Chapter - 1

Introduction
Chapter - 1
Introduction

Evolution of cyanobacteria about 3.5 billion years ago on the Earth, in the early ocean, enabled them to use the solar radiation for the reduction of Carbon-dioxide and the photolysis of water molecule to release oxygen molecule as an end product. This was a keystone step taken by nature to assist biological evolution in new direction, as available oxygen molecule through photosynthesis initiated the process of changing the Earth's atmosphere; reducing to oxidizing. Interestingly, till 2.3 billion years before present (bp) there was no free oxygen available; during the period 3.5-2.3 billion years bp all oxygen produced in photosynthesis was consumed by reduced iron and other silicious minerals. Only after the bulk of available reduced material got oxidized and got locked under the ocean bed, the free oxygen started building up in the atmosphere. Availability of the free oxygen created conditions conducive for the aerobic life forms to flourish. However, till 600 million years bp the diversity of life was confined to the lower photic zone of ocean and other water bodies to ensure filtering of energetic solar UV radiation (< 280 nm). During these times (600 million years bp) a second keystone step was initiated by nature to favor the aerobic life forms on earth. Once the level of free oxygen reached 0.1% of the present, the formation of a UV shield in the form of Ozone-Layer could be set in motion high in the atmosphere [Valen, 1971; Holland, 1984; Kasting, 1993]. As the ozone layer thickened, survival of life no longer was constrained to the lower photic zone of the ocean, and path was cleared for terrestrial life to evolve. Prior to 600 million years bp, only primitive life forms existed on the Earth. But, the protection provided by the ozone-layer paved the way for the rapid increase in the diversity of complex life forms to flourish on the Earth. In this sense, the role of Ozone layer is vital to allow the sustenance, survival and diversification of life on the Earth, which is linked with its chemical structural attributes.
Ozone, an allotrope of oxygen, is a natural constituent of the earth's atmosphere. The electronic configuration of ozone represents the sharing of outer most shell electrons between three oxygen atoms. This sharing endows Ozone (O₃) with resonance structure, whereby bond in ozone (O=O₂) can dissociate with exposure to light having λ< 1130 nm [Pitts and Pitts, 2000]. This characteristic of Ozone molecule makes it a powerful oxidant, which is capable of reacting with almost anything coming in its contact (gases, liquids or solids). The reactive nature of this molecule ensures its low residence time, which varies as a function of its location in the atmosphere and the processes underlying it's formation [Seinfeld and Pandis, 1998]. In atmosphere, it is present in trace amounts; most of the ozone concentration is present in the stratosphere. The process of ozone formation in the troposphere and the stratosphere differ significantly, and this aspect has considerable impact in modifying the surrounding atmospheric traits. Though the total concentration of Ozone (Stratosphere + Troposphere) is very small in comparison to the bulk atmospheric constituents (N₂ and O₂) but the role it plays in modifying the solar irradiance regime (filtering of high energy Ultraviolet solar radiations from reaching the Earth’s surface) is vital for the survival of all life forms on land [World Meteorological Organization, 2007]. This trait of ozone is coupled with the dynamics of its formation and destruction, involving a cycle of photochemical reactions occurring in the stratosphere. Any decrease in the total ozone present in a column having a unit area and extending from the surface of the earth to the top of the stratosphere will allow the passage of high energy UV component of solar radiation to reach ground [Xenopoulos and Schindler, 2001]. This is the precise reason as to why there is a world wide concern to continuously monitor the changes in the ozone column at different latitudes and analyze systematically the variability in its column concentration on temporal scale. The implications associated with the increased solar UV radiation reaching ground are: (a) threat to global food security, (b) enhanced selection pressure on microbes, and (c) threat to human health (skin cancer, suppression of immunity, and increase in the eye related
ailments) [Diffey, 1991; Dolin, 1994; Allen et al., 1998; Cockell and Blaustein, 2001].

1.1 Abundance of Ozone in the Atmosphere and its importance

Most of the Ozone (around 90%) resides in the lower stratosphere, between 15-38 kilometer height above the earth’s surface, and this expanse is commonly known as region where “Ozone Layer” confines [World Meteorological Organization, 1995]. The remaining Ozone (about 10%) is found in the troposphere. Ozone molecules have a relatively low abundance in the atmosphere. In the stratosphere where Ozone Layer confines, its abundance is 12,000 parts per billion (ppb); tropospheric abundance is typically in the range of 20-100 ppb [World Meteorological Organization, 1999].

The unit used to quantify the abundance of ozone is “Dobson Unit (DU)” named after G.M.B. Dobson, who investigated the ozone between 1920 and 1960. The abundance of ozone present in a column is expressed in terms of thickness. One Dobson Unit (DU) is defined as 0.01 mm thickness of ozone column formed at STP, when all the ozone in the air column above a unit area is collected; 100 DU correspond to 1 mm thick ozone layer [World Meteorological Organization, 2007].

1.1.1 Presence of Ozone in the Stratosphere and its importance

The presence of Ozone layer in the stratosphere is considered “good” for all life forms as it absorbs biologically active part of solar ultra-violet (UV) radiation. Investigations indicate that the absorption is almost complete for 220-290 nm (UV-C) but less strong in 290-330 nm (UV-B) region [Molina and Molina, 1986]. Any decrease in the stratospheric ozone leads to an increase in solar UV-B radiation at the Earth's surface; considering all other factors (cloudiness, turbidity etc.) remain constant [Madronich et al., 1998]. It is well established that exposure to UV-B induce skin cancer, cataracts, and suppresses the immune system; and it stands to reason that any additional
increase in the incoming solar UV-B will seriously impact human health, damage to terrestrial plant life, single-cell organisms, and aquatic ecosystems [Cockell and Blaustein, 2001].

The role of stratospheric Ozone layer in inverting the temperature gradient to positive above tropopause plays an important role by disallowing the mixing of tropospheric constituents into stratosphere. The positive temperature gradient in stratosphere is due to the interaction of solar radiation with ozone layer [Shen et al., 1995].

1.1.2 Presence of Ozone in the Troposphere and its importance

Presence of Ozone in troposphere arises from two sources: (1) natural; and (2) anthropogenic. The source of natural ozone in the troposphere is from the sinking of stratospheric air mass; this phenomenon is more pronounced at higher latitudes. Most of the tropospheric ozone arises from anthropogenic activities involving interaction between solar irradiance and emitted ozone precursors from fossil fuel combustion [Crutzen, 1995].

