Ganguly, Nandita D., 2006, “Study of atmospheric ozone concentration and its longterm variability (Climatology).”, thesis PhD, Saurashtra University

http://etheses.saurashtrauniversity.edu/id/864

Copyright and moral rights for this thesis are retained by the author

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge.

This thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the Author.

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the Author

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given.
STUDY OF ATMOSPHERIC OZONE CONCENTRATION
AND ITS LONGTERM VARIABILITY (CLIMATOLOGY).

Thesis Submitted to

Saurashtra University, Rajkot

for the Degree of Doctor of Philosophy in Physics

by

Nandita D. Ganguly

Guide: Prof K. N. Iyer

Department of Physics

Saurashtra University

Rajkot - 360005.

May, 2006.
**Statements under O. Ph.D. 7 of Saurashtra University**

The contents of this thesis are my own work carried out under the supervision of *Prof. K. N. Iyer* and leads to some contributions in Physics supported by necessary references.

(Nandita D. Ganguly)

This is to certify that the present work submitted for the award of the Ph. D. degree of Saurashtra University, Rajkot by *Ms. Nandita D. Ganguly* has been the result of about two and a half years of research work under my supervision and is a valuable contribution in the field of “Atmospheric Science”.

(Prof. K. N. Iyer)

Head, Department of Physics
Saurashtra University
Rajkot – 360005.
Gujarat.
India.
Dedicated to the divine mother Durga.
CONTENTS

Acknowledgments. ................................................................. 9

Publications in Journals, newspapers and presentations in
conferences. ................................................................. 11

List of abbreviations. ............................................................... 13

[1] Introduction. ................................................................. 15

1.1. Earth’s atmosphere.

1.2. Effect of ozone on global environment.

1.3 Absorption characteristics of ozone.

1.4 Processes controlling ozone distribution.

1.4.1 Stratospheric ozone production.

1.4.2 Stratospheric ozone destruction.

1.5 Possible causes for perturbation in the chemistry of stratospheric ozone.

1.5.1 Role of catalysts (NO\textsubscript{x}, CFC’S, CH\textsubscript{3}Br, HO\textsubscript{x}).

1.5.2 Aircraft emissions.

1.5.3 Lightning.

1.5.4 Volcanic eruption.

1.5.5 Nuclear testing.

1.5.6 Automobile exhaust.

1.5.7 El Nino southern oscillation (ENSO).

1.5.8 Quasi-Biennial Oscillation (QBO).
1.5.9 Solar storms.

1.5.10 Solar UV variations.

1.5.11 Temperature driven fluctuations.

1.6 Temporal Variations of ozone.

1.7 Review of literature on ozone studies.

1.8 Scope of the Thesis.

[2] Methodology for ozone measurement. ................................. 40

2.1 Chemical techniques.

2.2 Satellite based remote sensing techniques.
   2.2.1 SBUV (Solar Back Scattered Ultra Violet Technique).
   2.2.2 TOMS (Total Ozone Mapping Spectrometer).
   2.2.3 OMI (Ozone Monitoring Instrument).
   2.2.4 UARS (Upper Atmosphere Research Satellite).
   2.2.5 MLS (Microwave Limb Sounder).

2.3 Ground based remote sensing techniques.
   2.3.1 Dobson spectrometer.
   2.3.2 Microprocessor Controlled Total Ozone Portable Spectrometer (MICROTOPS II).

2.4 Calibration scheme with other techniques.

2.5 Model estimations.
   2.5.1 Tropospheric ozone residual method (TOR).
   2.5.2 Convective cloud differential method (CCD).
3.1 Introduction.

3.2 Monitoring site, meteorological conditions and measurements at Rajkot.
   3.2.1) Temperature.
   3.2.2) Humidity.
   3.2.3) Wind speed and direction.

3.3 Study of short term variation in ozone concentration at Rajkot using MICROTOPS II Sun photometer.
   3.3.1 Diurnal variation of ozone in 2004 / 2005.
   3.3.2 Monthly variation of ozone in 2004 / 2005.

3.4 Study of long term variation in ozone concentration at Rajkot using TOMS data.
   3.4.1) Seasonal variation of ozone from 1996 – 2004.

3.5 Effect of solar cycle variation on the total ozone concentration at Rajkot from 1980 – 2003.

3.6 Latitudinal variation of ozone in India.

3.7 Trend analysis of ozone in different atmospheric layers at Rajkot from 1982 – 2003 using SBUV technique.


4.1 Introduction.

4.2 Data and analysis.

4.3 Results and discussions.
4.3.1 Trend of columnar stratospheric and tropospheric ozone in India from 1980 – 2005 using CCD ozone data.

4.3.2 Trend of erythemal UV irradiance in India from 1979 – 2003.

4.3.3 Statistical estimation of upper and lower tolerance limits for tropospheric and stratospheric ozone in India.


5.1 Introduction

5.2 Effect of ENSO on the total ozone concentration.

5.3 Effect of ENSO on tropospheric ozone concentration.

5.4 Effect of ENSO on stratospheric ozone concentration.

5.5 Effect of ENSO on seasonal variation of total ozone.

5.6 Impact of solar storms on ozone concentration.

5.7 Impact of different solar storms on the ozone concentration of Srinagar.

5.8 Impact of 20th January 2005 solar proton event on the ozone concentration of Indian cities.


Bibliography. 135
I express with deep gratitude, my indebtedness to Prof. K. N. lyer for his invaluable guidance during the entire period of my work. His patience, encouraging attitude, powerful insight and willingness to discuss various topics in a simple and effective manner has made this short period of association with him very pleasant and memorable for me. I consider it fortunate to have worked under him.

I am deeply grateful to Prof. Shyam Lal, Physical Research Laboratory, Ahmedabad, for his encouragement, support, valuable suggestions and interest in the progress of my work. He has been a constant source of inspiration to me.

I am extremely grateful to Dr. Suraiya Ahmad, NASA Goddard Space flight Center for valuable suggestions and discussions, Dr. S. K. Peshin, IMD Delhi, for providing the Dobson spectrometer data, Dr. J. Fishman, A.E. Wozniak and J.K. Creilson, NASA, for providing TOR data, J. R. Ziemke, S. Chandra and P. K. Bhartia, NASA, for providing CCD data and the ozone processing team of the Atmospheric Chemistry & Dynamics Branch and the Distributed Active Archive Center at NASA Goddard Space Flight Center, Greenbelt, MD, for the production and distribution of TOMS ozone data. These activities were sponsored by NASA's Earth Science enterprise. The images presented in the thesis were created by NASA and taken from NASA’s website. The temperature, wind speed
and dew point measured at Rajkot airport was taken from the website www.wunderground.com.

Completing a thesis is an extensive learning process at many different levels and one of the most important lessons, which I have learned during this work, is the value of support from my family and friends. I express my heartiest regards to my parents for their constant encouragement, magnanimous support and ceaseless worry about my well being.

I also express my sincere thanks to Rev. Father Francis Parmar, S.J. honorable principal of St. Xavier’s College, Ahmedabad, for his encouragement and cooperation, the management of Physical Research Laboratory, Ahmedabad for providing library facilities and my co workers associated with various supporting facilities which I have received in connection with this work from Saurashtra University, Rajkot.
PUBLICATIONS IN JOURNALS


PRESENTATIONS IN CONFERENCES

[1] Poster presentation on “Study of variation in columnar ozone concentration at Rajkot.” in the 41st annual convention of Indian Geophysical Union, held on the 29th of Dec. 2004, at Hyderabad.


[1] Depleting ozone layer: B’lore feeling the heat? - Deccan Herald ...

Depleting ozone layer: B’lore feeling the heat? From Kalyan Ray DH News Service Bhopal. Bangalore may be at risk from depleting ozone layer. ... But barely anybody has looked into the problem, Ms Nandita Ganguly, a researcher from ...


[2] South Asian Media Net

BHOPAL: Bangalore may be at risk from depleting ozone layer. ... But barely anybody has looked into the problem, Ms Nandita Ganguly, a researcher from ...

www.southasianmedia.net/cnn.cfm?id=257238


Bangalore may be at risk from depleting Ozone Layer. ...

schema-root.org/science/environment/ozone_layer/

[4] Environmental Health News:

Bangalore may be at risk from depleting ozone layer.

www.environmentalhealthnews.org/archives.

__________________________________________________________
### List of abbreviations.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADEOS</td>
<td>Advanced Earth Observing Satellite.</td>
</tr>
<tr>
<td>BOBMEX</td>
<td>Bay of Bengal Monsoon Experiment.</td>
</tr>
<tr>
<td>CCD</td>
<td>Convective cloud differential method.</td>
</tr>
<tr>
<td>CIE</td>
<td>Commission Internationale de l'Éclairage</td>
</tr>
<tr>
<td>CTM</td>
<td>Chemical Transport Model.</td>
</tr>
<tr>
<td>DISC</td>
<td>Data and Information Services Center</td>
</tr>
<tr>
<td>ECHM</td>
<td>European Center Hamburg Model.</td>
</tr>
<tr>
<td>ENSO</td>
<td>El Nino southern oscillation</td>
</tr>
<tr>
<td>EOS</td>
<td>Earth Observing System.</td>
</tr>
<tr>
<td>EP</td>
<td>Earth Probe.</td>
</tr>
<tr>
<td>ET</td>
<td>Extra Terrestrial.</td>
</tr>
<tr>
<td>GCM</td>
<td>General Circulation Model.</td>
</tr>
<tr>
<td>GES</td>
<td>Goddard Earth Sciences</td>
</tr>
<tr>
<td>Giovanni</td>
<td>GES-DISC Interactive Online Visualization and Analysis Infrastructure.</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System.</td>
</tr>
<tr>
<td>HALOE</td>
<td>Halogen Occultation Experiment.</td>
</tr>
<tr>
<td>HIRDLS</td>
<td>High Resolution Dynamics Limb Sounder</td>
</tr>
<tr>
<td>IMD</td>
<td>India Meteorological Department.</td>
</tr>
<tr>
<td>INDOEX</td>
<td>Indian Ocean Experiment.</td>
</tr>
<tr>
<td>MICROTOPS</td>
<td>Microprocessor Controlled Total Ozone Portable Spectrometer.</td>
</tr>
<tr>
<td>MLS</td>
<td>Microwave Limb Sounder</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration.</td>
</tr>
</tbody>
</table>
NASDA  National Space Development Agency of Japan.
NMHC  Non Methyl Hydrocarbon.
NOAA  National Oceanic and Atmospheric Administration.
ODP   Ozone Depletion Potential.
OMI   Ozone Monitoring Instrument
ppbv  Parts per billion by volume
ppmv  Parts per million by volume
pptv  Parts per trillion by volume
PRL  Physical Research Laboratory.
QBO  Quasi-Biennial Oscillation.
SAGE  Stratospheric Aerosol and Gas Experiment.
SBUV  Solar Back Scattered Ultra Violet Technique
SCO   Stratospheric Column Ozone.
TCO   Tropospheric Column Ozone.
TES   Tropospheric Emission Spectrometer
TOMS  Total Ozone Mapping Spectrometer.
TOR   Tropospheric ozone residual method.
UARS  Upper Atmosphere Research Satellite
UNEP  United Nations Environment Programme.
UT    Universal Time.
UV    Ultra violet.
WMO   World Meteorological Organization.
[1.1] **The Earth’s atmosphere.**

The evolution of atmosphere of different planets and the diverse variety in their structures is mainly due to their distance from the sun. Atmosphere is the medium for life on the surface of the planet and is the transition zone between Earth and Space. It comprises of a mixture of gases exposed to the electromagnetic spectrum of the sun. The atmosphere does not have a well defined upper boundary, but its density decreases progressively with altitude and ultimately merges with the space environment. Evidence indicates that the Earth has a secondary atmosphere (one produced by gradual release of gases from its interior), rather than a primordial atmosphere retained by a planet at the time of its original formation. Support for this idea stems from the depletion of inert gases such as He, Ne and Ar on earth, relative to their observed abundance in the solar system.

The atmosphere can be divided into different regions on the basis of temperature profile as shown in *Figure 1.1*. In the lowermost region from the ground to about 15 km (~17 km at the tropics), it is found that the temperature decreases with height at the rate of ~10 °K / km (Lapse rate). This region is called the **Troposphere**. The primary heat source for this region is the ground itself and the heat is convected upwards by turbulent motion. Therefore the temperature decreases with height due to adiabatic cooling. The height at which this
temperature reaches a minimum is called **Tropopause**, signifying the end of Troposphere. Rain, cloud, winds, cyclones etc. take place in this region.

The region above the Tropopause from 15 to 50 km is called the **Stratosphere**. Here the temperature increases with height at the rate of $3 \text{ } ^\circ \text{K} / \text{km}$. Heating of this region is caused by the absorption of ultraviolet radiation by ozone. This creates a global "inversion layer" which impedes vertical motion into and within the stratosphere. Since warmer air lies above colder air, convection is inhibited in this region. Though ozone concentration is maximum at about 25 km, most intense absorption of solar radiation at around 250 nm takes place at 50 km altitude. Thus solar radiation below 300 nm does not reach the earth’s surface as it is absorbed in the upper atmosphere. **Stratopause** signifies the end of Stratosphere.

![Figure 1.1 Division of Earth’s atmosphere on the basis of temperature profile and composition.](image-url)
The next higher region from 50 to 85 km is called **Mesosphere**, where the temperature decreases with height reaching a minimum at the **Mesopause**. The decrease in temperature is caused by the presence of CO$_2$ and H$_2$O (*Figure 1.2*), which provide a heat sink by radiating in the infrared radiation. (*Degaonkar S S, 1975; Manuel L. P et al., 2000*). Above the Mesopause, extreme ultraviolet radiation ($\lambda<175$ nm) is absorbed by O$_2$, thereby producing photo ionization. The energy of the absorbed photons is very high (>12eV) which leads to rapid increase in temperature with altitude. This region is called **Thermosphere**.

![Figure 1.2 Atmospheric H$_2$O profile from UARS/HALOE](image)

*Figure 1.2 Atmospheric H$_2$O profile from UARS/HALOE*

On the basis of chemical composition, the atmosphere can be divided into two regions. In the region below 85 km, the chemical composition of the atmosphere is substantially the same at all heights and the mean molecular mass remains constant. This region is called **Homosphere** (*Figure 1.1*). The chemical composition and mean molecular mass vary with altitude above 85 km. This region is called **Heterosphere**.
[1.2] **Effect of ozone on Global environment.**

The intermediate region, which extends from 10 to 100 km altitude, is generally called the **Middle Atmosphere**. One of the most important constituents in the middle atmosphere is ozone, because it is the only atmospheric species that effectively absorbs ultraviolet solar radiation from 200 to 300 nm, protecting plant and animal life from exposure to harmful radiation. Therefore the stability of the ozone layer (with peak concentration near 25 to 30 km) is of prime importance in the study of the middle atmosphere.

Ozone is a relatively unstable molecule made up of three atoms of oxygen. It condenses to form a liquid at \(-111.9\) °C (1 atmospheric pressure) and to form a solid at \(-192.7\) °C. Ozone is exceedingly rare in the atmosphere (approx. 3 molecules of ozone for every 10 million air molecules.) About 90% of ozone is found in the stratosphere and the remaining 10% in the troposphere. If the entire amount of ozone present in the atmosphere were to be concentrated in a layer of pure ozone and compressed at one atmospheric pressure, the layer would be less than half a cm thick.

The total columnar ozone concentration in the atmosphere is expressed in Dobson Units, (DU) which is the thickness in milli cm of the total amount of ozone occupying a column overhead if brought to the earth’s surface at S.T.P.
In absolute terms, 1 DU is about $2.7 \times 10^{16}$ molecules/cm$^2$. The unit is named after G. M. B. Dobson, who carried out pioneering studies of atmospheric ozone between ~1920 -1960. There are about $10^{12}$ molecules/cm$^3$ at 15 km, rising to nearly $10^{13}$ at 25 km, and then falling to $10^{11}$ at 45 km. In relative terms: ~0.5 parts per million by volume (ppmv) at 15 km, rising to ~ 9 ppmv at ~32 km, falling to ~3 ppmv at 48 km (Figure 1.3). Even in the peak of the layer, ozone is a trace gas. The total columnar ozone concentration is least (250 DU) at the tropics where it is produced and highest (400 – 460 DU) at the poles to where it is transported from the tropics, and where photochemical losses are minimum.

The amount of ozone in the atmosphere varies substantially from day to day and also varies with season and latitude. Stratospheric ozone plays a beneficial role by absorbing most of the biologically damaging ultraviolet (UV) radiation. Decrease in stratospheric ozone will result in an increase in UV-B radiation which...
will have negative impacts on human health such as suppressed immune system, serious sunburn, cataracts, epidermal lesions, reduced vitamin D synthesis and skin cancer. In plants, exposure to enhanced ultraviolet radiation can inhibit photosynthesis and influence agricultural productivity. It may cause deterioration of synthetic materials like plastics.

However, as ozone is toxic to the living system, elevated tropospheric ozone concentration may damage the tissues of plants and animals and also cause the temperature of the atmosphere to rise. Intense exposure to tropospheric ozone is associated with persistent decrease in lung function, pneumonia, influenza, asthma, decrease in crop yield etc. Thus there is a great need to monitor the atmospheric ozone concentration.

