in ozone.
Recent findings have revealed that most of the ozone in the troposphere is locally produced by human activities and the increasing trend leading to an overall decrease in the oxidation efficiency of the atmosphere.

1.6 ATMOSPHERIC NITROGEN OXIDES

Nitrogen oxides are important chemical species in the PBL as well as in the free troposphere and the stratosphere. There are seven oxides of nitrogen that are present in the ambient air. They are NO, NO$_2$, NO$_3$, N$_2$O, N$_2$O$_3$, N$_2$O$_4$ and N$_2$O$_5$. Of these seven nitrogen oxides, the most important forms of reactive nitrogen in the air are nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$). NO$_2$ is a very reactive and significant species in the atmosphere. It plays an important role in the control of concentrations of radicals in the troposphere, in the production of tropospheric ozone, as an aerosol precursor, and in the production and deposition of acidic species directly or indirectly (Logan, 1983; Finlayson-Pitts and Pitts, 1986). The interconvertibility of NO and NO$_2$ in photochemical reactions has frequently resulted in their being grouped together under the designation NOx.

Ambient sources of NO$_x$ can be classified into anthropogenic and natural sources, but the major contribution is from anthropogenic sources. Anthropogenic sources of NO$_2$ emissions include transportation, stationary fuel combustion, various industrial processes, solid waste disposal, and others such as forest fires. Natural sources are lightning, biological and abiological processes in soil and stratospheric intrusion. Estimates of lightning based NOx emissions for North America range from 1.2 to 1.7 Tg/year of NO$_2$ (Placet et al., 1990). Crutzen and Schmailz (1983)
estimated that global NO\textsubscript{x} emissions from stratospheric injection to be 0.5Tg/year. The important indoor sources of NO\textsubscript{x} are gas stoves, unvented space heaters, kerosene heaters, wood stoves and tobacco products. Estimates indicate that about 95% of all NO\textsubscript{x} stationary combustion sources are emitted as NO which can be oxidized to NO\textsubscript{2} in ambient air in the presence of O\textsubscript{3} or in a photochemically reactive atmosphere. Another form of nitrogen oxide, the very reactive nitrate radical (NO\textsubscript{3}) is formed in the dark and this controls the chemistry of the night time atmosphere. Nitrogen oxides react with water to form nitric acid (HNO\textsubscript{3}). Nitric acid is not only a major contributor to acid rain but is also the main way in which nitrogen oxides are removed from the air, either by dry deposition of the acid directly or by removal in rain. Other important nitrogen gases in the atmosphere include Nitrous oxide (N\textsubscript{2}O) which is formed during microbiological degradation processes. It is an important greenhouse gas but does not react in the troposphere. In the stratosphere it destroys ozone.

NO\textsubscript{x} influences the oxidation capacity of the atmosphere through OH and nitrate. At wavelengths below 398 nm, photo dissociation of oxygen atoms occur (NO\textsubscript{2} + hv \rightarrow NO + O) giving rise to several significant inorganic reactions in addition to a host of atmospheric reactions involving organic species. Most chemical compounds which are oxidized and removed from the air or transformed into other chemical species come into touch directly or indirectly with NO or NO\textsubscript{2}. Figure 1.6 gives an overview of the role of nitrogen oxides in some of the most important processes in atmospheric chemistry (ESPERE, 2006).
The transport and dispersion of the various nitrogenous species are dependent on both meteorological and chemical parameters. Advection, diffusion, deposition and chemical transformations combine to dictate the atmospheric lifetime. Surface emissions are dispersed vertically and horizontally through the atmosphere by turbulent mixing processes that are dependent to a large extent on the vertical temperature structure and wind speed.

1.7 EFFECTS OF NITROGEN DIOXIDE

The toxicity of NO\(_2\) relates to its ability to form nitric acid with water. It is highly toxic to various animals as well as humans, highly reactive and corrosive to metals.

1.7.1 Health Effects

Health risks from nitrogen oxides may potentially result from NO\(_2\) itself or its reaction products including O\(_3\) and secondary particles. High levels may be fatal, while lower levels affect the delicate structure of lung tissues. Several epidemiological studies have shown consistent associations of long-term NO\(_2\) exposure with decreased lung function and increased risk of respiratory symptoms (Ackermann-Liebrich et al., 1997; Schindler et al., 1998; Panella et al., 2000; Smith et al., 2000). Exposure to 150-200 ppm of NO\(_2\) causes bronchiolitis fibrosa obliterans, a fatal condition within 3-5 weeks after exposure. Death generally results within 2-10 days after exposure to 500 ppm or more of NO\(_2\) (Gauderman et al., 2000). Chiusolo et al., (2011) found that there is a statistically significant association between increase of NO\(_2\) and mortality. Gurjar et al., (2010) estimated that elevated
SO₂, NO₂ and Total Suspended Particulates (TSP) concentrations resulted in 5,000 to 15,000 excess deaths per year in Mumbai and about 7,000 to 22,000 excess deaths per year in Delhi. NO₂ concentrations are also highly correlated with other pollutants either emitted by the same sources or formed through complex reactions in the atmosphere (Brook et al., 2007).