Contrary to the positive implications of the stratospheric ozone layer, the presence of ozone in troposphere is harmful to humans, plants, and other living systems. As stated earlier, ozone as an oxidant readily reacts with any molecule and gives rise to the formation of many altered chemical species. It is known that ozone exposure reduces crop yields and forest growth. In humans, exposure to high levels of ozone can reduce lung capacity; cause chest pains, throat irritation, and coughing; and worsen health conditions in case of any pre-existing cardio-pulmonary diseases [Lippmann, 1989; Sandermann Jr, 1996].

1.1.3 Ozone and Climate Change

Any change in the quantum of Ozone present in the stratosphere and the troposphere has important implications to climate change. A decrease in the mixing ratio of ozone in Stratosphere results in a negative radiative forcing. But, in the troposphere an increase in the Ozone concentration causes
a positive radiative forcing [Intergovernmental Panel on Climate Change, 2007].

1.2 Formation of Ozone

Ozone formation in stratosphere involves multiple photochemical steps. The process begins with an oxygen molecule \((O_2)\) being broken apart by high energy component of solar ultraviolet radiation, whereas in the lower troposphere ozone formation is initiated with the photolysis of nitrogen dioxide \(\text{(NO}_2\text{)}\) [Pitts and Pitts, 2000].

1.2.1 Formation of Ozone in the Stratosphere

Initially a mechanism for the formation and destruction of ozone in the undisturbed stratosphere was provided by Chapman [1930], further investigations fine tuned the reaction kinetics involved:

**Formation of Ozone**

\[
\begin{align*}
O_2 + \text{hv} (\lambda < 242 \text{ nm}) & \rightarrow O + O \quad (1.1) \\
O_2 + O (+M) & \rightarrow O_3 
\end{align*}
\]

**Photochemical Destruction of Ozone**

\[
\begin{align*}
O_3 + \text{hv} (\lambda < 320 \text{ nm}) & \rightarrow O_2 + O (^1D) \quad (1.3) \\
O + O_3 & \rightarrow 2O_2 \quad (1.4) \\
O + O (+M) & \rightarrow O_2 
\end{align*}
\]

Where, \(M\) represents a third molecule (usually \(\text{N}_2\)) which through collision helps to remove the excess energy released in the chemical reaction. Reaction (1.3) is the mechanism by which ozone shields the Earth's surface from the UV-B radiation.
The formation of odd oxygen in (1.1) is driven by UV light at wavelengths below 242 nm. UV light at these wavelengths is absorbed high up in the stratosphere and does not penetrate far down. This means, as the Sun's intensity is more in the tropics, the major region for ozone formation is also confined in the upper half of the stratosphere over the tropics [Seinfeld and Pandis, 1998].

A series of scientific investigations, focused on the Ozone formation mechanism, have been carried out, when a discrepancy arises between measured Stratospheric Ozone concentrations and the Stratospheric Ozone concentrations calculated by using Chapman mechanism. It was observed that the measured ozone concentrations in the stratosphere were less by a factor of 2 than what is predicted by Chapman mechanism. Thus, it can be concluded that there are additional Ozone destruction pathways other than explained in Chapman mechanism. First of all, Bates and Nicolet [1950] introduced the idea of a catalytic loss of Ozone involving hydrogen radicals, but the main breakthrough in the understanding of Stratospheric Ozone chemistry occurred, when pioneering work by Crutzen [1970] and Johnston [1971] revealed the role of nitrogen oxides in the stratospheric chemistry. Subsequent work done by Stolariski and Cicerone [1974], Molina and Rowland [1974], and Rowland and Molina [1975] elucidated the effect of chlorine-containing compounds on the Stratospheric Ozone chemistry.

The catalytic Stratospheric Ozone destruction processes that must be added to the Chapman mechanism can generally be expressed as:

\[
\begin{align*}
X + O_3 & \rightarrow XO + O_2 \quad \text{(1.6)} \\
XO + O & \rightarrow X + O_2 \quad \text{(1.7)}
\end{align*}
\]

\[\text{Net: } O_3 + O \rightarrow O_2 + O_2\]

where X is a free radical catalyst. X can be H, OH, Cl or Br.
1.2.2 Formation of Ozone in the Troposphere

For all practical purposes, (1.2) is the only reaction that produces ozone in the atmosphere, either in the stratosphere or in the troposphere. The major mechanism of odd oxygen formation in the troposphere is from the photolysis of nitrogen dioxide.

\[ \text{NO}_2 + \text{hv} (\lambda < 424 \text{ nm}) \rightarrow \text{NO} + \text{O} \quad (1.8) \]

Then ozone is formed through (1.2)

\[ \text{O}_2 + \text{O} (+\text{M}) \rightarrow \text{O}_3 \quad (1.2) \]

Once formed, \( \text{O}_3 \) has an option to react with \( \text{NO} \) to regenerate \( \text{NO}_2 \)

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (1.9) \]

In an unpolluted troposphere, reactions (1.8), (1.2) and (1.9) lead to a pseudo-stationary state for the concentrations of \( \text{NO} \), \( \text{NO}_2 \) and \( \text{O}_3 \). In a polluted troposphere \( \text{CO} \), \( \text{CH}_4 \) and other Volatile Organic Compounds (VOCs) form Peroxy Radical (\( \text{HO}_2 \) or \( \text{RO}_2 \)) after their reaction with Hydroxyl Radicals (OH). Peroxy Radical reacts with Nitrous oxide (NO) to produce net Nitrogen dioxide (\( \text{NO}_2 \)) and Hydroxyl Radical (OH), and this sequence shift the pseudo-stationary state in favor of net ozone formation in the troposphere.

To a small extent, under specific micro-climatic conditions, ozone can also be formed in troposphere following the mechanism akin to stratospheric ozone formation, without any involvement of Nitrogen Oxides (NOx) and VOCs [Attri et al., 2001].

1.3 Variations in the Total Ozone Column

Once formed, Ozone concentration at any location will be subjected to the dispersion enforced by the dynamic atmospheric factors operating over varying time scale (molecular diffusion, convection from solar heating, convergence and divergence of air masses, horizontal flow of air over specific-topographic features of the Earth, buoyancy changes influenced by the latent heat exchange in air parcels and pressure gradient induced motion of air masses etc.). The magnitude of atmospheric properties assisting the transport
of material and energy changes, not only with latitude but also vary significantly in the different regions of the troposphere and stratosphere [Holton et al. 1995; Seinfeld and Pandis, 1998; Holton, 2004].