In 1973, Molina M J and Rowland F S first discovered that man-made substances called chlorofluorocarbons (CFC’s) could play a major role in the destruction of stratospheric ozone. (Molina et al., 1974). This possibility, of a long term global ozone depletion due to catalytic reactions in the stratosphere involving chemicals released by anthropogenic activities and its possible impact on the biosphere, put ozone on the center stage of atmospheric research over the past few decades. The discovery of the Antarctic ozone hole in the mid eighties (Farman et al., 1985) highlighted the gravity of the problem. These studies led to the United Nations Environment Programme (UNEP) initiative to protect the ozone layer, which was signed in Vienna in 1985, and a protocol outlining proposed protective actions followed. The Montreal Protocol, signed in September 1987, was a benchmark treaty calling for a 50% reduction in CFC
production by 2000, and an eventual complete phase-out of ozone-depleting chemicals. The United States ratified the Montreal Protocol in 1988. A total of 161 nations including India, have since become parties to the treaty. The 1992 Copenhagen Agreement accelerated the phase-out schedule by four years. Recent NOAA measurements (Elkins et al., 1993, Montzka et al., 1996) show that the rate of increase of halocarbon concentrations in the atmosphere has decreased markedly since 1987. It appears that the protocols are being observed. Under these conditions total stratospheric chlorine is predicted to peak at 3.8 ppbv in the year 1998, 0.2 ppbv above 1994 levels, and to slowly decline thereafter (WMO, 1994). Very little depletion in ozone has been observed in the tropics and little is expected there. It is expected that after the year 2000, the ozone layer will slowly recover over a period of 50 years or so. The Antarctic ozone hole is expected to last until about 2045. Scientists are investigating ways to replenish stratospheric ozone, either by removing CFC’s from the troposphere or by tying up the chlorine in inactive compounds (WMO, 1989).

[1.3] Absorption characteristics of ozone.

Long wavelength photons have little energy, and when they are absorbed, they may cause the absorbing molecule to rotate or vibrate, but they cannot cause chemical changes. To cause chemical changes, the photon must have enough energy to disrupt the molecule by breaking the chemical bond that holds the molecules together. This process, in which the absorption of a photon leads to disruption of the absorbing molecule, is called photo dissociation. The atoms produced by photo dissociation are chemically very active, and they start a chain
of reactions leading to the production of new species. Two new species produced in the Earth’s atmosphere by the photo dissociation of molecular oxygen (O₂) by a wavelength of 242.4 nm, and subsequent chemical reactions, are atomic oxygen (O) and ozone (O₃) respectively.

Ozone absorbs solar radiation in the ultraviolet and visible region of the spectrum; resulting in a change in the electronic energy of the molecule. The strongest absorption occurs in the ultraviolet, with much weaker absorption in the visible. Ozone can also absorb the thermal infrared radiation of the earth-atmosphere system.

The solar UV radiation is classified as UV-A (320 - 400 nm), UV-B (280-320nm) and UV-C (200-280 nm), based on the wavelength of radiation (Figure 1.4). While UV-C radiation is completely absorbed by atmospheric ozone and other gases, most of the UV-A radiation reaches the earth’s surface which is however not harmful to biological life on earth (Figure 1.5). The UV-B radiation, which is partially absorbed by ozone and reaches the earth’s surface, is harmful to plants and animals as mentioned before.

**Figure 1.4** The spectrum of solar radiation that is incident on the top of the Earth's atmosphere.
The absorption by ozone in the solar spectral region is due to electronic transitions. The strongest ozone bands are the **Hartley bands**, which cover the region from 200 nm to 310 nm and are centered at 255.3 nm (*Figure 1.6*). The absorption of solar flux in these ozone bands takes place primarily in the upper stratosphere and mesosphere. The weak bands between 310 nm to 400 nm are called **Huggins bands**. The absorption of solar flux in these ozone bands takes place in the stratosphere and troposphere. Ozone also shows weak absorption bands in the visible and near infrared regions from about 400 nm to 850 nm. These bands are referred to as **Chappuis bands**. Absorption by ozone in the troposphere induces photo dissociation even at the surface. The absorption coefficients of these bands are slightly dependent on temperature. At wavelengths less than 200 nm, the absorption by ozone is related to the
existence of large bands superimposed on a continuum. This spectral region plays a very minor role in the photochemistry of the Ozonosphere (15 to 50 km altitude range) because these wavelengths are absorbed by molecular oxygen at altitudes far above the ozone layer. However in the Herzberg continuum (200 nm to 242 nm) both ozone and molecular oxygen contribute to the absorption of radiation.

![Image](image.png)

**Figure 1.6** The absorption spectra of the main absorbers of solar radiation in the upper atmosphere. Radiation with wavelength less than 200 nm is absorbed in the ionosphere and mesosphere by nitrogen N₂, O atoms and O₂ molecule. Radiation between 200 and 320 nm reaches further down into the stratosphere (below 50 km), where it is absorbed by ozone O₃. Finally, radiation with wavelengths greater than 320 nm, reaches the Earth's surface.

[1.4] **Processes controlling ozone distribution.**

1.4.1) **Stratospheric ozone production.**

The only process known to produce a significant amount of ozone is the photolysis of molecular oxygen by ultraviolet radiation followed by recombination of atomic oxygen with molecular oxygen. The band dissociation energy of oxygen is 5.1 eV, which corresponds to a wavelength of 242.4 nm.

\[
O₂ + h\nu \rightarrow O + O \quad \rightarrow J_1 \quad \rightarrow (1.1)
\]

\[
O + O₂ + M \rightarrow O₃ + M \quad \rightarrow K_1 \quad \rightarrow (1.2)
\]
where M is any molecule in the atmosphere needed for the conservation of both energy and momentum in the recombination process. \( J_1 \) represents the photo dissociation rate for molecular oxygen and \( K_1 \) the reaction rate coefficient. Chemical energy is released when oxygen atom and oxygen molecule combine to form ozone molecule. If the ozone molecule is unable to get rid of this excess energy, the oxygen atom and oxygen molecule will come apart again, recreating the original oxygen atom and oxygen molecule. In the reaction \( k_1 \), the ozone molecule gives up its excess energy in a collision with molecule M before it falls apart. The production of ozone by photolysis of oxygen is the largest in the tropical upper stratosphere.

1.4.2) Stratospheric ozone destruction.

Atmospheric ozone is continuously destroyed by the action of ultraviolet, visible and near infrared radiation. The threshold for ozone dissociation is 1.1 eV corresponding to a wavelength of 1180 nm. Hence ozone dissociation can take place at all levels in the atmosphere right down to the surface.

\[
O_3 + h\nu \rightarrow O + O_2 \quad J_2 \rightarrow (1.3)
\]

Occasionally, the atomic oxygen formed by photolysis in the above reaction reacts with another ozone molecule to form two molecules of oxygen.

\[
O + O_3 \rightarrow 2O_2 \quad K_2 \rightarrow (1.4)
\]

\( J_2 \) represents the photo dissociation rate for ozone, and \( K_2 \) the reaction rate coefficient. In the absence of additional chemical reactions or atmospheric transport processes, the ozone concentration at any altitude is given by:

\[
n (O_3) = \frac{[ n (O_2) n (M) J_1 K_1]}{[ J_2 K_2]} \rightarrow (1.5)
\]

Where \( n (M) \) is the total air density.
This expression gives a first order picture of the vertical distribution of ozone in the atmosphere as shown in Figure 1.3. Typical units for mixing ratios are parts-per-million, billion, or trillion by volume, designated as "ppmv", "ppbv", and "pptv" respectively. Equal volumes contain equal numbers of molecules. Thus 10-ppbv ozone mixing ratio at 25 km altitude means that 10 out of every 1 billion molecules in an air sample collected at that altitude would be an ozone molecule.

(Graedel et al., 1993)

[1.5] Possible causes for perturbation in the chemistry of stratospheric ozone.

1.5.1) Role of catalysts.

Compounds containing chlorine, fluorine and carbon (chlorofluoro carbons) are important man made ozone depleting gases that are used in aerosol spray cans as propellants, refrigeration, air conditioning, foam blowing, cleaning of electronic components and solvents. Oxides of Nitrogen (NO\textsubscript{x}), which are produced in the stratosphere by the reaction of O\textsuperscript{1}D with N\textsubscript{2}O (which is released from the biosphere below) and from the emission of supersonic aircraft, play an important role in the stratospheric chemistry by destroying ozone catalytically. NO\textsubscript{x} \((NO\textsubscript{x} = N + NO + NO\textsubscript{2})\) is the most important destroyer of ozone in the 25 - 45 km altitude region. Nitrogen oxides are a precursor to ground-level ozone, which can in turn trigger serious respiratory problems. It forms when fuel is burned at high temperatures, as in a combustion process. The primary sources of NO\textsubscript{x} are motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels.
The catalytic cycles of ozone destruction can be illustrated by

\[
\begin{align*}
O_3 + X & \rightarrow O_2 + OX \\
OX + O & \rightarrow O_2 + X
\end{align*}
\rightarrow (1.6)
\]

\[
NET O_3 + O \rightarrow 2 O_2
\]

Where X is a radical, which goes through the catalytic cycle, destroys ozone and is recovered at the end of the reaction cycle. X can belong to the NO\textsubscript{X}, CLO\textsubscript{X} or HO\textsubscript{X} family.

In the NO\textsubscript{X} cycle the radical that destroys ozone is NO, which can be obtained by

**Oxidation of N\textsubscript{2}O**: \( N_2O + O^1D \rightarrow 2 NO \)

**Photo dissociation of N\textsubscript{2}O**: \( N_2O + h\nu \rightarrow NO + N \) \((\lambda < 400 \text{nm})\)

**The catalytic cycle is**: \( NO + O_3 \rightarrow NO_2 + O_2 \) \rightarrow (1.7)

\[
NET O_3 + O \rightarrow 2 O_2
\]

Intensive use of nitrogen fertilizers has altered the natural nitrogen cycle by increasing the fixation of this element in the form of ammonia, amino acid and nitrates. During nitrification and denitrification, part of the nitrogen is emitted to the atmosphere in the form of \( N_2O \) rather than \( N_2 \). Since \( N_2O \) is the major source of NO in the middle atmosphere, the use of nitrogen fertilizers ultimately leads to an acceleration of ozone destruction as indicated above. This process is catalytic since NO initiates’ ozone destruction process, but is regenerated, so that no net consumption of NO occurs. Each stratospheric NO molecule can catalytically destroy about \( 10^{12} \) to \( 10^{13} \) ozone molecules during it's life time in the stratosphere. Thus possible perturbations in the NO content of the atmosphere could have significant effects on the ozone layer.
**Emission of chlorine compounds.**

In the chlorine cycle, CFC’s are photo dissociated in the stratosphere to release chlorine radical, which goes through the catalytic cycle to destroy ozone.

\[
\begin{align*}
CFC_3 + h\nu & \rightarrow CFCl_2 + Cl (\lambda < 226 \text{ nm}) \\
CF_2Cl_2 + h\nu & \rightarrow CF_2Cl + Cl (\lambda < 215 \text{ nm}) \\
Cl + O_3 & \rightarrow ClO + O_2 \quad \rightarrow (1.8) \\
ClO + O & \rightarrow Cl + O_2
\end{align*}
\]

\[\text{NET: } O_3 + O \rightarrow 2O_2\]

The quantitative model estimates of the effect of the industrial chlorine perturbation indicates that the time required for the middle atmosphere to respond to surface emission of industrial halocarbons is very long (several decades) and that the reduction of ozone concentration is greatest near 40 km altitude. The halocarbons are infrared active and can affect the atmospheric radiative balance.

**Effect of Bromine.**

Methyl bromide (CH\textsubscript{3} Br) is an important source of Br radical in the atmosphere. It has natural and man-made sources. It is used as a fumigant and is a product of automobile exhaust and biomass burning. It has a relatively short lifetime of 1.2 to 2 years. Br takes part in catalytic destruction of ozone and is 40 times more reactive than Cl\textsubscript{2} in ozone depletion.

\[
\begin{align*}
Br + O_3 & \rightarrow BrO + O_2 \\
BrO + O & \rightarrow Br + O_2 \quad \rightarrow (1.9) \\
\text{NET: } O_3 + O & \rightarrow 2O_2
\end{align*}
\]
**Effect of Hydrogen.**

In the hydrogen cycle, the radical, which destroys ozone, is the hydroxyl radical OH, which is produced at

1. **High altitudes by the photo dissociation of water vapour**
   
   \[ H_2O + \text{hv} \rightarrow OH + H \ (\lambda < 240 \text{ nm}) \]

2. **Stratospheric altitudes by reaction with O^1D**
   
   \[ O_3 + \text{hv} \rightarrow O_2 + O^1D \ (\lambda < 320 \text{ nm}) \]
   
   \[ O^1D + H_2O \rightarrow 2 OH \]
   
   \[ \text{and} \quad O^1D + CH_4 \rightarrow OH + CH_3 \]

The catalytic reaction is:

\[ \text{OH} + O_3 \rightarrow HO_2 + O_2 \]

\[ HO_2 + O \rightarrow OH + O_2 \]

\[ \text{NET: } O_3 + O \rightarrow 2 O_2 \]

Other members of the HO_X family which destroy ozone are H and HO_2

\[ H + O_3 \rightarrow OH + O_2 \]

\[ OH + O \rightarrow H + O_2 \]

\[ \text{NET: } O_3 + O \rightarrow 2O_2 \]

\[ HO_2 + O \rightarrow OH + O_2 \]

\[ OH + O_3 \rightarrow HO_2 + O_2 \]

\[ \text{NET: } O_3 + O \rightarrow 2O_2 \]

The ozone depletion potential (ODP) of a compound is a relative measure of its ability to destroy stratospheric ozone. The ODP of CFC-11 is defined to be 1.0, and the ODP’s of other compounds are calculated with respect to this reference point. Thus a compound with an ODP of 0.2 is roughly one-fifth as "bad" as CFC-
11. ODP of a compound "x" is defined as the ratio of the total amount of ozone destroyed by a fixed amount of compound x to the amount of ozone destroyed by the same mass of CFC-11

$$\text{ODP} (x) = \frac{\text{Global loss of ozone due to x}}{\text{Global loss of ozone due to CFC-11}}$$

1.5.2) Aircraft emissions.

The subsonic aircraft fleet adds NO\textsubscript{X} only to the lower most stratosphere (<13 km), where large-scale dynamics tend to prevent advection to higher altitudes. The net ozone production rate increases rapidly with NO\textsubscript{X} until a maximum is reached. At NO\textsubscript{X} concentration > 500 pptv, the net rate of ozone production is expected to decrease with increasing NO\textsubscript{X}. Depending on the background concentration of NO\textsubscript{X}, addition of NO\textsubscript{X} from aviation can increase or decrease the net ozone production rate. Field measurements of NO\textsubscript{X} in the middle and upper troposphere, have found NO\textsubscript{X} to be of the order of 50 to 200 pptv. (Emmons et al., 1997; Tremmel et al., 1998) At these concentrations, the rate of net ozone production increases almost linearly with NO\textsubscript{X}. As a result, injection of NO\textsubscript{X} by the present fleet is thought to increase ozone in the lower stratosphere.

1.5.3) Lightning.

Lightning is an important elevated source of NO\textsubscript{X}. The total amount of NO\textsubscript{X} produced by lightning is proportional to the lightning flash frequency. The energy available for NO\textsubscript{X} production is higher for cloud to ground flashes than for intra cloud flashes. This increases ozone production potential at high altitudes.
Changes in temperature will affect the lightning frequency, NO production and ultimately ozone concentration. (Wei-Chyung et al., 1995)

1.5.4) **Role of volcanic eruption.**

Volcanic eruptions are potential sources of SO$_2$, HCl and H$_2$O in the lower stratosphere. The eruption of Mt. Pinatubo in the Philippines in June 1991 injected SO$_2$ in the stratosphere, which got converted into H$_2$SO$_4$ and condensed into small aerosol particles. These aerosol clouds were transported pole wards in both the hemispheres, which provided an increased scope for heterophase chemistry and enhanced ozone depletion. During 1992/1993, severe ozone loss was observed in both the hemispheres in both vertical distribution and in total column content. (Gleason et al., 1993). While almost total removal of ozone at its peak region was observed in the Antarctic, the effect was also felt at lower altitudes.

1.5.5) **Nuclear Testing.**

During atmospheric testing of nuclear bombs, the temperature within the fireball of a nuclear explosion is sufficient to convert atmospheric nitrogen and oxygen into nitrogen oxides. The fireball can then reach the middle stratosphere and deposit the nitrogen oxides, which could participate in catalytic ozone destruction.

1.5.6) **Automobile exhaust.**

Nitrogen oxides and hydrocarbons present in automobile exhaust combine in the presence of sunlight to produce ozone which not only causes eye watering and respiratory distress in man but also increases respiration of leaves, thus
killing the plant by depleting its food. In urban atmospheres rich in hydrocarbons and nitrogen oxides, ozone is produced as a by product by the following reactions:

\[
\begin{align*}
CH_4 + OH & \rightarrow CH_3 + H_2O \\
CH_3 + O_2 + M & \rightarrow CH_2O_2 + M \\
CH_2O_2 + NO & \rightarrow CH_3O + NO_2 \\
NO_2 + h\nu & \rightarrow NO + O \\
O + O_2 + M & \rightarrow O_3 + M \\
CH_2O + O_2 & \rightarrow CH_2O + HO_2 \\
HO_2 + NO & \rightarrow NO_2 + OH \\
NO_2 + h\nu & \rightarrow NO + O \\
O + O_2 + M & \rightarrow O_3 + M \\
CH_2O + h\nu & \rightarrow CO + H_2 \\
CO + OH & \rightarrow CO_2 + H \\
H + O_2 + M & \rightarrow HO_2 + M \\
HO_2 + NO & \rightarrow OH + NO_2 \\
NO_2 + h\nu & \rightarrow NO + O \\
O + O_2 + M & \rightarrow O_3 + M \\
Net; CH_4 + 6 O_2 + h\nu & \rightarrow H_2O + H_2 + 3 O_3 + CO_2
\end{align*}
\]

1.5.7) El Niño southern oscillation (ENSO).