1.7.2 Effects on Vegetations

NOₓ have the potential for influencing plant growth through either the leaves or the roots of plants. However, the concentrations of gaseous nitrogen oxides in the atmosphere, by themselves or in combination with O₃ or SO₂, rarely are in large enough to influence plant growth. NO₂ in combination with SO₂ may enhance the phytotoxicity of these pollutants (Bennett et al., 1975).

1.7.3 Effects on Materials

NOₓ have been shown to cause or accelerate damage to materials exposed to the atmosphere. Strong evidence exists for the deleterious effects of NOₓ on dyes and fabrics. The effects observed are mainly fading, discoloration, and loss of strength of textile fibers. In indoors, NO₂ may react synergistically with SO₂ and its deposition on electronic components and magnetic recording equipment may lead to component or system failure. NOₓ have been reported to play a role in causing damage to paints and stones (EPA, 1993)

1.7.4 Effects on climate

The nitrogen oxides do not absorb infrared radiation, and, therefore, do not contribute to direct radiative "greenhouse" forcing but NO₂ is an efficient absorber of visible radiation, and it has been proposed as a possible source of additional climatic
influences (Wuebbles, 1989). NOx indirectly influences the radiation budget of the atmosphere through photochemical production of O₃, which possibly represents 10–15% of the total anthropogenic greenhouse radiative forcing in the atmosphere (Fishman et al., 1979; Lacis et al., 1990; Wild et al., 2001).

1.8 RISING OF NO₂ CONCENTRATION

The emissions of NOₓ, which lead to the formation of ozone are increasing dramatically in Asia as the region experiences rapid industrialization. The Global Ozone Monitoring Experiment (GOME), which observed the distribution of NO₂ column concentrations in the troposphere, provided evidence of this trend (Richter et al., 2005). Due to larger population and higher economical growth rates, emission of these gases are increasing in Asia and more so in the central South Asia (Lelieveld et al., 2001). According to Research Institute of Humanity and Nature (RIHN), NOₓ in Asia increased by about 2.5 times over the last two decades. Figures 1.7 (a) and (b) which compare distributions of NOₓ emissions in 1980 and 2000, show that increases are large in India (Ohara et al., 2005). Garg et al., (2001) estimated that the rate of increase of NOₓ is 5.5% / year in India, which relates to the economic growth of the nation. Akimoto, (2003) and Oltmans et al., (2006) have also shown that the NOₓ emission in Asia and India is increasing at a faster rate. Kunhikrishnan et al., (2006) have made a detailed study on NOₓ emission in Asian region and concluded that photochemical transformation and losses of NOₓ are uncertain because of lack of
sufficient observations. Table 1.2 shows the contribution of various emission sources of NO\textsubscript{x} in India (Lal, 2007).

**Table 1.2 Various emission sources of NO\textsubscript{x} in India.**

<table>
<thead>
<tr>
<th>Sector</th>
<th>NO\textsubscript{x} (in percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generation</td>
<td>27.9</td>
</tr>
<tr>
<td>Transport</td>
<td>32.0</td>
</tr>
<tr>
<td>Industry</td>
<td>19.2</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>18.7</td>
</tr>
<tr>
<td>Other sectors</td>
<td>1.9</td>
</tr>
<tr>
<td>Non energy sources</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Recently, The Energy and Resources Institute (TERI) (2011) has assessed the energy and emissions scenarios for the period 2005 to 2030 for various States and Union Territories of India based on the *Greenhouse Gas and Air Pollution Interactions and Synergies* (GAINS) Asia model for different pollutants like particulate matter, oxides of sulphur and nitrogen oxides. An inventory of NMVOCs emissions prepared for India shows that industrial sector dominates in the PM emissions, whereas transport sector has the major share in NO\textsubscript{x} and power plants contribute more to the SO\textsubscript{2} emissions. Biomass burning has the maximum share in NMVOCs emissions.