1.3.1 Daily, Seasonal and Annual Variations

The variations in the total ozone column at a given location (latitude and longitude) come about from two main reasons: (1) Movement of air masses between Ozone rich and poor region; and (2) Variation occurring in the photochemical kinetics underlying the Ozone production and its loss [Volk et al., 1996; World Meteorological Organization, 2007]. Interesting aspect about these two factors results in the unequal and surprising distribution of column ozone abundance with latitude. The production of Ozone is maximal in the column coinciding with the region lying above the equator, suggesting a strong correlation between available solar intensity and solar zenith angle [Trenberth, 1992; Seinfeld and Pandis, 1998]. It is equally interesting to note that the stratospheric regions above latitudes associated with higher ozone formation do not coincide with the regions showing the highest ozone column abundance. Maximum ozone concentrations are found at higher latitudes and poles; indicating that ozone concentration and splitting of O₂ (first step in the reaction) do not coincide. This behavior reflecting latitudinal variability of ozone column abundance is due to the complex vertical and horizontal transport of air masses from equatorial regions towards the poles; distributing ozone [World Meteorological Organization, 2007]. This complex phenomenon brings in the differences in the Ozone residence time in stratospheric and tropospheric regions; transport of Ozone formed in stratospheric region above equator to mid-latitudes takes about 3-4 months. The investigations in this regard show that the Ozone residence time ($\tau_{O_3}$) in stratosphere can vary from 1 day to three years as a function of region’s altitude and latitude [Dutsch, 1974; Johnston, 1975]. Tropospheric weather pattern that perturbs the atmospheric flow, not only in the troposphere but also at tropopause region and in the lowermost stratosphere, is mainly responsible for the day-to-day
variability observed in the total ozone column abundance. The extra-tropical total ozone values vary due to number of dynamical parameters such as the free tropospheric temperature, the lower stratospheric temperature, the geopotential height, the potential vorticity of the lowermost stratosphere, the tropopause height, and the tropopause pressure [Schubert and Munteanu, 1988; Tung and Yang, 1988a; Vaughan and Price, 1991; Ziemke et al., 1997; Staehelin et al., 1998; Steinbrecht et al., 1998; Appenzeller et al., 2000].

Total Ozone Column (TOC) abundance is lowest in the tropics and increases with latitude. The related influences on TOC are exerted by the strength of the seasonal cycle, which increases with latitude. The strength of these cycles in Northern Hemisphere is maximal in the regions around mid- and high-latitudes (late winter and early spring). As stated above, the main source of stratospheric ozone lies above the tropics, from where ozone is transported by the stratospheric mean diabatic circulation towards poles [Tung and Yang, 1988b]. This shows the importance of seasonal cycle’s role in affecting the TOC variability. The pole-ward and downward transport of ozone-rich air during winter progressively increases the TOC in the middle and high latitude regions. The downward transport of Ozone rich air mass from stratosphere to troposphere transports only a small amount of Ozone. These aspects are also reflected during southern winter (Southern Hemisphere), where the stratospheric circulation is approximately mirrored at the equatorial line, and fresh tropical ozone is transported into the Southern Hemisphere. In this region the maximal value occur during late spring at mid-latitudes, and during summer season the ozone abundance decreases; whereas during winter the polar ozone is substantially reduced over Polar Regions. Stratospheric transport processes thus determines, to a large extent, the annual cycle and the hemispheric budget of TOC [Dutsch, 1974].

1.3.2 Inter-Annual Variations

Inter-Annual Variability (IAV) observed in the TOC over a location is mainly contributed by additional different multi-annual cycles having diverse
origin. In tropical regions, the role of Quasi-Biennial Oscillation (QBO) of 26-28 month time-period on TOC is significant. These oscillations are a result of the reversal in the direction of stratospheric zonal winds [Baldwin et al., 2001]. These natural oscillations of the tropical atmosphere also influences total ozone in the mid-latitude regions, which leads to a differential transport of stratospheric ozone from the tropical source region to the mid-latitudes as a function of QBO’s strength. The El Nino-Southern Oscillation (ENSO) is an additional factor impacting the inter-annual variability present in the total ozone column [Bojkov, 1987], though this aspect is still to be resolved at scientific level. In northern-middle and high-latitudes, a good part of the observed multi-annual variability in TOC can be related to the changes in the dynamical structure of the atmosphere associated with the North Atlantic Oscillation (NAO) [Appenzeller et al., 2000]; also known as Arctic Oscillation (AO) [Thompson et al., 2000]. In addition to influences of above stated cycles, the variations in the TOC is also influenced by the natural 11-year Solar Cycle (SC); Solar Cycle has a significant influence on the TOC over sub-tropical and mid-latitude regions [Willett, 1962; Dutsch, 1979; Dutsch et al., 1991; Shindell et al., 1999].

1.4 Important features of Ozone absorption spectra

Absorption spectra of ozone manifest a strong absorption band between 200 to 300 nm spectral span (Hartley Bands). It is this absorption that is responsible for the filtering of Solar UV-C radiation (\(\lambda < 290\) nm). Another absorption band (Huggins Bands) lies in the wavelength range of 300 to 360 nm. Third absorption band (Chappuis Bands) falls in the wavelength range spanning 440 to 850 nm. The absorption by Ozone in the Huggins Band is responsible for the attenuation of biologically active Solar UV-B (\(\lambda = 290\) to 320 nm). Along with the Hartley bands and the Huggins band, the absorption of solar radiation in Chappuis band is responsible for the formation of odd oxygen species \(^{3}\text{P}_\text{O}\) atom. Further, the absorption in this band assigns green house gas (GHG) attributes to the Ozone molecule [Molina and Molina, 1986].
1.5 Measurement of Total Ozone Column abundance