Large scale variations in equatorial Pacific Ocean surface temperatures are known as ENSO. Normally, the waters of the eastern Pacific Ocean near South America are quiet cool as a result of upwelling ocean currents. The tropospheric trade winds normally traverse from east to west in this region. However in an El
Niño period, the trade winds weaken, allowing the warmer waters of the western pacific to migrate eastwards. This change in temperature of the sea surface water causes large-scale shifts in the global circulation patterns in the troposphere and the lower stratosphere. This in turn affects the transport of ozone in these regions. This oscillation is very irregular, with a period of 4 to 7 years between episodes. Ozone variations in response to ENSO are strongest at the tropics. The zonal mean ENSO variation is very small. Ozone effects reach into mid latitudes, although the effects are hard to separate from other variations.

1.5.8) **Quasi-Biennial Oscillation (QBO).**

The QBO is an oscillation in the average zonal winds in the tropical stratosphere. Roughly every 27 to 30 months, the tropical stratospheric winds in the 10mb to 100mb altitude range are observed to shift from westerly to easterly and then back again. The QBO develops as a result of disturbances or waves in the tropical troposphere propagating vertically into the lower stratosphere. These disturbances interact with the average wind in such a way as to cause the average wind to regularly reverse direction. Over the course of 30 months, the winds complete one cycle. This circulation enters the lower stratosphere in the tropics and leaves the middle stratosphere in the extra tropics. Air masses having different ozone concentration are transported between the two latitude regions. This induced (latitude / altitude) meridional circulation moves ozone poor air into the tropics and ozone rich air out of the tropics during one phase of QBO and then reverses this process during the other. Ozone in the tropics thus decreases and then increases as we go through the QBO cycle.
1.5.9) **Solar storms.**

Solar storms lead to the ejection of large amount of high-energy protons which penetrate the earth’s magnetic field near the poles. These protons penetrate into the atmosphere (40 to 80 km layer), causing ionization of air molecules. As the ionized particles recombine, they produce nitrogen and hydrogen oxides, which can affect ozone through the NO$_X$ and HO$_X$ catalytic cycles. These effects are short lived because the hydrogen oxides, which cause the primary ozone loss, recombine within hours. The effect of NO$_X$ can persist for several months.

1.5.10) **Solar ultraviolet variations**

The output of solar UV radiation is influenced by magnetically active regions (sun spots) on the sun. The period when sunspot activity is at its greatest during the 11 year cycle, is a solar maximum, while the period when sunspot activity is at its least is a solar minimum. The modulations in the solar UV output have a direct effect on ozone photochemistry and even column amount of ozone. The UV output of the sun increases as sunspot activity increases. The production of ozone is found to be more sensitive to variations in solar UV output (4 to 8%) than the loss rate of ozone (1%), (Ganguly et al., 2005). Thus the production rate of ozone is high when solar activity is at its maximum and it decreases when solar activity is at its minimum.

1.5.11) **Temperature driven fluctuations.**

Planetary waves propagating upwards from the lower atmosphere grow in magnitude as altitude increases. These waves lead to variations in temperatures, which then affect the photochemical reaction rates, since the reaction rate
coefficients that determine photochemical loss rates are temperature dependant. The rate coefficient for the reaction \( \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \) as a function of temperature is given by:

\[
K (\text{O}, \text{O}_3) = 8 \times 10^{-12} e^{-2060/T} \text{cm}^3/\text{molecule. sec.}
\]

Where \( T \) is the temperature on Kelvin scale.

Thus a 10 \( ^{\circ} \text{K} \) increase in temperature results in approximately 30 % decrease in ozone amount.


Our atmosphere is continuously in motion. These motions occur over different time scales, ranging from a single day to several decades. It is convenient to separate atmospheric variations into the following four time scale categories. (1) Short-term, (2) Seasonal, (3) Inter-annual (year to year) and (4) Long term.

The study of atmospheric motions makes up a branch of atmospheric sciences called dynamics. Ozone in the lower atmosphere (i.e. in the troposphere and the lower stratosphere) has a long lifetime, of the order of months to years. The lifetime of ozone molecule refers to the period between its creation and destruction. This is because, the photo chemical processes which create and destroy ozone occur very slowly in the lower atmosphere, since the UV radiation which drives ozone photochemistry is mostly screened out from the lower atmosphere by the ozone in the upper atmosphere. The primary source of variability in the lower atmosphere is therefore the transport processes. As a result, ozone in the lower atmosphere acts as a tracer of atmospheric motions.

**Short-term variability**: It refers to day-to-day and week-to-week variations.
**Seasonal variability**: It exhibits a general pattern that repeats every year. This repeating variation is called an annual cycle or a seasonal cycle.

**Inter annual variability**: The shape and amplitude of the annual distribution will not be precisely the same from year to year. This year-to-year variability is referred to as inter annual variability.

**Long-term variability**: Cyclic variability with a time scale longer than our available measurement record make up one class of long-term variability. One cause of long-term variability is a trend. e.g. Long-term variability in the ozone loss processes can result in a trend in ozone amounts. Such long-term variability can have other causes, such as the gradual built up (a trend) in the amount of ozone destroying Cl in the stratosphere from CFC's.

When analyzing ozone data for the long-term trend, it is possible that our data set may not be long enough to resolve some natural cyclic pattern. There could even be a non-cyclic factor unresolved by our limited data set. Some unknown factor contributing to a variation with a period longer than the period of our record might cause us to conclude erroneously the existence of a long-term trend in the data e.g. Solar activity exhibits 27 days solar rotation; 11 years sun spot cycle and 90 years Gleissberg cycle with peaks observed in 1780, 1870, and 1960. Thus a data set of only 20 years would not capture the effects due to the Gleissberg cycle.

[1.7] **Review of literature on ozone studies.**

The Tropical region is characterized by large biogenic and pyrogenic (due to biomass burning) emissions of trace gases, including NMHC’s, which combine
with high OH concentrations making it the most photochemically active region of the earth. (Andreae et al., 1997). Model simulations (European Center Hamberg Model) show that in the tropics the photochemical production of ozone predominates over the stratospheric transport, throughout the year. (Reolofs et al., 1995). Estimations made by using the Chemical Transport Model (NASA) showed that on increasing the anthropogenic emissions, ozone production efficiency was maximum over the Indian region, followed by Japan and China, which was explained on the basis of increase in OH and peroxy radicals (Berntsen et al., 1996). Apart from this, since India is a rapidly developing country, there may be large future changes in the atmospheric chemistry of this region.

The total columnar ozone over the observing station, its vertical distribution and its temporal variations are important basic data for studies on morphology and behaviour of atmospheric ozone in different parts of the globe. For the past several decades, ozone has been regularly monitored on a global scale by means of Total Ozone Mapping Spectrometer (TOMS) carried on Nimbus -7 satellite. In India, ozone is being monitored since last three decades by India Meteorological Department, (Mandal et al., 2004) which includes measurements of total ozone with Dobson Spectrometer as well as profiles of ozone from ozonesondes. Daily ozone measurements using Dobson Spectrometer in India were started by Physical Research Laboratory, Ahmedabad from 25th October 1951 at Mt. Abu(24°36’ N, 72°43’E). Since then regular ozone measurements have been made alternately from Mt. Abu (during 1951 – 1960 and 1969 – 1982)
and Ahmedabad (23°1’N, 72°39’E; from 1960 – 1969 and thereafter from 1982 onwards). This data is perhaps the largest ozone time series in the tropics (Angreji, 1989). There have also been a number of major campaigns like INDOEX 1998 and 1999 (Indian Ocean Experiment) and BOBMEX-99 (Bay of Bengal Monsoon Experiment), which provide insights of seasonal changes in ozone. Mandal et al., 2004; have studied the ozone scenario over India, and have found that although the total ozone has not changed significantly over the past three decades, there has been a considerable reduction in stratospheric ozone and substantial increase in tropospheric ozone. Long term variations in total columnar ozone were studied by Chakrabarty et al., 1979 and Chakrabarty et al., 1984 using TOMS and Dobson Spectrometer data. Chakrabarty et al., 1997 also studied the behavior of ozone over Indian region after the Pinatubo eruption. Variations in the vertical ozone profile over India were studied by Mani et al., 1973, Subbaraya et al., 1990 and Subbaraya and Lal, 1999. Long term trends in tropospheric ozone over the Indian tropical region were studied by Saraf et al., 2004. Singh et al., 2002 studied the effect of El Niño on total ozone column. They observed anomalous high values of total column ozone around Jan-Mar 1998 at Delhi, Lhasa and Beijing, which was found to coincide with high SST increase over the equatorial Indian Ocean due to the strong El Niño effect. The effect of El Niño on ozone is being studied globally, but it needs investigation by the scientific community in greater details.

The diurnal variation of surface ozone has been studied by several workers like Kaushar Ali et al., 2004 over Himalayan region and Delhi, Satsangi et al., 2004 at
Agra and Kulshrestha et al., 1997 at Delhi. However apart from Raj et al., 2003 at Pune and Dani et al., 2003 during BOBMEX – 99, very little study has been reported on the diurnal variation of total columnar ozone in India.

[1.8] **Scope of the Thesis.**

The study of variations in ozone concentration at Rajkot has special significance because it is located in the tropical region, where most of the ozone formed is due to the availability of the high dose of solar UV radiation. In view of these considerations, the thesis is focused on the study of tropospheric, stratospheric and total ozone photochemistry at different Indian stations particularly at Rajkot in Gujarat since 1980. The modulating effect of meteorological conditions such as temperature, humidity, wind speed, and geophysical conditions such as 11-year solar cycle, volcanic eruptions, anthropogenic causes, along with the effects of ENSO and solar storms on the total ozone concentration has been investigated. The observed long term trend for ozone and erythemal UV irradiance in India has also been studied to determine whether Indian latitudes are safe from the lethal effects of erythemal UV. A calibration scheme for MICROTOPS II Sun photometer is presented.
Methodology for ozone measurement.

There have been significant changes and improvements in the techniques for ozone measurements since the last few years. In this chapter, a brief description of the different techniques used for ozone measurement with special emphasis on the techniques used in this work is presented.

[2.1] Chemical techniques.

The amount of ozone in the stratosphere can be measured with electrochemical sondes. Information can be obtained by sending the instruments into the stratosphere and making direct measurements. Small balloons routinely reach the lower and even the middle stratosphere, but very large balloons and rockets are needed to reach the upper part of the stratosphere.

[2.2] Satellite based remote sensing techniques.

Satellite based platforms have been used for the measurement of ozone concentration for more than 20 years. There are wide varieties of spectral techniques for ozone measurements. The occultation technique is the one in which ozone profiles at selected latitudes are determined by measurement of the absorption of visible or ultraviolet light during sunrise or sunset as well as by starlight.
2.2.1) The largest amount of satellite based ozone measurements comes from the **Solar Back Scattered Ultra Violet Technique**. In this method, the ratio of sunlight scattered back to the spacecraft from the earth-atmosphere system to that incident at the top of the atmosphere is used to determine the ozone amount. This technique works only during daytime and can be used to measure total ozone columns and vertical distribution. It divides the earth’s atmosphere into 13 layers and determines the columnar ozone for each of these layers. The classification of these layers and their corresponding altitude from the surface of the earth is shown in *table 2.1*.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>Altitude in km</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 to 15.5 km</td>
</tr>
<tr>
<td>2</td>
<td>15.5 to 21.5 km</td>
</tr>
<tr>
<td>3</td>
<td>21.5 to 25.5 km</td>
</tr>
<tr>
<td>4</td>
<td>25.5 to 28.5 km</td>
</tr>
<tr>
<td>5</td>
<td>28.5 to 31.5 km</td>
</tr>
<tr>
<td>6</td>
<td>31.5 to 34.5 km</td>
</tr>
<tr>
<td>7</td>
<td>34.5 to 37.5 km</td>
</tr>
<tr>
<td>8</td>
<td>37.5 to 41.5 km</td>
</tr>
<tr>
<td>9</td>
<td>41.5 to 45 km</td>
</tr>
<tr>
<td>10</td>
<td>45 to 48 km</td>
</tr>
<tr>
<td>11</td>
<td>48 to 52.5 km</td>
</tr>
<tr>
<td>12</td>
<td>52.5 to 56.5 km</td>
</tr>
<tr>
<td>13</td>
<td>56.5 km to the top of the atmosphere.</td>
</tr>
</tbody>
</table>

*Table 2.1* Classification of the Earth’s atmosphere into 13 layers according to the SBUV technique, and their corresponding altitude from the surface of the earth.
2.2.2) **Total Ozone Mapping Spectrometer (TOMS).**

TOMS was one of eight instruments designed to provide continuous, long-term monitoring of atmospheric, oceanic and surface parameters on a global basis throughout most of the 1980s.

**Nimbus - 7 TOMS.**

Nimbus –7 satellite was launched on 24th October 1978, and the measurements began about a week later from 1st November 1978 to 5th May 1993. The Total Ozone Mapping Spectrometer (TOMS) experiment on board NASA’s Nimbus –7 satellite is a source of high-resolution daily global information about the total ozone content of the atmosphere. It measures the ultraviolet sunlight back scattered from the clouds or the ground at wavelength bands centered at 312.34, 317.35, 331.06, 339.66, 359.88 and 379.95 nanometers to measure the total ozone amount. The first four wavelengths are sensitive to ozone; the two longer wavelengths are used for estimating the scene reflectivity necessary for deriving ozone amounts. Total column ozone is inferred from the differential absorption of scattered sunlight in the ultraviolet using the ratio of two wavelengths, 312nm and 331nm for instance, where one wavelength is strongly absorbed by ozone while the other is negligibly absorbed. TOMS scans in the cross-track direction in 3-degree steps from 51 degrees on one side of nadir to 51 degrees on the other, for a total of 35 samples. At the end of the scan, the mirror quickly returns to the initial position without taking any measurements on the retrace. The next scan begins 8 seconds after the start of the previous scan. Consecutive cross – scans overlap, creating a contiguous mapping of ozone as the spacecraft moves from...
south to north. Approximately 2,000,000 measurements are made on a daily basis during the sunlit portions of the orbits. Nimbus-7 is in a south-north sun synchronous polar orbit such that it is always close to a local noon/midnight beneath the satellite. Thus, ozone over the entire world is measured every 24 hours. It cannot measure nighttime ozone or make measurements in the winter polar darkness.

<table>
<thead>
<tr>
<th>Spatial coverage</th>
<th>90° N to 90° S and 180° E to 180° W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temporal coverage</td>
<td>1/11/78 – 6/5/1993</td>
</tr>
<tr>
<td>Orbit</td>
<td>Sun-synchronous, near polar</td>
</tr>
<tr>
<td>Nominal Altitude</td>
<td>955 km</td>
</tr>
<tr>
<td>Inclination</td>
<td>104.9 Deg</td>
</tr>
<tr>
<td>Equator Crossing Time</td>
<td>12.00 noon (ascending)</td>
</tr>
<tr>
<td>Number of views / scans.</td>
<td>35</td>
</tr>
</tbody>
</table>

**Table 2.2 Characteristic features of Nimbus-7 TOMS.**

**Meteor-3 TOMS.**

During the last days of the Cold War, Meteor-3 TOMS was the first and the last American-built instrument to fly on a Soviet spacecraft. Meteor-3 was launched on August 15, 1991 from Plesetsk, Russia on a Cyclone booster, and failed on 27th December 1994. The orbit drifted with respect to the sun angle with a period of 212 days. Because of the precessing nature of the Meteor-3 orbit (precession period = 212 days), the equator crossing time varied from noon (overhead sun,
solar zenith angle = 0 deg) to the terminator (solar zenith angle = 90 deg). Good quality data was obtained over a wider range of equator crossing times.

**Table 2.3 Characteristic features of Meteor-3 TOMS.**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altitude</td>
<td>1202 km</td>
</tr>
<tr>
<td>Orbit inclination</td>
<td>82.5 deg</td>
</tr>
<tr>
<td>Orbit precession</td>
<td>212 days</td>
</tr>
<tr>
<td>Launch time</td>
<td>12:15 Moscow standard time</td>
</tr>
<tr>
<td>1st ozone data</td>
<td>22/8/91</td>
</tr>
<tr>
<td>Wavelengths</td>
<td>312.35, 317.4, 331.13, 339.73, 359.0, 380.16 nm</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>1.1 nm</td>
</tr>
<tr>
<td>Cross-track scan angle</td>
<td>+/- 51 deg</td>
</tr>
<tr>
<td>Number of views/scan</td>
<td>35</td>
</tr>
</tbody>
</table>

**ADEOS TOMS.**

Advanced Earth Observing Satellite (ADEOS) was the first international space platform dedicated to Earth environmental research and was developed and managed by the National Space Development Agency of Japan (NASDA). The TOMS instrument along with NSCAT (a NASA Spectrometer designed to study wind speed and direction) was a major US component of the platform. ADEOS was launched on August 17, 1996 (at 01:53 UT) into a sun synchronous orbit at an altitude of approximately 830 km by an H - II launch vehicle from the Tanegashima Space Center in Japan. The instrument was designed to operate for 3 years at an altitude of 800 km orbit, giving full daily global coverage, and
used the following wavebands: 308.6, 312.5, 317.5, 332.2, 331.2, 360.0 nm. On June 30, 1997, the ADEOS Spacecraft failed and was replaced on task by NASA’s Earth Probe TOMS.