Similarly, the increase in VOC emissions is large. VOC emissions increased 1.9 times in Asia and 2.4 times in China from 1980 to 2000. The main causes of these
increases are due to increasing emissions from automobiles and evaporation from the use of solvents. As mentioned above both NO\textsubscript{X} and VOC emissions which lead to ozone formation, have been increasing dramatically in Asia particularly in India over the past quarter of a century. The growing importance of photochemical production of O\textsubscript{3} in the tropical region, such as the Indian subcontinent, is due to intense solar radiation and higher water content in the atmosphere along with increasing NO\textsubscript{X} (Andreae and Crutzen, 1997; Lelieveld \textit{et al.}, 2001).

Since the lifetime of NO\textsubscript{X} is substantially shorter than other O\textsubscript{3} precursors, such as carbon monoxide (CO) and hydrocarbons, NO\textsubscript{X} is often considered as the rate-limiting precursor for O\textsubscript{3} formation. In other words, photochemical production of O\textsubscript{3} is usually proportional to the abundance of NO\textsubscript{X} in the tropics. As a result, emissions of NO\textsubscript{X} can often lead to significant increase in O\textsubscript{3}. The increase in NO\textsubscript{X} concentration is responsible for increasing O\textsubscript{3} in the Indian subcontinent (Berntsen \textit{et al.}, 1996; van Aardenne \textit{et al.}, 1999; Debaje \textit{et al.}, 2003).

1.9 AMBIENT STANDARDS AND GUIDELINES

Many jurisdictions worldwide have established standards or guidelines for O\textsubscript{3} and NO\textsubscript{2}. Ambient standards and guidelines for surface ozone are aimed at protecting human health, sensitive ecosystems, and agricultural plants from the harmful effects of ozone. The EPA in USA has developed the \textit{Air Quality Index} (AQI) for reporting the levels of ozone and other pollutants, and their effects on human health. The AQI scale has been divided into different categories, which range from 0 to 300. Each
category corresponds to a different health impact. In addition to the national or supranational standards or guidelines the World Health organization has proposed an ozone guideline of 100 µgm$^{-3}$ (approximately 50 ppb) as an 8-hour average (WHO, 2005). Though India had adopted standards or guidelines for several criteria pollutants, adaption of standards for ozone (50ppb 8-hour mean) was made only in 2009 (Table 1.3).

Table 1.3 National Ambient Air Quality Standards (India)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Time Weighted Average</th>
<th>Industrial, Residential, Rural and Other Area (Concentration in Ambient Air (µg/m$^3$))</th>
<th>Ecologically Sensitive Area (Notifyed by Central Government)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>8 hours 1 hour</td>
<td>100 180</td>
<td>100 180</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Annual 24 hours</td>
<td>40 80</td>
<td>30 80</td>
</tr>
</tbody>
</table>


1.10 OBJECTIVES OF THE STUDY

Chemistry of formation of tropospheric ozone and nitrogen oxides is a major complex and nonlinear problem of atmospheric research. The reduction of surface ozone is an important objective of air quality policy for many governments. At present, ozone is measured in very few cities in India. Significant amount of research,
including monitoring and modelling of surface ozone pollution, is required to draft policies for its control.

The surface ozone concentrations depend sensitively upon meteorological parameters such as temperature, cloudiness, sunlight, wind speed and the mixed layer depth. So there’s a lot more to be learned about the links between climate and pollution. Since both surface ozone and NO\textsubscript{2} have adverse effects on human health, understanding the link is important. Hence, a comprehensive study of both surface ozone and nitrogen dioxide is attempted through this study.

Increase in tropospheric O\textsubscript{3} from industrialization in developing countries was found to contribute to accelerate warming in the tropics during the latter half of the century (Shindell et al., 2006). Also, it was realized that increased surface ozone was not only a problem of urban locations but also of rural locations (Kalabokas et al., 2003). Hence observation for this study is planned to have at a semi-urban tropical site.

In this present work an attempt has been made to address briefly some of the important issues, relevant to the changing climate scenario, with special emphasis on temporal (diurnal and seasonal) variations in surface ozone and one of its precursors, NO\textsubscript{2} with available meteorological parameters (Relative humidity, Temperature, Rainfall, and Wind speed) over a tropical semi-urban location, Nagercoil, in the southernmost region of India. In summary, the objectives of this study are,

- To execute statistical analysis of ozone and its precursor NO\textsubscript{2} data collected for the period of three years at the observation site.
• To analyze the ozone and NO\textsubscript{2} data in terms of their diurnal, seasonal and annual variations.

• To explain the observed ozone concentration with meteorological parameters to determine if there is any correlation and to identify the most important factors in determining ozone levels.

• To explain the interaction between ozone concentration and its precursor nitrogen dioxide in the observation site.

In general, this research is an attempt to bring forth the physical and chemical characteristics of this semi-urban atmosphere by applying sophisticated and reliable instruments of investigation and to support the surface ozone research in India.