There are different techniques used to measure the abundance of ozone in the atmosphere; some are specifically used to measure the online concentrations of Ozone in the ambient air and others specifically do the measurement of Ozone column abundance. The underlying principles for the measurement exploit Ozone-specific physical or chemical traits. The instruments that measure ozone can be placed on the ground or attached to a weather monitoring balloon, aircraft or be a part of the satellite based monitoring system. The measurements of atmospheric ozone abundance are done by the instruments that draw the air directly into an instrument. For instance Ozonesonde, a commonly used technique, where Ozone passes through a sensor cell containing iodide solution and its reaction with Ozone liberates free iodine. The iodine on contact with platinum electrode, having active carbon anode, allows the measurement of the current produced by 2 electrons released per molecule of Ozone. The conducted current is proportional to the number of Ozone molecules present in a given volume of air. The instruments exploiting the electrochemical principal are known as “Ozonesondes,” which are lightweight, ozone-measuring modules suitable for launching on small balloons. The balloons ascend far enough in the atmosphere to measure ozone in the stratospheric ozone layer and communicate the information to the ground stations as a function of height between 0–35 km altitude. On the other hand the localized ozone-measuring instruments using optical or chemical detection schemes are also used routinely by placing them on research aircrafts to measure the distribution of ozone in the troposphere and lower stratosphere. High-altitude research aircraft can reach the ozone layer at most locations over the globe and can reach farthest into the layer at high latitudes in the Polar Regions. The approaches stated have limitations as they provide the estimate of Ozone column distribution within a limited slice of altitudes.
On the other hand, the indirect-remote sensing methods measure Ozone column abundance rely on the absorption of UV radiation by ozone in a vertical column. The UV source is either Solar irradiance or the wavelength-specific-laser beam. For example, satellite based detectors can use the absorption of UV-sunlight profile by the atmospheric column or they can detect the absorption profile of sunlight scattered, arising from the column of atmosphere extending from the surface of Earth. The analysis of the detected absorption profile is used to measure the ozone abundance at any location of the Earth on daily basis. A network of ground-based detectors measure column ozone by analyzing the amount of the Sun’s UV light that reaches Earth’s surface.

1.5.1 Measurement of Total Ozone Column abundance from the ground

Total Column Ozone measurements at ground stations have been done by using mainly three different kinds of instruments; all exploit the optical property of the Ozone. These instruments are: (a) Dobson Spectrophotometer developed by G. M. B. Dobson in 1920; (b) Filter Ozonemeters; and (c) The Brewer instrument developed in the 1980s.

Dobson Spectrophotometer measures the ratio of differences in the intensities at two pairs of wavelengths in the Huggins band (300 to 360 nm). One member of each pair of wavelength is selected where ozone strongly absorbs UV; and the other where weak UV absorption occurs. By using the ratio of intensities at these two wavelengths, the effects of changing ozone amounts can be separated from other factors affecting the amount of UV reaching the ground. The use of two wavelength pairs removes much of the wavelength-dependent effects (mainly arising from the aerosols), which are assumed to be zero when one pair of wavelengths is used [Dobson, 1957; World Meteorological Organization, 1999]. The precision of well maintained Dobson spectrophotometers is expected to be of the order of ±2%.

The filter Ozonemeters have been used since 1960s in Russia and other former Soviet bloc countries. These instruments use an optical filter for
selective wavelength recordings. The bandwidth of these Filter Ozonometers is wider than that of used in the Dobson instrument [Gustin, 1963].

The Brewer instrument is based on the principal of Sun photometry and approximately use the same UV range as used by the Dobson spectrophotometer [Kerr et al., 1985]. The instrument makes use of more modern detection devices by using a holographic grating as a dispersive element instead of a prism, and its operation is fully automated. The main difference in the design from the Dobson spectrometer is that the absolute measurements are done at four wavelengths instead of analyzing the differences only at two wavelength pairs.

In 1957, as a part of the International Geophysical Year, a global network of ground-based, total-ozone observation stations were established. At present, World Meteorological Organization (WMO) controls a global network of about 100 ground stations distributed throughout the world extending from South Pole, Antarctica (90°S), to Ellesmere Island, Canada (83°N). Routine measurements of total ozone column are done by using Dobson instruments. The accuracy of these observations is maintained by regular calibrations and inter-comparisons.

1.5.2 Measurement of Total Ozone Column abundance from the space

Total Column Ozone monitoring from space has been performed by mainly four different sensors placed aboard on various Sun-Synchronized polar satellites since October 1978.

The Total Ozone Mapping Spectrometer (TOMS) measures solar irradiance and the radiance backscattered by the Earth's atmosphere at six wavelengths extending from 310 to 380 nm [Heath et al., 1975]. The Ozone absorption in the Huggins band is used to calculate the total ozone column abundance. The average instrumental calibration long-term drift of TOMS Nimbus 7 data is less than 1% per decade. TOMS data are rather insensitive to the changes in the tropospheric ozone. The TOMS instrument on Nimbus 7 uses 312.3, 317.3, 331.1, 339.7, 360.0, and 380.0 nm wavelengths for the
measurements. This instrument had a long lifetime (October 1978 to May 1993), which makes this data series very useful for the long-term trend analysis. Meteor 3 TOMS had a design nearly identical to the Nimbus 7 TOMS instrument using the same wavelengths, but the satellite had a different orbit than Nimbus 7. The instrument was in operation from August 1991 to December 1994. In July 1996, Earth Probe (EP) TOMS was launched. The six wavelengths for this TOMS instrument are 308.5, 312.3, 317.3, 331.1, 339.7, and 360.0 nm.

The Solar backscatter ultraviolet radiometers (SBUV) have been flown on a number of NASA and NOAA satellites over the last 20 years. SBUV instruments measure column ozone in a manner similar to TOMS.

The TIROS-N Operational Vertical Sounders (TOVS) on NOAA polar-orbiting satellites measure ozone by using infrared wavelength (9.7 μm), where ozone absorbs: high-resolution infrared sounder (HIRS). These instruments are sensitive to lower stratospheric ozone and provide near-global coverage even during polar night. The accuracy of the instrument is questionable because it’s poor sensitivity in mid-stratospheric region. That is why, though TOVS data are available from February 1979 to the present, but these data-sets are not used for long-term trend determination.

Lately, the Global Ozone Monitoring Experiment (GOME), used an instrument placed on the second European Remote Sensing Satellite (ERS-2), which was launched in April 1995. Ozone column measurements, in this case, are done by using the principle of differential ozone absorption spectroscopy (DOAS), near-global maps of total ozone can be made from the measurements taken over 3 days.

1.5.3 Comparison of the measurements of Total Ozone Column abundance from the ground and from the space

Measurements done by ground based instruments (mainly by Dobson Spectrophotometer) and by space based instruments board on satellites (mainly TOMS) are reliable individually and compliment to each other, and it
is possible to draw a comprehensive picture of long-term global or local trends present in total column ozone. Both of these instruments have some limitations; e.g. the accuracy of the Dobson instrument is affected by the Total Column Ozone variations occurring within a day over a location. The monitoring by TOMS is limited severely by the presence of clouds. Extensive comparisons of the data acquired by these two instruments have been made, so that the best use can be derived from their complementary capabilities. The comparison of the version 7 TOMS data with the primary Dobson instrument operated at Mauna Loa show a good long-term stability between the two instruments in the period 1979-1993 [Bojkov et al., 1988; McPeters and Komhyr, 1991; World Meteorological Organization, 1995]. The comparison of the global network of Dobson spectrophotometers and Nimbus 7 TOMS overpass data revealed a systematic long-term drift of less than 1% per decade over its entire lifetime, which is believed to be the long-term stability associated with this instrument. The measurements of the Earth Probe TOMS instrument are approximately 1% higher than the average of 30 northern mid-latitude ground-based stations [World Meteorological Organization, 1999]. A very good agreement ($R^2 \approx 0.98$) between ground based Dobson data and space based TOMS data for Delhi, India was reported by Sahoo et al., 2005. Precise total ozone observations from the ground are valuable for reliable long-term trend determination at a single site as well as for ascertaining the estimate of possible long-term instrumental drifts of satellite instruments.