**Earth-Probe TOMS.**

Earth-Probe TOMS was launched on 2nd July 1996. The satellite was flown in a 500 km polar orbit, rather than the 950 km orbit that was originally planned. The lower orbit increased the satellite’s resolution and also the probability of making measurements over cloudless scenes. The lower orbit also improved the ability of the TOMS instrument to make measurements of UV-absorbing aerosols in the troposphere, a capability that was recently developed using earlier TOMS data. The increased probability of making measurements over cloud-free areas will enhance the capability of converting the TOMS aerosol measurements into geophysical quantities such as optical depth. The increased resolution available with the lower orbit may even result in the ability of the TOMS instrument to detect urban aerosols such as pollution.

### Table 2.4 The wavelengths used by Earth-Probe TOMS.

<table>
<thead>
<tr>
<th>Band</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band 1</td>
<td>360.0 nm</td>
</tr>
<tr>
<td>Band 2</td>
<td>331.2 nm</td>
</tr>
<tr>
<td>Band 3</td>
<td>322.3 nm</td>
</tr>
<tr>
<td>Band 4</td>
<td>317.5 nm</td>
</tr>
<tr>
<td>Band 5</td>
<td>312.5 nm</td>
</tr>
<tr>
<td>Band 6</td>
<td>+/- 0.1 nm</td>
</tr>
</tbody>
</table>
Because of continuing changes in the optical properties of the front scan mirror (the reason for which could not be understood), a latitude dependent error was observed which could not be corrected by a simple calibration correction. The calibration appeared to be stable near the equator. But by 50 degrees latitude, a -2% to -4% error in TOMS was observed. Therefore, in view of the good performance of Ozone Monitoring Instrument (OMI) and the calibration problems with EP TOMS, Earth Probe TOMS data has been discontinued from January 1, 2006 and has been replaced by the OMI data.

2.2.3) Ozone monitoring instrument (OMI).

The OMI instrument can distinguish between aerosol types, such as smoke, dust, and sulfates, and can measure cloud pressure and coverage, which provide data to derive tropospheric ozone. It will continue the TOMS record for total ozone and other atmospheric parameters related to ozone chemistry and climate. OMI measurements will be highly synergistic with the other instruments on the EOS Aura platform.

The OMI instrument measures solar backscatter radiation in the visible and ultraviolet region. It will improve the accuracy and precision of the measurements of total ozone and will also allow for accurate radiometric and wavelength calibration over the long term. The instrument is a contribution of the Netherlands's Agency for Aerospace Programs in collaboration with the Finnish Meteorological Institute (FMI) to the EOS Aura mission.
2.2.4) **Upper Atmosphere Research Satellite (UARS).**

The Halogen Occultation Experiment (HALOE) was launched on the Upper Atmosphere Research Satellite (UARS) spacecraft on September 12, 1991, and after a period of out gassing; it began science observations from October 11, 1991. The experiment uses solar occultation to measure vertical profiles of O$_3$, HCl, HF, CH$_4$, H$_2$O, NO, NO$_2$, aerosol extinction at 4 infrared wavelengths, and temperature versus pressure with an instantaneous vertical field of view of 1.6 km at the Earth's limb. Latitudinal coverage is from 80°S to 80°N over the course of 1 year and includes extensive observations of the Antarctic region during spring. The altitude range of the measurements extends from about 15 km to 60-130 km, depending on the species. Nitric oxide measurements extend through the lower thermosphere. Experiment operations have been essentially flawless, and all performance criteria either meet or exceed specifications. Internal data consistency checks, comparisons with correlative measurements including satellite, in situ and ground-based observations are in good agreement.

2.2.5) **Microwave Limb Sounder (MLS).**

**Microwave Limb Sounder (MLS)** focuses on the upper troposphere and stratosphere, measuring microwave radiation emitted by ozone, chlorine compounds and many other traces gases. It studies how water vapour and ozone destroying compounds like chlorine and bromine pass between the troposphere and stratosphere. MLS is a microwave sensor, which is able to measure trace gases inside the clouds.
Ground based remote sensing techniques

2.3.1) The **Dobson Spectrophotometer** is a ground-based instrument, which is widely used for measuring the total columnar ozone content in the atmosphere *(Figure 2.1)*. Gordon Dobson designed it in the 1930’s. It uses the fact that ozone has a series of bands in the ultraviolet absorption spectrum and by measuring the solar ultraviolet radiation transmitted to the surface at several pairs of wavelength’s, one close to an absorption maxima, and one away from it, the total columnar ozone content can be calculated. It uses a Quartz prism as a dispersing element. Light can be separated into its individual wavelengths by passing it through a prism. In the visible region, the wavelength corresponds to the colour of the light. Since the human eye does not respond to light in the UV region, a sensitive electronic eye is used to observe the light intensity. Each type of molecule absorbs certain wavelengths of light in a characteristic pattern, known as a spectrum. The spectrum of ozone peaks in the UV and thus, ozone absorbs UV. At wavelengths where ozone absorbs only part of the solar radiation, the amount of light that reaches the ground depends on the abundance of overhead ozone. Thus, measurement of the light intensity at a wavelength where light is partially absorbed by ozone allows us to quantify the abundance of overhead ozone.

Dobson Spectrophotometer measures ultraviolet light from the Sun at 2 to 6 different wavelengths from 305 to 345 nm. One of the wavelengths used to measure ozone is absorbed strongly by ozone (305 nm), whereas the other wavelength is not absorbed by ozone (325 nm). Therefore the ratio between the
two light intensities is a measure of the amount of ozone in the light path from the sun to the observing spectrophotometer. The ratio between the two intensities is determined by an R-dial located on the top of the Dobson spectrophotometer. The R-dial controls a filter wedge that gradually blocks out the 325 nm light. As the R-dial rotates from 0 to 300 degrees, the filter wedge increasingly blocks out more light. At 0 degrees the wedge does not block out any light. At 300 degrees, the wedge nearly blocks all of the light. The filter wedge gradually blocks more and more light until the intensity of the 325 nm and 305 nm light are equal. The R-dial is calibrated with the filter wedge, so that the original intensity of the 325nm light can be determined from the R-dial reading. By taking the R-dial reading when the intensities of the two wavelengths are equal, their ratio is determined. Aerosols present in the atmosphere scatter light at both wavelengths equally. Thus, aerosols have no affect on the ratio of light intensities between 305 and 325 nm.

Figure 2.1 Photograph (Left) and internal construction (Right) of Dobson Spectrophotometer.
2.3.2) **Microprocessor Controlled Total Ozone Portable Spectrometer**

(MICROTOPS II)

Dobson spectrophotometer is a universally accepted ground based ozone monitoring instrument for measuring total column ozone. However, since it is expensive, bulky and heavy, a need for a more portable, compact instrument with reasonable accuracy led to the development of Microtops – II Sun photometer. The Microtops II sun photometer is a 5 channel, hand held, multi-band sun photometer designed by the Solar Light Company, Inc, USA (Morys et al., 2001) and is capable of quick and inexpensive measurements of the total ozone column and optionally the water vapour column as well as aerosol optical thickness at 1020 nm (Figure 2.2)

![Block diagram of Microtops II Sun photometer.](image)

**Figure 2.2 Block diagram of Microtops II Sun photometer.**

**Principle of operation.**

MICROTOPS II measures the direct solar radiation at 305, 312, 320, 936 and 1020 nm using narrow band interference filters. The instrument is equipped with five accurately aligned optical collimators; capable of a full field view of 2.5°.
Internal baffles are also integrated into the device to eliminate internal reflections. Each channel is fitted with a narrow-band interference filter and a photodiode suitable for the particular wavelength range. The collimators are encapsulated in a cast aluminum optical block for stability.

A sun target and pointing assembly is permanently attached to the optical block and laser aligned to ensure accurate alignment with the optical channels. When the image of the sun is centered in the bull’s eye of the sun target, all optical channels are oriented directly at the solar disk. A small amount of circumsolar radiation is also captured, but it makes little contribution to the signal. Radiation captured by the collimator and band pass filters radiate onto the photodiodes, producing an electrical current that is proportional to the radiant power intercepted by the photodiodes. These signals are first amplified and then converted to a digital signal by a high resolution A/D converter. The signals from the photodiodes are processed in series. However, with 20 conversions per second, the results can be treated as if the photodiodes were read simultaneously.

Short wavelengths of UV radiations are much more readily absorbed by ozone than the longer wavelengths in the same UV band. This means that the amount of ozone between the observer and the sun is proportional to the ratio of two wavelengths of the sun’s UV radiation. MICROTOPS II uses that relationship to derive the total ozone column (the equivalent thickness of the pure ozone layer at standard pressure and temperature) from measurements of three wavelengths in the UV region. Similarly, as in the traditional Dobson instrument, the
measurement at an additional 3rd wavelength enables a correction for particulate scattering and stray light. The total ozone column is calculated from the wavelengths 305, 312 and 320nm, the site’s latitude and longitude, universal time, altitude and pressure. An in built pressure transducer facilitates the measurements of atmospheric pressure. Calculation of the ozone column requires knowledge of the actual air mass. This is calculated by the MICROTOPS II based on the time from a built in clock and the user entered coordinates of the measurement site.

Best results can be obtained during clear sky conditions with the sun high in the sky. Haze and thin clouds increase the measurement’s variability, but the ozone readings are still valid.

**Characteristic features**

1) **High accuracy:** High-grade filters are embedded in a solid cast aluminum housing that assures accurate, stable optical alignment. Low noise electronics and a 20-bit A/D converter ensure high linearity, resolution and dynamic range.

2) **Easy to use:** No computer knowledge is required to take the readings. Once the geographical coordinates of the measurement site are entered, the operator has to simply aim the meter at the sun, align the image of the sun with the bull’s eye and push the button. The result is displayed on the LCD within seconds.

3) **Portable:** It is a compact, hand held, battery operated device and can therefore even operate in places where the mains power is not available.
4) **Computer interface:** A serial interface allows the transfer of data and remote control of the instrument from any computer.

5) **GPS interface:** MICROTOPS II can be linked directly to a hand held GPS (Global Positioning System) receiver via serial cable. Accurate location parameters are calculated by the receiver based on a combination of signals emitted from satellites orbiting the earth.

6) **Instantaneous results:** The ozone and total water vapour calculation algorithms are programmed in the MICROTOPS II and the results of all the stored scans can be conveniently viewed on the LCD. The raw data is also stored to allow retrospective adjustments of calibration constants.

7) **Non-volatile memory:** The raw data collected by MICROTOPS II, as well as calculated results are stored in the non-volatile memory. Each data point is annotated with date, time, site coordinates, solar angle, altitude, pressure and temperature.

8) **Low cost:** By implementing the latest technology, the instrument cost has been brought below that of comparable ozonometers, without sacrificing accuracy or features.

![Figure 2.3 Photograph of Microtops II Sun photometer.](image-url)
Calibration and measurement of ozone.

As the solar radiation penetrates into the earth’s atmosphere, it is progressively absorbed and scattered. Consider monochromatic extra terrestrial solar radiation of intensity $I_0$ at the top of the atmosphere. The transmitted flux $I$ reaches the earth’s surface after traveling an optical distance “$m$” in the atmosphere.

Calibration of the MICROTOPS II instrument requires that the intensity of radiation measured at each channel be analyzed assuming the validity of the Lambert – Beer law $I = I_0 e^{-m x}$ which when applied to ozone absorption and Raleigh scattering by the atmosphere, gives the simple equation

$$I = I_0 e^{-\alpha \mu \Omega \cdot m \beta \frac{P}{P_0}} \rightarrow (2.1)$$

where $I_0$ = intensity of the radiation of a particular wavelength at the top of the atmosphere.

$I$ = intensity of the radiation after all processes attenuating the incident radiation has occurred. (Reduced solar irradiance at the surface of the earth)

$\Omega$ = amount of ozone.

$\mu$ = ratio of actual and vertical path lengths of the radiation through the ozone layer.

$P$ = the atmospheric pressure in mb

$P_0$ = standard pressure = 1013.25 mb

$\chi$ = total atmospheric optical thickness or attenuation coefficient.

$m$ = the air mass. ($m = 1/cos \theta$)

It is the thickness of the atmosphere between the observer and the Sun

$\alpha$ and $\beta$ are the ozone and Rayleigh absorption cross-sections respectively.
Every time the angle of the sun changes, the air mass changes. When the sun is overhead, its light passes through a certain thickness of the atmosphere (air mass \( m = 1 \)). The air mass increases as the sun moves closer to the horizon.

\[
\mu = \frac{R + h}{\left[ (R + h)^2 - (R + r)^2 \sin^2 \theta \right]^{1/2}} \rightarrow (2.2)
\]

where \( R = \text{mean earth radius (6371 km)} \)

\( r = \text{height of the measurement site above sea level in km.} \)

\( h = \text{height of ozone layer above the sea level.} \)

\( \theta = \text{solar zenith angle. It is the angle of the sun with respect to the zenith. The zenith angle is 90^\circ \text{ when the sun is at the horizon and 0^\circ when the sun is directly above. When } m = 0, \text{ there is no air mass. This is the signal that the photometer would measure if it were taken to the top of the atmosphere. It is known as the extra terrestrial constant (ET).} \)

In the atmosphere, extinction is caused by various processes with attenuation coefficients \( \chi_{rs}, \chi_{aerosol} \) and \( \chi_{ma} \).

Since all extinction processes occur independently of each other, the overall optical depth due to all processes can be written as the sum of individual optical depth. \( \chi = \chi_{rs} + \chi_{aerosol} + \chi_{ma} \)

Where \( \chi_{rs} \) is the Rayleigh scattering optical depth (scattering due to air molecules.)

\( \chi_{ma} \) is the optical depth due to absorption by air molecules like ozone, water vapour etc.
The formula for corrected ozone calculation is given by:

\[
\Omega = \frac{\ln \left( \frac{I_{01}}{I_{02}} \right) - \ln \left( \frac{I_1}{I_2} \right) - \ln \left( \frac{I_{02}}{I_{03}} \right) - \ln \left( \frac{I_2}{I_3} \right) - (\beta_1 - \beta_2)\cdot(\beta_2 - \beta_3)\cdot m \cdot \frac{P}{P_0}}{\left( \alpha_1 - \alpha_2 \right) - \left( \alpha_2 - \alpha_3 \right) \cdot \mu}
\]

The indexes 1, 2 & 3 identify the three channels: 305.5, 312.5 and 320 nm respectively. \(b\) is the extraterrestrial constant of the channel. \(I\) is the measured signal, \(m\) and \(\mu\) are optical air masses for air and ozone, \(\alpha\) and \(\beta\) are the ozone and Rayleigh absorption cross-sections respectively and \(P\) and \(P_0\) are the barometric pressure and normal pressure respectively.

The Microtops II Sun photometer, however needs to be calibrated at regular intervals on clear days by comparison with other instruments with a known calibration history. Best results are obtained during clear sky conditions with the sun high in the sky.

[2.4] **Calibration scheme with other techniques.**

The performance of Total ozone mapping spectrometer (TOMS) has been compared with that of Dobson spectrophotometers at Delhi and Pune from 1996 to 2003 and at Ahmedabad in 2004 (Jan to Dec.). These three Dobson Spectrophotometers have been intercompared with the national standard spectrometer at New Delhi, which had earlier been standardized with the world standard during the International intercomparison of Dobson Spectrometers held at Boulder, U.S.A, in 1977. *(Mandal et al., 2004)* The calibration factor = the slope of the regression line as shown in figures 2.4a, 2.4b and 2.4c. Figure 2.4a indicates that the monthly mean Dobson spectrophotometer ozone values at
Pune are 0.9795 times the monthly mean TOMS ozone values in Dobson unit. 

*Figure 2.4b* indicates that the monthly mean Dobson spectrophotometer ozone values at Delhi are 0.9899 times the monthly mean TOMS ozone values in Dobson unit. The daily local noon Dobson spectrometer values at Ahmedabad (*Figure 2.4c*) are found to be 1.0064 times the daily local noon TOMS ozone values in Dobson unit. Thus the TOMS values are found to correlate well with respect to the Dobson spectrophotometer values. This proves that TOMS is reliable for ozone measurements. Since we do not have a Dobson spectrophotometer at Rajkot, I have calibrated the MICROTOPS - II Sun photometer with respect to TOMS. The daily local noon values of columnar ozone measured by MICROTOPS II Sun photometer at Rajkot for each month have been compared with the corresponding daily local noon values obtained from TOMS by plotting a scatter plot between the two data sets for each month. A typical plot for the month of July 2004 is shown in *figure 2.4d*, which indicates that the ozone values measured by MICROTOPS II Sun photometer in July are 1.0459 times those measured by TOMS. Therefore all the readings for the month of July have been divided by 1.0459 to make them equivalent to TOMS readings. The readings for the other months have been divided by similar correction factors, which are indicated in *figure 2.5*. 

57
Figure 2.4 Comparison between TOMS & Dobson Spectrometer ozone values for (a) Pune and (b) Delhi from 1996-2003 (c) Ahmedabad in 2004 and (d) comparison between TOMS and MICROTOPS II ozone at Rajkot in July 2004.
Figure 2.5 Correction factor by which the Microtops II readings for the corresponding months have been divided to make them equivalent to TOMS.


2.5.1) Tropospheric Ozone Residual Method (TOR)

Dr. Jack Fishman et al., (2003) at NASA Langley Research Center in Hampton developed the TOR method of deriving tropospheric ozone from satellite measurements. The TOR was initially developed by utilizing coincident observations of total ozone from the Total Ozone Mapping Spectrometer (TOMS) and stratospheric ozone profiles from the Stratospheric Aerosol and Gas Experiment (SAGE). At present, although the total ozone from the TOMS instrument is being used, the stratospheric ozone profiles from SAGE have been replaced by the Solar Backscattered Ultraviolet (SBUV) instrument. The change from the SAGE instrument to the SBUV instrument was made because of the much greater data density provided by the SBUV instrument. Gridded global
values of tropospheric column ozone can be derived between 50°N and 50°S with 1° latitude by 1.25° longitude horizontal resolution. The distributions are determined by subtracting the empirically corrected stratospheric column ozone amount derived from the SBUV instrument from the total column ozone measurements made by TOMS.

2.5.2) Convective cloud differential method (CCD).

Pacific averaged (120°W to 120°E and 50°S to 60°N, in steps of 5 degree by 5 degree bins); monthly mean stratospheric (SCO) and tropospheric column ozone (TCO) from TOMS measurements can be obtained from the CCD method of Ziemke et al., (1998). Measurements for latitudes south of 50°S and north of 60°N are not included because there are not enough suitable clouds for using the CCD method. Time coverage extends from January 1979 through December 2005. Total column ozone is derived from low reflectivity (R<0.2) measurements and SCO from nearby column ozone measurements taken above the top of tropopause level clouds under conditions of high reflectivity (R>0.9). Above-cloud column amounts are first evaluated in the Pacific region where tropopause/near-tropopause level clouds are common. SCO is then derived for every 5 degree latitude band for 120°E eastward to 120°W using only the lowest values of above-cloud column amount. These SCO values from the Pacific region are then assumed to represent SCO at all other longitudes in a given latitude band. This assumption is based on the zonal characteristics of tropical SCO as inferred from the ozone data based on Stratospheric Aerosols and Gas Experiment (SAGE), Upper Atmosphere Research Satellite (UARS) microwave limb sounder (MLS)
and halogen occultation experiment (HALOE). TOMS version 8 level -2 footprint measurements were used to construct the data. Sigma uncertainty in these monthly measurements of both stratospheric and tropospheric column ozone is 2.5 DU.
[3.1] Introduction.

The amount of ozone in the atmosphere varies substantially from day to day and also varies with season and latitude. Total columnar ozone over the observing station, its temporal variations and the vertical distribution of ozone are important basic data for studies on morphology and behavior of atmospheric ozone in different parts of the globe. Importance of monitoring of ozone levels on a global basis has increased, in view of the recognition in the early seventies of the possibility of a long term global ozone depletion due to catalytic reactions in the stratosphere involving chemicals released by anthropogenic activities and its possible impact on the biosphere (Subbaraya and Lal, 1999). The discovery of the Antarctic ozone hole in the mid eighties by Joseph Farman, Brian Gardiner and Jonathan Shanklin; a research group from The British Antarctic Survey highlighted the gravity of the problem. The diurnal variation of surface ozone has been studied by several workers like Kaushar Ali et al. (2004) over Himalayan region and Delhi, Satsangi et al. (2004) at Agra and Kulshrestha et al. (1997) at Delhi. However diurnal variation of total ozone in India has been reported by comparatively fewer workers like Raj et al. (2003) at Pune from 1998 – 2003 and Dani et al. (2003) during BOBMEX – 99. The study of variations in columnar
ozone concentration in India has special significance because it is located in the tropical region, where most of the ozone formed is due to the availability of the high dose of solar UV radiation. In view of these considerations, a study of the diurnal and seasonal variations in total ozone concentration at different Indian stations, particularly at Rajkot has been presented in this chapter.

3.2 Monitoring Site, meteorological conditions and measurements at Rajkot.

The total columnar ozone concentration at Rajkot (22.3°N, 70.8°E) is being monitored since June 2004 with the help of Microtops II Sun photometer to study the diurnal and seasonal variability of total ozone. The variations in total columnar ozone and its trend in different atmospheric layers has also been studied using TOMS and SBUV data respectively over the period from 1980 to 2004. Variation of ozone trends with sunspot activity has been studied for Rajkot from 1980-2003. Seasonal variation of ozone at different Indian latitudes has also been studied. The measurements for different meteorological parameters at Rajkot have been obtained from the website www.wunderground.com. The observed results are discussed in this chapter.

Rajkot (22.3°N, 70.8°E) is situated in the Saurashtra region of Gujarat. Total columnar ozone was measured at the Physics department of Saurashtra University from June 2004 to June 2005 using Microtops-II Sun photometer. The measurement site is located on the outskirts of the city. It is a major residential, educational and commercial area. However there are no major industrial areas nearby.
The variation in ozone concentration observed at Rajkot is a combined effect of local meteorological conditions, photochemical processes and long range transport processes which can be seen from the study of diurnal and seasonal variation. A hot summer and dryness in non-rainy seasons characterize the climate of Rajkot district. The year may be divided into four seasons. The winter season extends from December to February followed by summer from March to June, monsoon from July to September and post monsoon (autumn) in October and November.

3.2.1) **Temperature.**

The temperature at Rajkot is found to rise consistently from March to May. May is the hottest month with the mean daily maximum and minimum temperature at about 43 °C and 27 °C respectively. The onset of southwest monsoon by the middle of June slightly lowers the temperature, but the relief from heat is not significant due to the increase in humidity. With the withdrawal of monsoon after mid-September, days become hotter and in October, a secondary maximum in day temperature is reached. The nights become progressively cooler. After mid-November, both day and night temperatures drop rapidly till January which is the coldest month with the mean daily maximum and minimum temperature at 28 °C and 16 °C respectively (*Figure 3.1a*).
3. 2. 2)  **Humidity.**

Dew point is the temperature to which the air must be cooled before it becomes saturated and dew or liquid water will drop out of the air. Closer the
temperature and the dew point, higher is the level of humidity of the air (Figure – 3.1.c). The average rainfall in Rajkot district is about 596 mm. (IMD Report., 1995.) About 95 % of the annual rainfall is received during the southwest monsoon season.ie from June to September, July - August being the months with highest rainfall.

![Humidity levels](image)

**Figure 3.1.c** Humidity levels (Temperature - Dew point in °C) observed at Rajkot in 2004

During the southwest monsoon, the relative humidity is generally over 60 % and the skies are heavily clouded to overcast on most of the days. In the rest of the year, the air is comparatively dry and clear or lightly clouded skies prevail.

3.2.3) **Wind speed and direction.**

Winds are generally moderate, but in summer and southwest monsoon season, they become stronger. The prominent wind directions during summer are NW and W. During monsoon, winds blow from the SW direction. During post
monsoon, the winds blow from ESE, ENE and NE directions. During winter NE, NW and N flow is predominant (Sahu, 2004; Chand et al., 2003).

The total ozone concentration obtained from TOMS at Rajkot is found to vary negligibly with surface temperature (Figure 3.1.e) and wind speed (Figure 3.1d). The dependence of ozone concentration on wind speed is higher in summer compared to the other seasons of the year, which may be due to air blowing from a more polluted area and hence having a higher ozone concentration.

A comparison of columnar ozone measured by TOMS and surface temperatures for different seasons of the year 2004 - 2005 obtained from the website www.wunderground.com indicates that the columnar ozone is directly correlated with surface temperature in summer and monsoon and is inversely correlated with surface temperature in post monsoon (autumn) and winter. This may indicate the dominance of photochemical production of tropospheric ozone over transport processes during monsoon at Rajkot. However, the high level of ozone concentration during summer may be due to a combination of local photochemical production and transport processes. During post monsoon (autumn) and winter, for every $1^\circ$K decrease in temperature, the columnar ozone is found to increase by 9.4 DU and 7.8 DU respectively which may be because the rate coefficient for the loss rate of ozone given by the reaction $O + O_3 \rightarrow 2O_2$, is

$$K(O, O_3) = 8 \times 10^{-12} e^{-2060/T} \text{cc/mol.sec}$$

Thus as temperature decreases, $K(O, O_3)$ decreases, which in turn increases the ozone concentration during post monsoon (autumn) and winter.
Figure 3.1d Variation in total columnar ozone (DU) measured by TOMS at Rajkot with wind speed (meters per hour) in 2004 - 2005.
Figure 3.1e Variation in total columnar ozone (DU) at Rajkot measured by TOMS with surface temperature (°K) in 2004 - 2005.

Summer (March - June)
\[ y = 0.1762x + 261.87 \]
\[ R^2 = 0.4121 \]

Monsoon (July - September)
\[ y = 0.4649x + 273.09 \]
\[ R^2 = 0.2531 \]

Post monsoon (October, November)
\[ y = -0.1065x + 436.23 \]
\[ R^2 = 0.118 \]

Winter (December - February)
\[ y = -0.1286x + 333.31 \]
\[ R^2 = 0.1558 \]
3.3 Study of short term variation of ozone at Rajkot using MICROTOPS II Sun photometer.

3.3.1 Diurnal variation of ozone from June 2004 to June 2005.

The nature of diurnal variation is helpful in determining whether the observational site experiences photochemical production or destruction during the day. A strong diurnal variation during summer with maximum ozone amplitude during afternoon throughout the year indicates ozone production from anthropogenic precursor emissions. The diurnal variation of columnar ozone from June 2004 to June 2005 at Rajkot is found to be in phase with the diurnal variation in surface temperature (Figure 3.1b). Observations for diurnal variation of ozone have been recorded at intervals of twenty minutes to half an hour and have been averaged on an hourly basis for the entire month for days under clear weather conditions. There are fewer observations (of about 6 - 8 days per month) during monsoon and higher number of observations (about 20 days per month) during the rest of the year.

The diurnal variation of ozone measured by MICROTOPS II Sun photometer indicates a higher vertical column density of ozone during morning compared to evening hours (Figure 3.2). The ozone concentration is found to be generally low at sunrise; increase to a maximum in the afternoon (around 12 to 2 pm), and decrease in the evening. This may be due to an increase in temperature from morning to afternoon hours causing corresponding increase in ozone by photochemical formation, as higher temperatures increase the emission rate of ozone precursors. (Valente et al., 1993).
Figure 3.2 *Diurnal variation of total columnar ozone measured with Microtops II Sun photometer at Rajkot from June 2004 to June 2005.*

The daytime temperature at Rajkot is generally low at sunrise, increases rapidly to a maximum in the afternoon (around 1.30 to 2.30 pm) and gradually decreases in the evening (*Figure 3.1b*). The ozone concentration is thus found to follow the diurnal variation of surface temperature. However, unlike the ozone concentration which is found to be maximum around 12.30 pm, the temperature at Rajkot is found to be maximum around 2.30 pm. This time lag indicates, that temperature rise beyond a certain limit might lead to the saturation of photochemical production of ozone. It may also be possible, that there could have been deficiency of ozone precursors at the time when the temperature was at its peak at 2.30 pm. Also, the concentration of ozone at previous hour may be expected to influence the concentration of ozone at the
current hour. (Kaushar Ali et al., 2004) Similar results were observed by Satsangi et al., 2004 at Agra, Kaushar Ali et al., 2004 over Himalayan region and Delhi and Kulshrestha et al., 1997 at Delhi for surface ozone. The amplitude of diurnal variation of ozone observed in different seasons at Rajkot is approximately 3.35% of the total column content. The NO\textsubscript{x} family mainly governs these small diurnal variations in ozone.

The observed pattern of diurnal variation in ozone is found to be almost smooth and similar in summer, monsoon and winter. However, during post–monsoon, the ozone concentration is found to increase sharply from 11.00 am to 12.30 pm and thereafter decrease sharply till 2.00pm. During the rest of the day, the variation is almost smooth and similar to that observed during the other seasons. This may be because the prominent wind direction which is normally from NW and W during summer, SW during monsoon and from NE, NW and N during winter, varies between ESE, ENE and NE during post–monsoon.

Chemical reactions involving ozone production and removal occur within a time scale of few hours (Raj et al., 2004). Ozone is produced through NO\textsubscript{x}-CO-HC reactions during daytime and removed through NO reactions. It may be possible that the wind blowing over Rajkot from ESE, ENE and NE directions during post–monsoon has significant amount of NO\textsubscript{x}, CO and HC concentration providing the potential for ozone production between 11 am to 12.30 pm. Moreover, vehicular traffic is also at its peak between 10.30 am to 12 pm resulting in enhanced ozone concentration in the lower troposphere. However, systematic measurements of NO\textsubscript{x}, CO, methane and NMHC’s which
are currently not available at Rajkot, along with ozone measurements are required to arrive at any definite conclusion.

The amount of ozone present in the upper stratosphere (above 40 km) is about 3% of the total column content and the time required to attain photochemical equilibrium is less than one day. Here the variations in ozone occur with the daily rising and setting of the sun and are therefore called diurnal because they happen every day. At such altitudes, photo dissociation processes within the odd oxygen family govern the daily ozone cycle. (Brasseur et al., 1986) The diurnal variation of ozone above 40 km, as observed by Wilson et al., 1980 and Chapman, 1930 indicates a rapid decay at sunrise, followed by a daytime minimum around 4 pm and a rapid rise at sunset due to recombination of atomic oxygen forming ozone. This is opposite to the diurnal pattern of total ozone observed at Rajkot which may indicate a comparatively smaller influence of upper stratospheric ozone and a larger contribution of the ozone present below 5 km altitude, which also has a short lifetime. (Mandal et al., 2004). The diurnal variation in ozone concentration at Rajkot indicates a maximum standard deviation (SD) in winter, followed by monsoon, autumn & summer. Similar results have been observed by London., 1979 for different latitudes in the northern hemisphere.
### Monthly variation of ozone in 2004 – 2005

[Figure 3.3](#) *Monthly mean ozone measured with Microtops II Sun photometer at Rajkot from June-2004 to June 2005. Bars indicate $2\sigma$ variation.*

The factors affecting photochemical formation of ozone are intensity of solar radiation, air temperature, wind speed and direction. Monthly mean maximum and minimum temperature measured at Rajkot airport is shown in *figure 3.1a*. An examination of the monthly mean values of ozone obtained from MICROTOPS II Sun photometer indicates marked temperature dependence with maximum amplitude in June / July and a minimum in December suggesting the dominance of photochemical production (*Figure 3.3*). The ozone concentration at Rajkot is found to be maximum around June - July. It decreases during monsoon and post monsoon and reaches a minimum in December. Thereafter it gradually increases throughout the winter and reaches a peak in summer. The amount of ozone in the troposphere and lower stratosphere in general depends on both dynamics
and chemistry. The dynamical influences include wave driving of the stratospheric circulation and tropopause folds. The chemistry part includes the photochemical production and destruction of O$_3$.

The primary cause of large values of ozone in June may be the high solar flux acting upon a pool of accumulated NO$_x$ and hydrocarbons built up during winter resulting in local photochemical production.

\[
\begin{align*}
OH + CO &\rightarrow H + CO_2 \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow NO_2 + OH \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M \\
\text{Net: } CO + 2O_2 &\rightarrow CO_2 + O_3
\end{align*}
\]

\(\text{(3.1)}\)

The general wind pattern from NW & W direction takes the polluted continental air down to Rajkot during summer. The Asian region is a fast developing region with increasing levels of pollution from industries and other manmade sources. O$_3$ is produced by the photo oxidation of pollutants (carbon monoxide & hydrocarbons) in the presence of adequate amount of nitrogen oxides at lower altitudes. Once O$_3$ is produced it gets transported along with the wind resulting in a high concentration in summer. A factor more recently linked to the annual ozone cycle is the intercontinental transport of pollution. The same atmospheric mechanism responsible for the transport of Asian desert dust during spring has been shown to transport primary emissions and ozone (Vingarzan, 2004). The Arabian Sea lies to the south and west of Rajkot. During monsoon the pristine air
from the Arabian Sea blows over Rajkot resulting in decrease in O₃ concentration due to wash out effects by pure monsoonal air masses.

The reaction rate coefficients that determine photochemical loss rates are temperature dependant. The rate coefficient for the reaction O+O₃ → 2 O₂ as a function of temperature is given by:

\[ K(O, O_3) = 8 \times 10^{-12} e^{-2060/T} \text{ cc/mol/sec} \]

Thus the loss rate of ozone decreases by about 30% for every 10 deg fall in temperature in winter.

Another factor that contributes for the increase in ozone concentration from December to February is the long photochemical lifetime of ozone in winter (approximately 200 days) in the lower stratosphere. This is because the sun’s angle is quite low during winter and the lower stratospheric ozone is effectively shielded from the UV radiation by the ozone in the upper stratosphere. Thus ozone in the lower stratosphere is safe from destruction by photochemical processes. This accumulation of ozone rich air over the entire winter period leads to an increase in concentration from December to February in winter.

**[3. 4] Long term variation of total ozone at Rajkot using TOMS data.**

The total ozone at Rajkot and its distribution in various atmospheric layers has been studied using TOMS and SBUV data respectively over the period from 1980 to 2004.

3. 4.1) **Seasonal variation of ozone from 1996 – 2004.**

The amount of ozone in the upper stratosphere (above 40km) is about 3% of the total ozone. Thus the variations occurring above 40 km have little measurable
effect on the total ozone column. The variation of ozone in the lower stratosphere where its density is maximum (87%) and in the troposphere (10%) has a measurable effect on the total amount of ozone. Seasonal variation of total columnar ozone is difficult to account for, since the major contribution to total columnar ozone comes from the lower stratosphere, where photochemical life times are of the order of several months to years. (Banks and Kockarts., 1973) Thus seasonal changes in columnar ozone are not expected unless there is a significant variation in tropospheric ozone below 5 km.