1.6 Depletion in Total Ozone Column abundance

Systematic measurements have revealed that the total ozone in a column over a location in many regions of the globe have decreased markedly since about 1980 [Reinsel et al., 1994]. This decrease varies in magnitude as factors affecting Ozone depletion, too, are inflicted with variations. For instance the natural cycles, having variable time-periods, can have cycles spanning months to years and their influence is moderated in location-specific manner. The decrease in ozone column, observed in recent decades is real but
this trend at global level can not be explained merely on the basis of the variations associated with natural factors alone. Even the longest available high-quality ground based Dobson total column ozone record at Arosa (Switzerland), which dates back to the 1920 also manifest the larger-scale changes as interpreted from TOMS based satellites records [Staehelin et al., 1998].

1.6.1 Chemistry of anthropogenic Ozone depletion

The first explanation for the stratospheric ozone depletion was based on the chain reactions of Nitrogen Oxides emitted by supersonic transport planes (SST) [Crutzen, 1970]. Subsequently, the role of Chlorine and Chlorine Oxides were linked with the stratospheric ozone depletion in catalytic manner, in chain reactions similar to the one observed in case of Nitrogen Oxides [Stolarski and Cicerone, 1974]. Startling revelation by Molina and Rowland [1974] investigations unfolded the mechanism, where chlorofluorocarbons (CFCs) known as chemically inert and highly volatile species (used chiefly as aerosol propellants and as refrigerants) were involved. The catalytic chain reaction with Ozone in this case involved photochemical dissociation of Cl from so far considered inert CFC molecule. Further investigations showed that the chlorine radicals in the stratosphere were responsible for significant stratospheric ozone depletion. The findings from these investigations opened the field of atmospheric chemistry centered around the causes of Ozone column depletion, where the role of CFCs was investigated in significant details along with the factors causing their transport into the stratosphere [World Meteorological Organization, 1995; 1999; 2007].

Many human centric activities emit synthetic volatile compounds containing the halogens chlorine and bromine for variety of usage. The class of these compounds is commonly known as Chlorofluorocarbons (CFCs), and they are inert in tropospheric radiation regime, and the presence of halogens is a part of their structure. Once in troposphere these compounds are
On entering stratosphere, halogen part of these molecules (CFCs) on interaction with high energy ultraviolet radiation available in stratosphere releases halogen part. The released halogen atoms react chemically to destroy ozone in catalytic cycle in the stratosphere. The average depletion of total ozone attributed to these reactive halogens is small in the stratospheric regions above tropics and maximal at high latitudes. In Polar Regions, the presence of polar stratospheric clouds (PSCs) that greatly increases the abundance of the most reactive halogen gases result in the destruction of Ozone in an accelerated manner. The process results in a substantial ozone destruction in Polar Regions during winter and spring. Eventually, after a few years, air in the stratosphere returns to the troposphere, bringing along with it the reactive halogen molecules where they are removed from the atmosphere by rain and other form of precipitation and deposition on the Earth’s surface [Solomon, 1999].

Fig. 1.1: Pools of anthropogenically emitted halogen source gases in the troposphere and photo-chemically converted reactive halogen species in the stratosphere.

The general reaction scheme relevant to the Ozone depletion due to CFC class of compounds follows the schematic sketched above that provides
the overview of the class of compounds sharing the common catalytic pathway to remove ozone from the stratosphere. First step in the reaction involves the photo-dissociation of halogen atom from the parent CFC by solar UV radiation.

\[ \text{CFCl}_3 + \text{hv (} \lambda < 230 \text{ nm)} \rightarrow \text{Cl} + \text{CFCl}_2 \quad (1.10) \]

It is evident that the release of halogen radicals from CFCs requires high-energy solar UV radiation (\( \lambda < 230 \text{ nm} \)) that is only available in the upper stratosphere. Once halogen radical forms the catalytic destruction of ozone follows.

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (1.11) \]
\[ \text{O}_3 + \text{hv (} \lambda < 320 \text{ nm)} \rightarrow \text{O}_2 + \text{O} \quad (1.3) \]
\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + 2\text{O}_2 \quad (1.12) \]

\[ \sum \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \]

Reactions (1.11) and (1.12) can be repeated many thousand times given the sufficient availability of Solar UV-B radiation and Oxygen atoms. It is estimated that a single halogen radical can destroy millions of Ozone molecules before it is deactivated by their conversion into an inactive reservoir compounds.

\[ 2\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3\text{Cl} \quad (1.13) \]

The reservoir compounds can be reactivated by further stratospheric reactions if they do not exit the stratosphere. The slow transport of the reservoir species to the tropopause and their washout by rain is the only path to their removal.
The steps in reactions (1.11) and (1.12) are common to Bromine, as well as for Nitrogen Oxides. The reactions of the species belonging to different radical families strongly influence the reaction rates of the gas phase radical chemistry. The pure gas phase ozone depletion only occurs significantly in the upper stratosphere. Additional heterogeneous reactions on particles are important in the lower stratosphere, as they provide a means for the conversion of the reservoir species into an active (radical) form; once the available chlorine is converted into its active forms, the ozone depletion occurs rapidly in the presence of sunlight [World Meteorological Organization, 2007].

1.7 Long-term variation in the Total Ozone Column, globally

Pioneering work done by Komhyr [1971] paved the way for the studies aimed to analyze the long-term variations in the total column ozone content, globally. Their investigations showed that there was an increase in the total ozone column content at many stations throughout during the period spanning between 1960-70.

Initial attempts in this regard were further extended by Angell and Korshover [1973] and they used monthly mean data obtained from the “ozone data for the world”, and they also reported an increase in total ozone of 3.9% per decade in Northern Hemisphere, and a decrease of 1.2% per decade in the Southern Hemisphere. A world-wide average increase of 1.5% per decade was estimated during 1951-1970.

Time-series analysis done by London and Kelley [1974] on the mean monthly global distributions of total ozone for the 13-year period from 1957 through 1970 revealed an upward trend of about 7.5 percent per decade in the Northern Hemisphere and about 2.5 percent per decade in the Southern Hemisphere.

The study done by Reinsel et al. [1987] reported long-term trends in the monthly averaged total ozone data through 1984 for 36 ground based Dobson stations, which included Srinagar, New Delhi, Varanasi, Mount Abu and
The approach used was a non-linear regression model that took into account the seasonal affects, linear trend, contribution of solar cycle, and the presence of random noise in the monthly averaged total ozone time-series data. Their estimate of overall global trend in total ozone column during the period 1970-1984, with associated 95% confidence limits, was \(-0.26 \pm 0.92\) percent per decade. For the stations located in India their analysis reported annual trends (percent per year) with estimated standard errors as: Srinagar 0.052 \pm 0.075; New Delhi -0.092 \pm 0.112; Varanasi 0.245 \pm 0.079; Mount Abu 0.318 \pm 0.211; Kodaikanal 0.047 \pm 0.197.

A Study was done by Bojkov et al. [1990] to estimate a seasonal trend analysis on monthly means of Dobson total ozone column data from 29 stations located between 19°N and 64°N latitudes. Their study did not include Dobson total ozone data from any Indian station. They also used a non-linear model much similar to the model used by Reinsel et al. [1987]. Their model included an additional component that took into consideration the affect of QBO in the monthly averaged total ozone time-series. The analysis showed significantly more negative trends during the winter months (December - March) than during the summer months (May - August); the trends in winter were more negative with increasing latitude. The winter trends were of the order of -1.2%, -2.1%, and -3.0% per decade for latitudes 35°N, 45°N, 55°N, respectively. The estimated trends during the summer months were of the order of -0.6% per decade with no distinct pattern as a function of latitude. The year-round trend or annual trend over all latitudes was estimated to be about \(-0.84 \pm 0.82\)% per decade.

Reinsel et al. [1994] extended their earlier analysis to undertake more comprehensive seasonal trend analysis of monthly mean Dobson total ozone data through 1991 for network of 56 stations, which included six Indian stations viz. Srinagar, New Delhi, Varanasi, Ahmedabad, Poona and Kodaikanal. In this analysis, they used three different data sets covering a period viz. 1964-1991, 1971-1991, 1978-1991. In this study, they used the non-linear model as used by Bojkov et al. [1990]. For the longest data set of 1964-
1991, substantial negative trends in the total ozone column over the higher northern latitude regions during winter and spring were estimated. Negative trend in the higher southern latitudes (30°S-55°S), during all seasons and trend close to zero for all seasons at locations extending from 30°S-30°N latitude were estimated. The Dobson total ozone trends (percent per decade) for Indian stations estimated by them are tabulated:

Table 1.1: Long-term trends (percent per decade) in the monthly mean Total Ozone Column data in three different time segments, through 1991 for six Indian stations as estimated by Reinsel et al. [1994].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Srinagar</td>
<td>34.1°N</td>
<td>-1.05 ± 0.69</td>
<td>-0.70 ± 0.97</td>
<td>-4.93 ± 1.74</td>
</tr>
<tr>
<td>New Delhi</td>
<td>28.6°N</td>
<td>0.86 ± 0.55</td>
<td>0.16 ± 0.62</td>
<td>-1.17 ± 1.16</td>
</tr>
<tr>
<td>Varanasi</td>
<td>25.3°N</td>
<td>-1.95 ± 0.63</td>
<td>-3.21 ± 0.49</td>
<td>-2.92 ± 0.84</td>
</tr>
<tr>
<td>Ahmedabad</td>
<td>23.0°N</td>
<td>0.49 ± 0.54</td>
<td>-0.16 ± 0.76</td>
<td>0.95 ± 2.10</td>
</tr>
<tr>
<td>Poona</td>
<td>18.5°N</td>
<td>-0.25 ± 0.64</td>
<td>-1.04 ± 0.90</td>
<td></td>
</tr>
<tr>
<td>Kodaikanal</td>
<td>10.2°N</td>
<td>0.60 ± 0.63</td>
<td>0.17 ± 0.71</td>
<td>1.95 ± 0.96</td>
</tr>
</tbody>
</table>

As the global concern towards the depletion of global ozone column abundance increased, a more detailed investigation was undertaken by Bojkov and Fioletov [1995]. They analyzed total ozone data collected from over 150 Global Ozone Observing System stations to deduce the basic global ozone characteristics both for pre-ozone-hole and during "ozone hole" periods. They also analyzed Total Ozone Mapping Spectrometer (TOMS) data for 1979-1993 time-span to find out the monthly zonal variations. They reported less than 1% difference between the estimations of monthly zonal variations by using data collected from ground-based and TOMS data between the latitudes 40°S-60°N covering the time period of 1979-1993. They also estimated around 3% lowering in the global average of total ozone during 1984-1993 when compared with 1964-1980 time-period analysis. The cumulative year-round global ozone decline was estimated as 4.8±0.6%. Long-term total ozone seasonal trends with 95% confidence limits between 10°N-

Table 1.2: Season-wise and Year-round long-term trends (percent per decade ± 2σ) in the zonal monthly mean Total Ozone Column data over two different time-spans (1970-1994 and 1980-1994) for 10°N-35°N latitude zone as reported by Bojkov and Fioletov [1995].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec-Mar</td>
<td>-1.3 ± 0.8</td>
<td>-2.3 ± 1.4</td>
</tr>
<tr>
<td>May-Aug</td>
<td>-0.3 ± 0.7</td>
<td>-0.6 ± 1.3</td>
</tr>
<tr>
<td>Sept-Nov</td>
<td>-0.5 ± 0.7</td>
<td>-1.1 ± 1.1</td>
</tr>
<tr>
<td>Year-Round</td>
<td>-0.7 ± 0.7</td>
<td>-1.3 ± 1.1</td>
</tr>
</tbody>
</table>

Bojkov et al. [1995] estimated a continuous year-round total ozone decline in the middle latitude (35°-60°) of the order of -4.3%, and -4.1% per decade for the period January 1979 - March 1994 in the northern and southern hemispheres respectively. These trend estimates (decrease) for 1979-1994 were about 1.5% per decade; and this decrease was stronger in middle latitude regions when compared with the trends estimates from 1970-1994 data sets.