![Graph showing monthly mean total ozone values obtained from the TOMS for Rajkot from Aug. 1996 to June 2004.](image)

**Figure 3.4** Monthly mean total ozone values obtained from the TOMS for Rajkot from Aug. 1996 to June 2004.

The monthly mean columnar ozone values obtained for the location of Rajkot from the TOMS data are plotted against months for the period from Aug. 1996 to June 2004 (Figure 3.4). It shows a clear seasonal variation that is repeated consistently year after year. The ozone concentration is found to be maximum around May –June. It decreases during monsoon and autumn and
reaches a minimum in December. Thereafter it gradually increases throughout the winter and spring and reaches a peak in summer. This trend is consistently observed in all the years from 1996 to 2004 (as shown in Figure 3.4). Chakrabarty et al., 1979 have observed similar results for other Indian stations.


Variation of ozone trends with sunspot activity has been studied for Rajkot from 1980 - 2003 (Figures 3.5 & 3.6). The UV output of the sun increases as sunspot activity increases. The production rate of ozone should be high when solar activity is at its maximum and decrease when solar activity is at its minimum. It is found that the monthly averaged ozone variation is in phase with the monthly averaged sunspot variations. Ruderman et al., 1975 have suggested that during solar minimum condition, there is an increase in the low energy cosmic rays in the earth’s atmosphere, which will increase NOx and decrease ozone. Thus the ozone concentration is expected to decrease during solar minima, which is observed in this study (as in 1986 and 1996). Similarly, the ozone concentration during solar maxima (1989 and 2000) is found to be higher than that observed during the other remaining years of the solar cycle.
Figure 3.5 11-Year solar cycle.

Figure 3.6 Total columnar ozone measured by TOMS over Rajkot from 1979 to 2003.
[3. 6] **Latitudinal variation of ozone.**

The monthly mean ozone data for different Indian stations obtained from TOMS for the year 2003 indicates that the columnar ozone concentration increases as we move northwards from Kanyakumari to Srinagar, *(Figure 3.7)* i.e. with increasing latitude. This is because ozone is produced at the tropics and then transported to the poles where it is relatively inert photo chemically. *Chakrabarty et al., 1979* have observed similar results for other Indian stations. The Hadley cell circulation observed in India is different compared to that observed globally due to the presence of the Himalayas *(Chakrabarty et al., 1984; Mani et al., 1973; Chakrabarty et al., 1997)* The air ascends near $24^\circ$N and descends in the higher latitudes near the Himalayas to give a pole ward drift in the upper air, with a return current towards $24^\circ$N at the surface. The upwelling of the Hadley cell circulation is usually felt up to the tropopause, but sometimes it also reaches the lower stratosphere. This reverse Hadley cell circulation may have a pronounced effect on the distribution of the ozone at different locations in the Indian subcontinent resulting in an earlier peak in ozone concentration during summer at Srinagar ($34^\circ$N) compared to Kanyakumari ($8^\circ$N).
Figure 3.7 Seasonal variation of total ozone measured by TOMS in the year 2003 at different latitudes.

The atmospheric circulation is such that it transports ozone during winter from low latitudes to poles. This transport is responsible for springtime maxima at higher latitudes. The transport is less rapid during summer and the maxima gradually decays and moves to lower latitudes. (Goody et al., 1972.)


Singh et al., 2002 have reported an increasing trend in columnar ozone for the period 1996 - 2000 for Kodaikanal and Delhi, which matches with the observations for Rajkot (Figure 3.6). However if the period of observation is extended to 2004, then an over all down ward trend in the total O₃ is observed from 1996 to 2004 (Figure 3.4). It is observed from the trend analysis, that there is an insignificant change in the columnar ozone concentration from 1996 to
2004, which may be due to the global decrease in CO concentration. (Novelli. et al., 1994; Khalil et al., 1994). The production of tropospheric ozone is mainly from CO and CH$_4$ in presence of hydrocarbons and nitrogen oxides. Hence a decrease in chemical fuels may ultimately lead to a decrease in the production of NO$_2$, consequently affecting the ozone production. (Saraf et al., 2004.)

![Figure 3.8](image.png)

**Figure 3.8** Variation in spring time ozone in different atmospheric layers at Rajkot from 1982 to 2003 using SBUV technique.

The average ozone concentration from 1$^{st}$ to 15$^{th}$ March has been used to study the distribution of ozone and its variations in different atmospheric layers during springtime at Rajkot using SBUV data. It is observed that the stratospheric ozone concentration at Rajkot has decreased consistently from 1982 to 1999. (Figure 3.8) This may be due to the catalytic destruction of ozone by CFC’s, bromine and oxides of nitrogen (NO$_x$), which are produced in the stratosphere by
the reaction of O¹D with N₂O (which is released from the biosphere below) and from the emission of supersonic aircraft. NOₓ is the most important destroyer of ozone in the 25 - 45 km altitude region. Bromine takes part in catalytic destruction of ozone and is 40 times more reactive than Cl₂ in ozone depletion.

The catalytic cycles of ozone destruction can be illustrated by:

\[
\begin{align*}
O_3 + X & \rightarrow O_2 + OX \\
OX + O & \rightarrow O_2 + X \\
\text{NET: } O_3 + O & \rightarrow 2 O_2
\end{align*}
\]

Where X is a radical, which goes through the catalytic cycle, destroys ozone and is recovered at the end of the reaction cycle. X can belong to the NOₓ, ClOₓ, HOₓ or Br family. (Subbaraya et al., 1999)

The ozone concentration is found to have increased suddenly in 2000 and further in 2001. Thereafter it decreased in 2002 and again increased in 2003. This recovery may be attributed to the efforts of international agreements like Montreal Protocol to reduce emissions due to CFC’s.

It is observed from figure 3.8, that maximum variation in ozone concentration is observed in the altitude range from 15.5 to 37.5 km. Thus the variation in ozone concentration in this altitude range has a measurable effect on the total amount of ozone. Beyond 37.5 km, the O₃ profile is found to remain constant from 1982 - 2003.
Every living organism has limits to the environmental conditions it can endure. Temperature, moisture level, living space, solar radiation and other environmental factors must be within appropriate levels for life to persist. Ecologist Victor Shelford stated in 1913, that each environmental factor has both minimum and maximum levels called tolerance limits beyond which a particular species finds it difficult to survive (Odum, 1971). The greatest abundance of any species along an environmental gradient is around the optimum level of the critical factor most important for that species as shown in figure 4.1. Near the tolerance limits, the abundance decreases because fewer individuals are able to survive the stress imposed by limiting factors.
The role of atmospheric ozone to protect living organisms and vegetation from the harmful effects of ultraviolet irradiation is well known. Although ozone represents only a tiny fraction of the atmosphere, it is crucial for life on Earth. Depending on where ozone resides, it can protect or harm life on Earth. In the Earth's stratosphere (about 15 to 50 km altitude from the Earth's surface), ozone acts as a shield to protect the Earth's surface from the sun's harmful ultraviolet radiation. Without this shield, we would be more susceptible to sunburn, skin cancer, cataracts and suppressed immune systems. Closer to Earth, in the troposphere, (up to about 15 km altitude from the earth's surface) however, in the
air which we breathe, ozone is a harmful pollutant that causes damage to lung tissue and plants and also causes the global temperature to rise. The amount of "good" and "bad" ozone in the atmosphere depends on a balance between the processes that create ozone and those that destroy it. An upset in the ozone balance can have serious consequences for life on earth. Human production of chlorine-containing chemicals such as chlorofluorocarbons (CFC’s) has created an additional ozone-destroying force.

Most of the UV radiation reaching the surface is UV-A. Due to the higher energy levels of UV-B, however, the UV-B component has more effect on flora and fauna than UV-A. An action spectrum is a parameter function, which describes the relative effect of energy at different wavelengths in producing a certain biological response. These effects may be at a molecular level, such as DNA damage, or at the level of the whole organism, such as plant growth. The CIE action spectrum for erythema (reddening of the skin due to sunburn) was proposed by McKinlay et al., 1987 and was adopted as a standard by the International Commission on Illumination.

The erythemal UV index is integration between 280 and 400 nm of the UV irradiance at ground level, weighted with the erythemal action spectrum. The DNA-damage UV index is integration between 256 and 370 nm of the UV irradiance at ground level, weighted with the DNA-damage action spectrum. The mammalian non-melanoma skin cancer action spectrum lies between the erythemal and DNA-damage action spectrum.
The consequences of increased exposure of the human body to UV-B radiation will in the first instance be characterized by the physical properties of this type of radiation. UV-B radiation does not penetrate far into the body; most of it is absorbed in the superficial tissue layers of 0.1 mm depth (Figure 4.2). This limits the primary effects to the skin and the eyes. There are, however, also systemic effects, which start with a primary reaction in the superficial layers, but have consequences throughout the body.

**FIGURE 4.2:** A cross-section of the human skin and underlying tissue, showing the depth to which UV radiation penetrates.

The thickness of the epidermis, roughly 50 micro-meters, is about half the thickness of a page of paper. The sunlight reaching us consists of only approximately 0.5% UV-B radiation, in terms of radiant energy. Yet this small fraction is responsible for most of the effects of sunlight on the body. It is the main cause of sunburn and tanning, as well as the formation of vitamin D$_3$ in the skin, and it has influences on the immune system. UV-B radiation is also the main cause of snow blindness and an important factor in the induction of
cataracts. UV-B radiation contributes significantly to the aging of the skin and eyes, and is effective in causing skin cancer.

The World Meteorological Organization (WMO) after serious deliberations recommended during the seventies that a good network of ground-based measurements of solar UV-B radiation be established to monitor the magnitudes of these radiations and their long and short-term trends on regional and global basis. Realizing the importance of these recommendations, National Physical Laboratory at New Delhi in India, started the regular measurements of UV-B radiations as early as 1979 (Singh et al., 2004). Later on similar measurements were extended to 6 additional sites to cover the different types of geographic and environmental conditions in India during the Indian middle atmospheric programme in the eighties. Extensive ground based and satellite measurements and model calculations have thereafter been done to analyze the UV irradiance, particularly in the UV-B and erythemal region both in India and abroad (Blumthaler et al., 1994; Zerefos et al., 1995; Herman et al., 1996; Bodhaine et al., 1997; Herman et al., 1999).

In view of these considerations, the lethal effects of stratospheric ozone depletion and the ozone and erythemal UV scenarios for different Indian latitudes varying from $10^\circ$N to $35^\circ$N from 1979 to 2005 have been discussed in this chapter. The expected upper and lower tolerance limits (UTL and LTL) for tropospheric and stratospheric ozone respectively in these latitude ranges have also been estimated statistically (Gupta et al, 1993), from mean chart using

[4.2] **Data and analysis.**

The monthly mean erythemal UV irradiance data obtained from Nimbus - 7 and Earth probe TOMS and the monthly mean tropospheric and stratospheric ozone data obtained from convective cloud differential (CCD) method of Ziemke et al., 1998; have been used to study the trend of erythemal UV, the stratospheric column ozone (SCO) and tropospheric column ozone (TCO) concentration respectively at different Indian latitudes varying from 10°N to 35°N over a period from 1979 - 2005. The expected upper and lower tolerance limits for tropospheric and stratospheric ozone respectively at these latitudes have been estimated statistically from mean chart using CCD data from 1979 – 2005. TOMS version 8 level - 2 footprint measurements were used to construct the CCD data. Sigma uncertainty in these monthly measurements of both stratospheric and tropospheric column ozone is 2.5 DU.

There may be errors due to instrumental uncertainties in the data of erythemal UV for different Indian cities obtained from TOMS and the ones estimated by the CCD method. I have not made any effort to synthesize them, and have assumed that these uncertainties have been reduced while taking the average of a large number of observations over a period of 27 years, which have been directly taken from TOMS and CCD model.
[4.3] Results and discussions.

4.3.1) **Trend of columnar stratospheric and tropospheric ozone in India from 1980 – 2005.**

The variations in columnar stratospheric and tropospheric ozone over a period of 27 years from 1979 – 2005 for different Indian latitudes using monthly mean convective doud differential (CCD) ozone data are indicated in *figures 4.3 and 4.4* respectively.
Figure 4.3  Trend of monthly mean stratospheric column ozone in Dobson Unit (DU) determined from CCD method of Ziemke et al., 1998 for Indian latitudes from 1979 - 2005.
Figure 4.4 Trend of monthly mean tropospheric column ozone in Dobson Unit (DU) determined from CCD method of Ziemke et al., 1998 for Indian latitudes from 1979 - 2005.

The observed depletion in columnar stratospheric ozone (SCO) and increase in columnar tropospheric ozone (TCO) at different Indian latitudes during this period are indicated in table 4.1.

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

Table 4.1 Observed depletion in columnar stratospheric ozone (SCO) and increase in columnar tropospheric ozone (TCO) at different Indian latitudes from 1979 – 2005 using CCD data.

According to the estimates made by Vander Leun et al., 1993, 1% decrease in total stratospheric columnar ozone will lead to 2.3 % increase in non-melanoma
skin cancer, 2% increase in cutaneous melanoma and 0.5 % increase in the incidence of cataracts. Therefore, the expected increase in non-melanoma skin cancer, cutaneous melanoma and the incidence of cataracts at different Indian latitudes over a period of 27 years from 1979 – 2005 according to the estimates made by Vander Leun et al; can be summarized as shown in table 4.2.

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Non melanoma skin cancer</th>
<th>Cutaneous melanoma</th>
<th>Cataracts</th>
</tr>
</thead>
<tbody>
<tr>
<td>10° N to 15° N</td>
<td>0.529%</td>
<td>0.46 %</td>
<td>0.115 %</td>
</tr>
<tr>
<td>15° N to 20° N</td>
<td>0.723 %</td>
<td>0.63%</td>
<td>0.16 %</td>
</tr>
<tr>
<td>20° N to 25° N</td>
<td>1.07 %</td>
<td>0.93 %</td>
<td>0.23 %</td>
</tr>
<tr>
<td>25° N to 30° N</td>
<td>1.27 %</td>
<td>1.10 %</td>
<td>0.28 %</td>
</tr>
<tr>
<td>30° N to 35° N</td>
<td>1.55 %</td>
<td>1.35 %</td>
<td>0.34 %</td>
</tr>
</tbody>
</table>

**Table 4.2** Expected increase in non-melanoma skin cancer, cutaneous melanoma and incidence of cataracts at different Indian latitudes from 1979 – 2005 according to the estimates made by Vander Leun et al., 1993

Hence according to the survey and calculations done by Vander Leun et al, it appears that the columnar stratospheric ozone concentration in India from 1979 – 2005 was within safe limits and its insignificant decrease might not have had any additional major negative impact on human beings. Minassian et al., (1990), estimated that 3.8 million people in India become blind from cataract each year. It is however difficult to determine practically, the actually observed percentage of increase in new cases of non-melanoma skin cancer, cutaneous melanoma and cataracts in India due to decrease in SCO, as the population in India is increasing rapidly and there is also an increase in average overall life time. As a
result of these two factors, the population aged over 60 years will double during the next 20 years from approximately 400 million now, to around 800 million in 2020 (Foster Allen, 2000). This increase in the elderly population will result in a greater number of people with cataracts.

It is also observed that the tropospheric ozone level has not increased significantly for Indian latitudes over the past 27 years. This implies that Indian latitudes may be safe from the lethal effects of ozone pollution and global warming due to ozone.

4.3.2) **Trend of erythemal UV irradiance in India from 1979 – 2003.**

A study of monthly mean erythemal UV irradiance at Chennai (13.08°N, 80.19°E, 60 m above sea level), Pune (18.29°N, 73.57°E, 560 m above sea level), Rajkot (22.3°N, 70.8°E, 182 m above sea level), New Delhi (28.38°N, 77.17°E, 213 - 305 m above sea level) and Srinagar (34.5°N, 74.5°E, 1730 m above sea level) indicates that there is an insignificant change in UV irradiance from January 1979 to July 2003 (Figure 4.5).

The erythemal UV levels in India are found to increase as latitude decreases as shown in *figure 4.5*. The monthly mean erythemal UV irradiance is found to decrease negligibly at Chennai, Pune and Rajkot and is found to increase insignificantly at New Delhi and Srinagar from 1979 to 2003 as shown in *table 3*, indicating that Indian latitudes lie within safe limits of the negative impacts of ozone depletion and increase in erythemal UV irradiance.
Figure 4.5 Trend of monthly mean erythemal UV irradiance measured by TOMS over Indian cities from 1979 to 2003.
According to the estimates made by *Ratan Dasgupta et al., 1995*, it is likely that 10% decrease in SCO will lead to 20% increase in UV irradiance. However, since the observed increase in erythemal UV at these stations is less than that estimated by *Ratan Dasgupta et al., 1995*, it may imply that apart from stratospheric ozone, which is the most important factor, other atmospheric conditions such as boundary layer aerosol (tropospheric particulates), clouds, boundary layer ozone, urban pollutants, surface elevation and reflectivity may also have a significant impact on the amount of erythemal UV reaching the ground. *Kuchinke et al., 1999*, estimated the amount of UV-B erythemal irradiance transmitted by clouds at two locations in southwest Sweden and found that the cloud transmission of UV-B irradiance decreases with increasing cloud cover. Overcast cloud conditions reduce transmissions by an average of 75%. In addition, cloud type affects the amount of ground incident irradiant flux. Fractus clouds afford the least UV-B transmission (0.16), while cirrus filaments afford the most (0.95). *Norris J R (2001)*, observed high concentrations of soot aerosol over the northern Indian Ocean during the Indian Ocean Experiment (INDOEX – 1999) in January-April, when air flows offshore from India. The soot particles were found to absorb and scatter a substantial amount of solar radiation. He also observed that soot aerosols have greatly increased over the past fifty years due to population growth and development in India. This absorption along with scattering led to a large reduction of UV and visible wavelength solar radiation at the surface (*Ramanathan et al., 2005*). Apart from this, *Norris, J. R., 2001*, has observed that the total cloud cover and low-level cloud cover has also increased
between 1952-69 and 1980-96 at all latitudes over northern Indian Ocean. Latitudinal trends are smallest at Northern Hemisphere middle latitudes. Basu BK (2001), found that cloud cover is less over the central and northern parts of India. These may be the reasons why the observed increase in erythemal UV in India from TOMS data is less than that estimated by Ratan Dasgupta et al., 1995. This also supports the fact that the erythemal UV irradiance is found to exhibit a decreasing trend at places like Chennai, Pune and Rajkot located at low latitudes due to increase in cloud cover and soot aerosol, and a negligible increasing trend at Delhi and Srinagar located in northern India due to comparatively lesser cloud cover.