Harris et al. [2003] calculated total ozone growth rates using flexible tendency curves method for three different kinds of data-sets (ground based Dobson data-set and two homogenized satellite data sets, one constructed at NASA/Goddard Space Flight Center and the other developed at New Zealand’s National Institute of Water and Atmospheric Research) for eleven stations covering 46.8°N to 45°S latitude stations. This method improved on the traditional trend analysis using a simple regression linear fits. Their results showed declining trend at all stations ranging from -0.06% per decade for Samoa (14.5°S) to -3.12% per decade for Arosa (46.8°N).

1.8 Long-term variation in the Total Ozone Column over India

Kundu and Jain [1993], by using a statistical model having terms for different variabilities such as linear trend, six monthly, seasonal and biennial
oscillations, as well as, long term solar variability, obtained linear trend in monthly averaged total ozone column data obtained from Dobson spectrometer operated at three Indian stations (Srinagar, New Delhi and Kodaikanal) spanning the period 1965-91; except for Srinagar where data was available only up to 1988. They reported that the trend near the equator, though small, is positive, which become negative at higher latitudes.

Chakrabarty et al. [1998] analyzed the Dobson data of time series spanning 23-45 years for six different Indian stations viz; Kodaikanal, Pune, Mount Abu/Ahmedabad, Varanasi, New Delhi and Srinagar. By applying simple linear regression on monthly averaged data they derive the following trends on total column ozone at respective stations:

Table 1.3: Long-term trends (percent per decade) in the monthly averaged Total Ozone Column time-series for six Indian stations as estimated by Chakrabarty et al. [1998].

<table>
<thead>
<tr>
<th>Station</th>
<th>Duration</th>
<th>Trend (percent per decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kodaikanal</td>
<td>Jul 1957-Mar 1994</td>
<td>+1.98</td>
</tr>
<tr>
<td>Pune</td>
<td>Mar 1973-Dec 1996</td>
<td>0.00</td>
</tr>
<tr>
<td>Ahmedabad</td>
<td>Oct 1951-Dec 1996</td>
<td>+2.33</td>
</tr>
<tr>
<td>Varanasi</td>
<td>Dec 1963-Dec 1996</td>
<td>-1.02</td>
</tr>
<tr>
<td>New Delhi</td>
<td>Jul 1957-Dec 1996</td>
<td>+1.85</td>
</tr>
<tr>
<td>Srinagar</td>
<td>Jul 1957-Nov 1989</td>
<td>+0.68</td>
</tr>
</tbody>
</table>

They also analyzed the NASA Nimbus TOMS overpass total ozone data for all the six stations for the time span Nov 1978 to April 1994, where Varanasi station data was analyzed over a shorter time span (Nov 1978 to Dec 1987). They noticed a good agreement between Dobson and TOMS data of the corresponding durations, at all stations except at Kodaikanal and Ahmedabad. They obtained a declining trend for TOMS total column ozone data at all the stations studied except at Kodaikanal where trend was zero.

Sahoo et al. [2005], applied linear regression technique to the Nimbus and Earth Probe Total Ozone Mapping Spectrometer (EP-TOMS) data to study the total Ozone trends during 1997-2003. The rate of decline of ozone
was found to be higher in these years over the northern parts of India. The monthly averaged total ozone contents were corrected for missing values by a 3×3 pixels spatial moving average filter. The time series at each grid location was de-seasonalized by calculating the deviations from the climatological mean annual cycle; i.e. Monthly Total Ozone Anomalies. A regression time series model was fitted to the de-seasonalized monthly mean values after subjecting the data to a five month smoothing filter. Their results showed that the observed trends were lower than the trends predicted earlier on the time-series data spanning 1979-1993 for the stations located in the northern part of India. No total ozone data was available for the duration 1994-1996. They extrapolated estimated trends for the Total Ozone anomaly content from time-series 1979-1993 and got predicted trend for time-span 1997-2003. The recent trends observed by them for the period 1997-2003 were compared with the predicted trends for the same period.

Table 1.4: Long-term trends (DU/decade) in the monthly Total Ozone (anomalies) time-series bifurcated in two (1979-1993 and 1997-2003) for Indian stations as reported by Sahoo et al. [2005].

<table>
<thead>
<tr>
<th>Station</th>
<th>Predicted (1979-1993) trend per decade (DU)</th>
<th>Observed (1997-2003) trend per decade (DU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trivandrum</td>
<td>-10.6</td>
<td>-12.4</td>
</tr>
<tr>
<td>Bangalore</td>
<td>9.5</td>
<td>9.1</td>
</tr>
<tr>
<td>Madras</td>
<td>-8.1</td>
<td>-9.5</td>
</tr>
<tr>
<td>Nagpur</td>
<td>-6.0</td>
<td>-8.3</td>
</tr>
<tr>
<td>Kolkata</td>
<td>-10.8</td>
<td>-32.3</td>
</tr>
<tr>
<td>Mount Abu</td>
<td>-8.2</td>
<td>-8.1</td>
</tr>
<tr>
<td>Varanasi</td>
<td>-11.3</td>
<td>-33.8</td>
</tr>
<tr>
<td>Delhi</td>
<td>-15.0</td>
<td>-36.8</td>
</tr>
</tbody>
</table>

Ganguly and Iyer [2006] found declining trends in monthly averaged Stratospheric Ozone Column (SOC) data applying a simple linear regression on the monthly mean of columnar stratospheric ozone data of 27 year spanning from 1979 to 2005 for different Indian stations. They observed variations (mostly positive) in Tropospheric Ozone Column (TCO).
Table 1.5: Long-term trend (%) in monthly averaged zonal Stratospheric Ozone Column and Tropospheric Ozone Column time-series from 1979 to 2005 for 10°N-35°N latitude zone as reported by Ganguly and Iyer [2006].

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Depletion in SCO (%)</th>
<th>Variation in TCO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 to 15°N</td>
<td>0.23</td>
<td>- 0.04</td>
</tr>
<tr>
<td>15 to 20°N</td>
<td>0.31</td>
<td>+ 0.44</td>
</tr>
<tr>
<td>20 to 25°N</td>
<td>0.46</td>
<td>+ 0.39</td>
</tr>
<tr>
<td>25 to 30°N</td>
<td>0.55</td>
<td>+ 0.37</td>
</tr>
<tr>
<td>30 to 35°N</td>
<td>0.68</td>
<td>+ 0.49</td>
</tr>
</tbody>
</table>

1.9 Recovery of the Ozone layer

With the support of scientific observations on Ozone column abundance and the recognition that "ozone hole" was forming every spring over Antarctica [Farman et al., 1985; Jones and Shanklin, 1995], the demand for an international regulation to curb the emission of ozone depleting gases gained momentum. Consequently, in 1985, a treaty called the "Vienna Convention for the Protection of the Ozone Layer" was signed by 20 nations in Vienna. The signatory nations agreed to take appropriate measures to protect the depletion of stratospheric ozone layer from human induced activities. The Vienna Convention supported research, exchange of information, and the development of the future protocols to reverse the depletion trend. In response to the growing concern, the "Montreal Protocol on the substances causing the depletion of the Ozone Layer" was signed in 1987, and the ratification of this protocol came into force in 1989. The Protocol established legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion; primarily used as refrigerant, perfumes, part of aerosol sprays and many other activities [Weatherhead and Andersen, 2006].
Subsequent to this treaty, calculations predicted that ongoing decrease in the total ozone content should lessen, then eventually turn around and recover. Of course, the anticipated recovery in the stratospheric Ozone contents is likely to occur in stages and will depend on many other factors playing a role in the pace of its recovery. Question arises as how to detect if the recovery has started in the depleted stratospheric Ozone layer? The likely signs of this can be estimated by measuring: (1) The decline in the rate of Ozone column abundance decrease; and (2) the positive trends (increase) in the Ozone column abundance. The negation of the impact of ozone depletion substances finally will reflect only the variations in the total ozone contents explained on the basis of natural dynamical factors affecting its variation.

Recent study done by Reinsel et al. [2002] shows that for mid-latitudes (30°-60°) regions a positive change in the trend in Ozone column abundance can be detected within around 7-8 years from the reversal date that is somewhere in 1996-1997. They also derived that a positive trend recovery can require roughly 15-20 years for southern mid-latitude zonal average, and 20-25 years for northern mid-latitude zonal average to reflect it in the recorded data of Ozone column abundance.

Another investigation to look into the impact of the ban on Ozone depleting substances done by Andersen et al. [2006] in their comprehensive study compared the estimated trends in the total column ozone using 10 two-dimensional and 4 three-dimensional models on SBUV-2 satellite observations covering the time period 1979-2003. The estimated trends for the past (1979-2000) was compared with the recent 7 years (1996-2003), and the future (2000-2050) trends. They reported that if the hockey stick method, with a turnaround point in 1996, is employed in the models, a positive trends can be derived for both the Northern and Southern Hemispheres.

These conclusions were countered by Weatherhead and Anderson [2006], they cautioned that although recent data suggest that total column ozone abundances have not decreased over past eight years for most of the world, but it is still uncertain whether this improvement is due to decline in
the amount of ozone-depleting substances in the Earth’s atmosphere or on account of the solar cycle and other natural dynamical fluctuation’s affect on Ozone layer.

1.10 Objectives and importance of the present study

It is evident from the previous studies that there are trends of total ozone depletion in the tropical zones but, ironically it is also this region over the tropical zone that has the least total ozone layer thickness even though there is high incoming solar irradiance. Consequently, even a small decrease is likely to have far reaching implications on life forms in general. The tropical region is responsible for more than fifty percent of global ozone production, most of which is transported to mid-latitudes. Putting together, and taking into consideration that tropical regions sustain more than ninety percent of global bio-diversity, the assessment of total Ozone column abundance over tropical regions is an extremely important scientific query for investigation.

India, with topical-subtropical climate, is endowed with a large biological diversity and inhabits a human population of 1028.7 million [Census of India-2001], and is a signatory of the Montreal Protocol. The likely implication of even a small decrease in the Ozone layer will have far reaching impacts on agriculture, human life and life in general. Thus the global issue of Ozone layer depletion, perhaps, is more important for the tropical regions.

Globally, there has been a significant amount of work done to comprehend the long-term variations in the total ozone column at many locations. However, not many studies have been done in Indian context; some studies done are still tentative at best, as robust statistical analysis approach is limited. The groups which have looked at the Ozone column trends at Indian stations in robust manner for Indian subcontinent are few [Angell and Korshover, 1973; Reinsel et al., 1987 & 1994; Bojkov and Fioletov, 1995], and their analysis is not recent. The most recent work, where the investigations were focused on Ozone column variability on many Indian stations were reported by few groups [Chakrabarty et al., 1998; Sahoo et al.,
2005; Ganguly & Iyer, 2006]. However, their analysis employed simple regression approach to determine the trends on data sets where seasonal imprints were not accounted for. Moreover, their analysis was limited to trend estimates only. No information was provided on the seasonal and inter-annual variability's effects on the total ozone column. Close appraisal of all studies done, where data from stations located in India was part of the analysis; unequivocally shows that analysis done by Bojkov and Fioletov [1995] and Reinsel et al. [1987, 1994] were robust.

Keeping in view the far reaching importance of total column abundance over tropical region, and the available current status of scientific knowledge from the past investigations, a detailed statistical analysis of the trend and variability in total Ozone column at 15 locations in India have been undertaken. To cover the tropical region with respect to latitude spread (1.3° N to 34.5° N) we also included the data from Singapore station. The analysis done in the present investigation entails following objectives:

1. Use of TOMS Overpass monthly mean Total Ozone Column time-series data sets 1979-1993 and 1997-2005 for total 16 locations;
2. De-seasonalization of each time-series data-set;
3. Determination of seasonal variation in the ozone column at each station;
4. Estimation of long term trend at each station with appropriate statistics of regression fits;
5. Detection of Inter Annual Variation (IAV) in de-sesonialized and de-trended time-series of Total Ozone Column at respective stations.

In Chapter-2, a brief account on the TOMS Overpass monthly mean Total Ozone Column data-set along with an over-view of various methodologies used to analyze the time-series data of climatic variables and
the details of the approach used in the present work for time-series analysis of monthly mean Total Ozone Column data-sets are presented.

In Chapter-3, the estimated long-term linear trends in the de-seasonalized monthly mean Total Ozone Column time-series are compared between past (1979-1993) and recent (1997-2005) time-series for all stations with the objective to detect any sign of recovery in Total Ozone Column abundance in recent times.

In Chapter-4, the seasonal (annual) and inter-annual variations present in the monthly mean Total Ozone Column time-series at different stations are discussed as a function of latitudinal variability (1.3° N to 34.5° N). The estimated inter-annual variation in time-series for each station was subjected to Discrete Fourier Transform to deconvolute the presence of known natural or dynamical multi-annual cycles like QBO.

In Chapter-5, the estimated long-term trends, seasonal (annual) as well as inter-annual variations present in the monthly mean Total Ozone Column time-series are discussed in the view of the existing scientific knowledge about Total Ozone Column dynamics.

The conclusions of the present work are presented in Chapter-6.