<table>
<thead>
<tr>
<th>Indian City</th>
<th>Depletion in SCO from 1979 - 2005</th>
<th>Variation in erythemal UV from 1979 - 2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chennai (13.08°N, 80.19°E)</td>
<td>0.23 %</td>
<td>0.19 % decrease</td>
</tr>
<tr>
<td>Pune (18.29°N, 73.57°E)</td>
<td>0.31 %</td>
<td>0.11 % decrease</td>
</tr>
<tr>
<td>Rajkot (22.3°N, 70.8°E)</td>
<td>0.46 %</td>
<td>0.08 % decrease</td>
</tr>
<tr>
<td>Delhi (28.38°N, 77.17°E)</td>
<td>0.55 %</td>
<td>0.55 % increase</td>
</tr>
<tr>
<td>Srinagar (34.5°N, 74.5°E)</td>
<td>0.68 %</td>
<td>0.54 % increase</td>
</tr>
</tbody>
</table>

Table 4.3 Observed depletion in SCO from CCD ozone data and variation in erythemal UV irradiance from TOMS data for different Indian cities.
4.3.3) **Statistical estimation of upper and lower tolerance limits for tropospheric and stratospheric ozone in India.**

A statistical control chart is essentially a time plot of observations with control limits (tolerance limits) added. The control limits indicate that, when the variability of the process is large, some special cause is likely to be operating. When an observation exceeds the upper tolerance limit (UTL), or lies below the lower tolerance limit (LTL), a search for the special cause should be initiated. The upper and lower tolerance limits for tropospheric and stratospheric ozone respectively at different Indian latitudes has been calculated statistically \cite{Gupta et al, 1993} from the mean control chart using the monthly mean convective cloud differential (CCD) ozone data from 1979 – 2005.

The LTL for stratospheric ozone and UTL for tropospheric ozone are given by the relations

\[
\text{LTL} = \bar{X} - A_2 \bar{R}
\]

\[
\text{UTL} = \bar{X} + A_2 \bar{R}
\]

Where \( \bar{X}_k \) is the yearly mean columnar ozone for \( n = 12 \) months of the \( k^{th} \) year. Range \( R_k = (\text{Maximum ozone} - \text{Minimum ozone}) \) observed for the \( k^{th} \) year. \( k = 1, 2, 3, \ldots, 25 \) (years from 1979 – 2005; data for the years 1994 and 1995 are not available.)

\[
\bar{X} = \frac{\sum \bar{X}_k}{25}
\]

\[
\bar{R} = \frac{\sum R_k}{25}
\]
The value of constant $A_2$ corresponding to $n = 12$ is 0.266, and is obtained from standard statistical control table (Gupta et al, 1993).

<table>
<thead>
<tr>
<th>Latitude</th>
<th>LTL for stratospheric ozone</th>
<th>UTL for tropospheric ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°N to 15°N</td>
<td>224.36 DU</td>
<td>28.25 DU</td>
</tr>
<tr>
<td>15°N to 20°N</td>
<td>224.74 DU</td>
<td>32.46 DU</td>
</tr>
<tr>
<td>20°N to 25°N</td>
<td>226.52 DU</td>
<td>37.19 DU</td>
</tr>
<tr>
<td>25°N to 30°N</td>
<td>231.50 DU</td>
<td>40.45 DU</td>
</tr>
<tr>
<td>30°N to 35°N</td>
<td>237.00 DU</td>
<td>47.1 DU</td>
</tr>
</tbody>
</table>

**Table 4.4** The upper tolerance limit (UTL) for tropospheric ozone and lower tolerance limit (LTL) for stratospheric ozone at different Indian latitudes, calculated statistically (Gupta et al, 1993) from the mean control chart using the monthly mean convective cloud differential (CCD) ozone data from 1979 – 2005

The tropospheric ozone values at different Indian latitudes should ideally be less than the respective upper tolerance limit indicated in table 4.4. However, the tropospheric ozone in the 10°N to 15°N latitude range is found to be slightly higher by 1.43 DU in 1993 and in the 15°N to 20°N latitude range by 0.03 DU in 1990 respectively than the UTL as shown in figure 4.6. The observed negligible high value of ozone in 1990 may be because the year 1990 lies close to the 11 year solar maxima, which is associated with maximum sunspot activity. The UV output of the sun increases as sunspot activity increases. The production of ozone is more sensitive to variations in solar UV output than the loss rate of ozone. Thus the production rate of ozone should be high when solar activity is at its maximum.
Similarly, the columnar stratospheric ozone values at different Indian latitudes should be ideally higher than the respective lower tolerance limit as indicated in table 4.4. However, the stratospheric ozone in the 10°N to 15°N, 15°N to 20°N and 20°N to 25°N latitude ranges are found to be lower than the LTL in the year 1993 by 6.21 DU, 10.64 DU and 2.22 DU respectively and in the 25°N to 30°N and 30°N to 35°N latitude ranges in 1996 by 4.3 DU and 12.7 DU respectively as shown in figure 4.7.

Volcanic eruptions are potential sources of SO$_2$, HCl, BrO and H$_2$O in the lower stratosphere. SO$_2$ emitted from the volcanoes gets converted into H$_2$SO$_4$ and condenses into small aerosol particles in the stratosphere. These aerosol clouds provide an increased scope for heterophase chemistry and enhanced ozone depletion. Volcanic particles generally take two or three years to settle out of the stratosphere. The low value of stratospheric ozone observed in 1993 may be due to the effect of a major volcanic eruption from Mount Pinatubo on the island of Luzon (15°N, 120°E) in Philippines in June 1991. After this eruption, ozone loss by different amounts was reported from different parts of the world in 1992 – 1993 (Gleason et al. 1993). The low value of ozone in observed in 1996 in the 25°N to 30°N and 30°N to 35°N latitude ranges may be due to the effect of a major volcanic eruption from Kliuchevskoi (56.06°N, 160.64°E), which is one of the most active volcanoes of the Kamchatka Peninsula in far eastern Russia. On 1st October 1994, a giant eruption occurred and a cloud of ash rose 15 - 20 km above the volcano. Apart from this, the year 1996 also corresponds to solar minima. Ruderman et al., 1975, have suggested that during solar minimum
condition, there is an increase in the low energy cosmic rays in the Earth’s atmosphere, which will increase NO\textsubscript{x} and decrease ozone. The depletion in stratospheric column ozone observed 1996 may be due to the combined effects of the Kliuchevskoi volcanic eruption in Russia and solar minima.
Figure 4.6 Mean chart representing the upper tolerance limit (UTL) for tropospheric column ozone (TCO) for Indian latitudes calculated using yearly mean CCD data from 1979 – 2005.
Figure 4.7 Mean chart representing the lower tolerance limit (LTL) for stratospheric column ozone (SCO) for Indian latitudes calculated using yearly mean CCD data from 1979 – 2005.
CHAPTER 5

Effect of El Niño southern oscillation (ENSO) and solar storms on the ozone concentration of Indian cities.

The Earth’s atmosphere is a dynamic system. Storms, volcanic eruptions and pollution shove particles up into the stratosphere, while large storms pull ozone down from the stratosphere into the lower atmosphere. The mechanism that causes the chemicals to move up and down between the layers of the atmosphere is of prime interest to scientists’ worldwide.

[5.1] Introduction.

The effect of El Niño southern oscillation (ENSO) on the ozone concentration at Kanyakumari (8°N, 77.6°E), Rajkot (22.3°N, 70.8°E), Delhi (28.5°N, 77.3°E) and Srinagar (34°N, 75°E) is studied using the data obtained from Total Ozone Mapping Spectrometer (TOMS) and Tropospheric ozone residual method (TOR).

The El Nino current arises as the ocean and atmosphere interact to balance Earth’s thermal energy. Large scale weakening of the trade winds and warming of the surface layers in the eastern and central equatorial Pacific Ocean characterizes El Niño. El Niño events occur irregularly at intervals of 2 - 7 years, although the average is about once every 3 - 4 years. They typically last for about 12 -18 months. During El Niño, unusually high atmospheric sea level pressure develops in the western tropical Pacific and Indian Ocean regions, and unusually low sea level pressure develops in the southeastern tropical Pacific.
The coupled oceanic-atmospheric character of ENSO can be explained with the help of the Multivariate ENSO Index (MEI). The MEI is a weighted average of the main ENSO features contained in the following six variables: sea-level pressure, the east-west and north-south components of the surface wind, sea surface temperature (SST), surface air temperature, and total amount of cloudiness.

![Multivariate ENSO Index](image)

*Figure 5.1a Multivariate ENSO index*

When this index is negative, we have a La-Niña (or ocean cooling), and when it is positive, we have an El-Niño (or ocean warming) as shown in Figure 5.1a. The seven biggest El Niño events since 1950, including 1997/98 are compared in Figure 5.1a. The first three events (1957/58, 65/66, and 72/73) featured an early warming in the far eastern Pacific and reached their standardized peaks before the end of the first year. The more recent El Niño events (1982/83, 86/87, and 91/92) took longer to mature, typically reaching their peaks in the spring of the second year. Early 1983 saw the peak of the biggest El Niño of the century, while 1997/98 featured two peaks just below the 1982/83 El Niño, one in July/August 1997, and one in February/March 1998.
Normally, the waters of the eastern Pacific Ocean near South America are quiet cool as a result of upwelling ocean currents. The tropospheric trade winds normally traverse from east to west in this region. However in an El Niño period, the trade winds weaken, allowing the warmer waters of western Pacific to migrate eastwards. This change in temperature of the sea surface water causes large-scale shifts in the global circulation patterns in the troposphere and lower stratosphere, which in turn affects the transport of ozone in these regions (Figures 5.1 b & c). This oscillation is very irregular, with a period of 4 to 7 years between episodes. Although there is a general tendency to hold El Niño responsible for almost anything unusual that happens anywhere, relationships between El Niño and rainfall, floods and droughts are well established. The effect of El Niño on ozone is being studied globally, but it needs investigation by the scientific community in greater details.

**Figure 5.1b** Global circulation pattern in the troposphere and lower stratosphere, during El Niño condition.
Figure 5.1c Global circulation pattern in the troposphere and lower stratosphere, during normal condition.

Hasebe, 1984 studied the interannual variations of total ozone (1970-1977) and found the oscillation with a period of about four years (FYO). The sea surface temperature in the equatorial eastern Pacific and the FYO of total ozone have a good correlation. When El Niño takes place, the Brewer-Dobson circulation enhances the ozone transport in the stratosphere. Therefore, the total ozone increases in the extratropics and decreases in the tropics (Koji Yamazaki et al, 1988) Singh et al. 2002 studied the effect of El Niño on total ozone. They observed anomalous high values of total ozone around Jan-Mar 1998 at Delhi, Lhasa and Beijing, which was found to coincide with high SST increase over the equatorial Indian Ocean due to the strong El Niño effect. Chandra., 1998 observed that during an El Niño period, total ozone decreases by 4-8 DU in the eastern Pacific and increases by about 10-20 DU in the western Pacific.

The effect of El Niño southern oscillation on the total ozone concentration at Kanyakumari (8°N, 77.6°E), Rajkot (22.3°N, 70.8°E), Delhi (28.5°N, 77.3°E)
and Srinagar (34°N, 75°E) is studied using the data obtained from Total Ozone Mapping Spectrometer (TOMS). The tropospheric ozone data obtained from the Tropospheric Ozone Residual (TOR) method for the years 1980 - 1998 for these stations has also been studied to determine the impact of El Niño on tropospheric ozone. There may be errors due to instrumental uncertainties in the data of different Indian cities obtained from TOMS and the ones estimated in the TOR method. I have not made any effort to synthesize them, and have assumed that these uncertainties have been reduced while taking the average of a large number of observations which have been directly taken from TOMS and TOR model.

[5.2] **Effect of ENSO on the total ozone concentration.**

An examination of the yearly mean values of total ozone from 1980 to 2003 (Figure 5.2) indicates that the total ozone concentration decreases in the tropics (Kanyakumari) and increases in the extra tropics (Srinagar and Delhi) during an El Niño period. This is because, when El Niño takes place, the Brewer-Dobson circulation enhances ozone transport in the stratosphere. *Koji Yamazaki et al., 1988* observed similar results in their atmospheric general circulation model (GCM). The total ozone concentration at Rajkot, situated close to the border of tropical and extra-tropical region, is found to be higher during an El Niño period compared to neutral period except in 1990 and 2000. This may be because the neutral years 1990 and 2000 also correspond to the solar maxima years of the 11 year solar cycle, which is associated with maximum sunspot activity. The UV
output of the sun increases as sunspot activity increases which in turn increases the production rate of ozone (Ganguly et al., 2005).

Figure 5.2 Effect of El Niño southern oscillation on total ozone concentration obtained from TOMS.

[5.3] **Effect of ENSO on tropospheric ozone concentration.**

An examination of the effects of El Niño on the tropospheric ozone (Figure 5.3) derived from Tropospheric Ozone Residual method (TOR) at these four stations indicates that the tropospheric ozone is higher at Srinagar, Delhi and Rajkot during an El Niño period compared to neutral period except in 1990 -1993 (Srinagar and Delhi) and 1989 – 1990 (Rajkot). This low value of observed ozone level in the period 1990 – 1993 may be due to the effect of a major volcanic eruption from Mount Pinatubo in Philippines in June 1991. After this
eruption, ozone loss by different amounts was reported from different parts of the world in 1992 – 1993 (Gleason et al., 1993). No significant ozone trend is observed at Kanyakumari (Figure 5.3).

Figure 5.3 Effect of El Niño southern oscillation on tropospheric ozone determined from TOR method.


The Tropospheric ozone values for these stations obtained from the TOR model were subtracted from the total ozone values obtained from TOMS to obtain and study the variations in stratospheric ozone (Figure 5.4). Unlike the Tropospheric ozone, the stratospheric ozone at Kanyakumari is found to decrease during an El
Niño period similar to the variations in total ozone. The trend of stratospheric ozone at Srinagar and Delhi is found to be opposite to that of total and tropospheric ozone. The stratospheric ozone at these stations is found to be lower during an El Niño period compared to neutral period except in 1985/86. This may indicate a downward transport of stratospheric ozone into the troposphere at these places, enhanced by Brewer-Dobson circulation during an El Niño period. The low value of observed ozone level in 1985/1986 may be because the neutral years 1985/1986 also correspond to the solar minima years of the 11-year solar cycle, which is associated with an increase in low energy cosmic rays in the earth's atmosphere, which will increase NOX and in turn decrease ozone (Ganguly et al., 2005). No significant trend in stratospheric ozone is observed at Rajkot.

![Figure 5.4 Effect of El Niño southern oscillation on the stratospheric ozone concentration.](image-url)
Effect of ENSO on the seasonal variation of total ozone.

The effect of El Niño on total ozone was found to be different at these four stations during summer (Mar-Apr-May), monsoon (Jun-Jul-Aug), autumn (Sep-Oct-Nov) and winter (Dec-Jan-Feb) (Figures 5.5a, 5.5b, 5.5c & 5.5d respectively). During El Niño period, the ozone concentration at Srinagar, Delhi and Rajkot was found to be less than that during neutral period by ~ 10 -15 DU in winter (except in 1991/1992 & 2000/2001) and higher than that during neutral period by ~ 10 - 25 DU in summer. (Except in 2000/2001 due to the effect of solar maxima). During monsoon, the ozone concentration is higher during an El Niño period except in (1989/1990 and 2000/2001 due to the effect of solar maxima). During autumn, the ozone concentration at Srinagar and Delhi is higher during an El Niño period (except in 1987/1988 which corresponds to solar minima) but lower at Rajkot compared to neutral period. At Kanyakumari, the ozone concentration is found to be lower during an El Niño period compared to neutral period during summer as well as winter (except in 1987/1988) and no significant trend is observed during monsoon and autumn. The passage of tropospheric weather patterns not only changes the ozone content at the tropopause, but also affects the ozone mixing ratios in the lower stratosphere. The breakdown in ozone - ENSO relationship at different places in India and the typical behavior of ozone at places like Rajkot located close to the border of tropics and extra-tropics may be due to the interference of the annual waves in the two hemispheres, which is further modulated by the Quasi Biennial Oscillation. (Kumar et al., 1999; Helsenrath, et al., 1979). Moreover, factors like the 11-year
solar cycle; volcanic eruptions, long time trend, the seasonal cycle in ozone, consequences of global warming and anthropogenic causes can also be considered as sources leading to the breakdown of ozone – ENSO relationship in certain years.

**Figure 5.5a** Relation between *El Niño* and total ozone during summer.

**Figure 5.5b** Relation between *El Niño* and total ozone during monsoon.
Tropopause plays an important role in the vertical distribution of ozone at a particular place. If the tropopause height decreases, ozone increases and vice versa. The Indian atmosphere is mainly dominated by tropical tropopause. Chakrabarty et al., 1984 have observed that the tropopause height is lower in winter than in summer for latitudes higher than 20°N and reverse for latitudes less than 20°N. In an El Niño period, the waters of western Pacific warm up to above normal values. This in turn causes additional convection (thunder storms) to develop in the western Pacific Ocean, carrying tons of warm moist air upwards.
into the atmosphere. *(Figures 5.1a & b)*. This warm moisture translates its energy into wind, yielding a stronger sub tropical jet stream, which then flows eastwards, bringing about a change in the longitudinal structure of tropopause height *(Wilson et al., 1980)*. According to *Gage et al., 1987*, tropopause potential temperature and tropopause height are well correlated with southern oscillation index. Majority of the cut off lows (upper level cyclones which become cut off or separated from the main flow of the upper tropospheric jet stream) form during summer months. The tropopause is subjected to significant gaps or breaks which are associated with jet streams *(Ramanathan et al., 1960)*. As a result of this break in the tropopause, there is an advection of air and ozone in the troposphere from the extra tropical latitudes. Whenever this circulation accelerates, the ozone concentration increases in the lower stratosphere and when it weakens, ozone will decrease or remain constant depending upon its leakage into the troposphere. During winter, it is possible that deep convection reaching the tropopause warms the upper troposphere and by overshooting the tropopause, cools the lower stratosphere and lifts the tropopause. This results in a decrease in ozone concentration. The air temperature measured at Rajkot airport indicates that the temperature is higher during an El Niño period compared to neutral period *(Figure 5.5e)*. The global temperature is also found to be high during an El Niño period *(Figure 5.5f)*. High temperature during an El Niño period leads to an increase the emission rate of ozone precursors *(Valente et al., 1993)*.
Figure 5.5e Comparison of surface temperature observed at Rajkot during El Niño and neutral period using data obtained from website wunderground.com

Figure 5.5f Global tropospheric temperature anomalies from 1979 – 2002 obtained from NASA website.
Large solar storms rain electrically charged particles called protons down on Earth’s atmosphere, which break up molecules of gases like nitrogen and water vapour, producing HO\textsubscript{x} and NO\textsubscript{x} which catalytically deplete the upper-level ozone for weeks to months thereafter. The enhanced ionization affects not only the ionosphere but also some of the minor neutral constituents between upper stratosphere and the mesopause. Odd hydrogen \((\text{HO}_x = H + \text{OH} + \text{HO}_2)\) and odd nitrogen species \((\text{NO}_x = N + \text{NO} + \text{NO}_2)\) are produced by proton and secondary electron impact on \(\text{N}_2\). When nitrogen gas molecules split apart, they create molecules, called nitrogen oxides, which last several weeks to months depending on where they end up in the atmosphere. Once formed, the nitrogen oxides react quickly with ozone and reduce its amounts. When atmospheric winds blow them down into the middle stratosphere, they can stay there for months, and continue to keep ozone at a reduced level. Protons similarly affect water vapour molecules by breaking them up into forms where they react with ozone. However, these molecules, called hydrogen oxides, last only during the time period of the solar proton event. These short-term effects of hydrogen oxides can destroy up to 70 percent of the ozone in the middle mesosphere. At the same time, long-term ozone loss caused by nitrogen oxides destroys a maximum of about nine percent of the ozone in the upper stratosphere.

Between January 15\textsuperscript{th} and 19\textsuperscript{th}, 2005, four powerful solar flares erupted from sunspot 720. Then on January 20, the fifth explosion produced a coronal mass
ejection (CME) that achieved velocities incomparably greater than anything astronomers had seen before. While it generally takes more than 24 hours for the charged particles of a solar outburst to reach the earth, this one was a profound exception. Just thirty minutes after the explosion, Earth (some 96 million miles away from the sun) was immersed in what NASA scientists called the most intense proton storm in decades. The solar energetic particle event of January 20, 2005 has been the most intense in 15 years, with greater than 100 MeV proton intensity comparable to that of the October, 1989 event.

The ozone data obtained from Nimbus-7 and Earth probe Total Ozone Mapping Spectrometer (TOMS) for the years 1989-2005 has been used to study the impact of solar storms on the total columnar ozone in India. The variation in columnar ozone values determined from satellite-based TOMS data is supported with ground-based ozone data measured with Dobson Spectrometer at Delhi. The total columnar ozone values obtained from AURA Ozone Monitoring Instrument (OMI) and vertical ozone profiles measured by Microwave Limb Sounder (MLS) have been obtained through GES-DISC Interactive Online Visualization and Analysis Infrastructure (Giovanni).

[5. 7] A comparison of the impacts of different solar storms on the ozone concentration of Srinagar.

A comparison of columnar ozone obtained from Nimbus - 7 and Earth - probe TOMS for three to six consecutive days after different SPE's observed at Srinagar (34°N, 74.8°E) is shown in Figure 5.6. It is observed that although the
20\textsuperscript{th} Jan., 2005 SPE was the most intense in the last 15 years, with >100 MeV proton intensity comparable to that of the October, 1989 event, the ozone depletion was found to be maximum in the 23\textsuperscript{rd} March, 1991 event followed by 20\textsuperscript{th} Jan., 2005, 4\textsuperscript{th} Nov., 2001, 19\textsuperscript{th} Oct., 1989 and 28\textsuperscript{th} Oct., 2003 events. This may be because a volcanic eruption Hekla was reported in Iceland on the 17\textsuperscript{th} January, 1991. The eruption cloud was north of the terminator in the polar night region for the first few days of atmospheric residence, and then it moved south across Russia and was detected by TOMS near the Black Sea. Volcanic eruptions are potential sources of SO\textsubscript{2}, HCl, BrO and H\textsubscript{2}O in the lower stratosphere. SO\textsubscript{2} emitted from the volcanoes gets converted into H\textsubscript{2}SO\textsubscript{4} and condenses into small aerosol particles in the stratosphere. These aerosol clouds provide an increased scope for heterophase chemistry and enhanced ozone depletion. Volcanic particles generally take two or three years to settle out of the stratosphere. The large depletion in ozone levels observed after the 23\textsuperscript{rd} March, 1991 SPE may be due to the combined effects of the Hekla volcanic eruption in Iceland and SPE.
Figure 5.6 Comparison of columnar ozone for three to six consecutive days in different SPE’s observed at Srinagar.

[5.8] **Impact of 20th January 2005 solar proton event on the ozone concentration of Indian cities.**

A comparison of ozone values for different Indian cities after the 20th January, 2005 SPE indicated that the observed decrease in ozone values was found to vary with latitude. The ozone values were found to decrease sharply at places situated at higher latitudes like Srinagar and Delhi (*First solid line and first dotted line respectively in Figure 5.7*) compared to places located in the tropics like Rajkot, Trivandrum and Hyderabad (*Second, third and fourth solid lines respectively in Figure 5.7*). This is because solar storms lead to ejection of large
amount of high-energy protons that can penetrate the Earth’s magnetic field near the poles. These protons penetrate into the atmosphere, (40 to 80 km layer) causing ionization of air molecules. As the ionized particles recombine, they produce nitrogen and hydrogen oxides, which can affect ozone through the NO_x and HO_x catalytic cycles.

The decrease in ozone values using TOMS data was observed for a short period from 20\textsuperscript{th} January to 25\textsuperscript{th} January after which the ozone levels started recovering to normal values (Figure 5.7). Similar results were observed for ground based columnar ozone values measured with Dobson spectrometer at Delhi from 19\textsuperscript{th} January to 28\textsuperscript{th} January (Figure 5.8). These effects are short-lived because the hydrogen oxides which cause the primary ozone loss recombine within hours.

![Figure 5.7](image.jpg)

**Figure 5.7** Columnar ozone measured by TOMS over different Indian cities from 20th to 31st January, 2005.
Figure 5.8 *Columnar ozone recorded at Delhi using Dobson Spectrometer from 19th to 28th January, 2005.*

An examination of total columnar ozone values obtained from AURA Ozone Monitoring Instrument (OMI) indicates that the ozone levels in northern and central India on the 24\(^{th}\)/25\(^{th}\) January, 2005 were lower by about 20 to 30 Dobson units compared to 20\(^{th}\)/21\(^{st}\) January, 2005. The ozone levels thereafter started recovering gradually around the 30\(^{th}\)/31\(^{st}\) January, 2005 (*Figure 5.9*). The recovery in ozone levels was observed to be faster in northern India, compared to central India.
NO\textsubscript{x} is the most important destroyer of ozone in the 25-45 km altitude region. In the NO\textsubscript{x} cycle, the radical that destroys ozone is NO.

The catalytic cycle is: \( NO + O_3 \rightarrow NO_2 + O_2 \)

\[
\begin{align*}
NO_2 + O &\rightarrow NO + O_2 \quad \rightarrow(5.1) \\
NET: O_3 + O &\rightarrow 2O_2.
\end{align*}
\]

This process is catalytic since NO initiates’ ozone destruction process, but is regenerated, so that no net consumption of NO occurs. In the hydrogen cycle, the radical which destroys ozone, is the Hydroxyl radical (OH).

The catalytic reaction is:

\[
\begin{align*}
OH + O_3 &\rightarrow HO_2 + O_2 \\
HO_2 + O &\rightarrow OH + O_2. \quad \rightarrow(5.2) \\
NET: O_3 + O &\rightarrow 2O_2
\end{align*}
\]
Other members of the HO\textsubscript{X} family which destroy ozone are H and HO\textsubscript{2}

\[ H + O_3 \rightarrow OH + O_2, \]
\[ OH + O \rightarrow H + O_2, \]
\[ NET: O_3 + O \rightarrow 2O_2. \rightarrow (5.3) \]
\[ HO_2 + O \rightarrow OH + O_2, \]
\[ OH + O_3 \rightarrow HO_2 + O_2. \]
\[ NET: O_3 + O \rightarrow 2O_2. \]

Figure 5.10 Ozone values at different pressure levels obtained from Microwave Limb Sounder from 20\textsuperscript{th} - 31\textsuperscript{st} Jan., 2005, for New Delhi.

An examination of ozone values obtained from Microwave Limb Sounder from 20\textsuperscript{th} – 31\textsuperscript{st} Jan., 2005 for New Delhi (Figure 5.10) indicates that the ozone mixing ratio in ppmv in the 7.0 to 3.0 hPa pressure range (approximately 32 to 40 km
altitude range) is found to decrease consistently from 21\textsuperscript{st} Jan., 2005 to 25\textsuperscript{th} Jan., 2005. The ozone levels are found to recover by the 31\textsuperscript{st} of January 2005. The SPE-produced NO\textsubscript{x} constituents in the upper stratosphere cause direct ozone losses. However, interference of the NO\textsubscript{x} constituents with the halogen loss cycles for ozone destruction might have actually led to some ozone production in the 15 to 25 hPa pressure range (approximately 27 to 29 km altitude range) on the 25\textsuperscript{th} and 26\textsuperscript{th} January. Jackman \textit{et al.}, 1999 observed similar results in their two-dimensional chemistry and transport atmospheric model. Since the solar proton event is found to deplete very little total ozone for a short period in India, its negative impacts on humans will be very little.
The Thesis is focused on the study of tropospheric, stratospheric and total ozone photochemistry at different Indian stations particularly at Rajkot in Gujarat since 1980. The modulating effects of meteorological and geophysical conditions such as temperature, humidity, wind speed and direction along with the effects of ENSO and solar storms on the total ozone concentration have been investigated. The trend of erythemal UV irradiance observed at Rajkot since 1980 has also been studied to determine whether Rajkot is safe from the lethal effects of erythemal UV.

The diurnal variation of ozone measured by MICROTOPS II Sun photometer at Rajkot, indicates a higher vertical column density of ozone during morning compared to evening hours. The monthly mean values of total ozone obtained from MICROTOPS II Sun photometer indicate a marked seasonal variation with a maximum around June - July and a minimum around December. Since the ozone concentration measured by Dobson Spectrometer and TOMS are found to correlate well, it is possible to calibrate MICROTOPS II Sun photometer with TOMS to get accurate diurnal ozone variations over locations where Dobson
data are not available. This will in turn reduce the inconvenience in carrying the Microtops Sun photometer to a Dobson center for calibration at regular intervals. The ozone data obtained from Total Ozone Mapping Spectrometer (TOMS) and Solar Back scatter Ultra Violet (SBUV) technique on Nimbus 7 satellite have been used to study the variability of the total column amount of ozone and ozone concentration in different atmospheric layers respectively at Rajkot (22.3°N, 70.8°E) over a period from 1980 - 2004. An examination of the monthly mean total ozone values obtained from TOMS indicates a marked seasonal variation with a maximum around June and a minimum around December. The SBUV profile of springtime ozone indicates that the stratospheric ozone concentration at Rajkot has decreased consistently from 1982 to 1999. The concentration is found to have increased suddenly in 2000 and further in 2001. Thereafter it decreased in 2002 and again increased in 2003. An insignificant overall downward trend is observed in the total column amount of ozone (0.85%) from 1997 to 2004 at Rajkot. Seasonal variation of ozone from Srinagar to Kanyakumari has also been studied for the year 2003, which indicates an increase in ozone concentration with latitude. The ozone values are found to peak earlier at Srinagar compared to Kanyakumari. The results are discussed in the light of photochemical and dynamical effects.

The monthly mean erythemal UV irradiance data obtained from Nimbus - 7 and Earth probe Total Ozone Mapping Spectrometer (TOMS) and the monthly mean stratospheric and tropospheric column ozone data obtained from the CCD method of Ziemke et al., 1998, has been used to study the variability of
erythemal UV irradiance, the stratospheric column ozone and tropospheric column ozone respectively at different Indian latitudes over a period of 27 years from 1979–2005. The columnar stratospheric ozone concentration in India from 1979–2005 has not been found to decrease significantly. It is also observed that the tropospheric ozone level has not increased significantly for Indian latitudes over the past 27 years. This implies that Indian latitudes may be safe from the lethal effects of stratospheric ozone depletion, tropospheric ozone pollution and global warming due to increase in tropospheric ozone. The monthly mean erythemal UV irradiance is found to decrease negligibly at Chennai, Pune and Rajkot and is found to increase insignificantly at New Delhi and Srinagar from 1979 to 2003, indicating that Indian latitudes lie within safe limits of the negative impacts of ozone depletion and erythemal UV irradiance. The tropospheric ozone values in the $10^\circ$N to $15^\circ$N latitude range and $15^\circ$N to $20^\circ$N latitude range are found to be slightly higher than the upper tolerance limit (UTL) in the years 1993 and 1990 respectively. Similarly, the stratospheric ozone values in the $10^\circ$N to $25^\circ$N latitude ranges are found to be lower than the lower tolerance limit (LTL) in the year 1993 and in the $25^\circ$N to $35^\circ$N latitude ranges are found to be lower than the LTL in the year 1996. The low value of stratospheric ozone observed in 1993 may be due to the effect of a major volcanic eruption from Mount Pinatubo in Philippines in June 1991. The low value of stratospheric ozone observed in 1996 may be due to the combined effects of the Kliuchevskoi volcanic eruption in Russia and solar minima.
The effect of El Niño southern oscillation on the total, tropospheric and stratospheric ozone concentration at Kanyakumari, Rajkot, Delhi and Srinagar is studied using the data obtained from Total Ozone Mapping Spectrometer (TOMS) and Tropospheric Ozone Residual method (TOR). An examination of the yearly mean values of total ozone from 1980 to 2003 and tropospheric ozone from 1980 to 1998 indicates that the total and tropospheric ozone concentration decreases in the tropics & increases in the extra - tropics during an El Niño period. The total ozone concentration at Rajkot, which is situated close to the border of tropical and extra - tropical region, is found to be higher during an El Niño period compared to neutral period. No significant trend in tropospheric ozone is observed at Kanyakumari. The trend of stratospheric ozone at Srinagar and Delhi is found to be opposite to that of tropospheric ozone indicating a probable leakage of stratospheric ozone into the troposphere during an El Niño period. The effect of El Niño on total ozone was found to be different at these four stations during summer, monsoon, autumn and winter. During an El Niño period, the ozone concentration at Srinagar and Delhi was found to be less than that during neutral period in winter and higher than that during neutral period in summer, monsoon and autumn. At Kanyakumari, the ozone concentration is found to be lower during an El Niño period compared to neutral period during summer as well as winter and no significant trend is observed during monsoon and autumn. Factors like the 11-year solar cycle, volcanic eruptions, long time trend, consequences of global warming, anthropogenic causes and the seasonal
cycle in ozone may be considered as sources leading to the breakdown of ozone – ENSO relationship in certain years at different places in India.

Ozone data obtained from Nimbus-7 and Earth-probe TOMS for the years 1989-2005 has been used to study the impact of solar storms on the total columnar ozone in India. A comparison of total ozone values for different SPE’s observed at Srinagar indicates that although the 20th Jan., 2005 SPE event was the most intense in the last 15 years, the ozone depletion was found to be maximum in the 23rd March, 1991 event followed by 20th Jan., 2005, 4th Nov., 2001, 19th Oct., 1989 and 28th Oct., 2003 events. The large depletion of ozone observed in 1991 may be due to the combined effects of the Hekla volcanic eruption in 1991 and SPE. The observed decrease in ozone values during the SPE was found to vary with latitude. The ozone values were found to decrease sharply at higher latitudes compared to places located in the tropics. The decrease in ozone values was observed for a short period of about 5 days, after which the ozone levels started recovering to normal values. Since the solar proton event is found to deplete very little total ozone for a short period in India, its negative impacts on humans will be very little.

**Future scope.**

The integrity of the Earth's ozone layer has been a subject of concern for over 20 years. An issue was first raised in the U.S in 1970, regarding the likely prospects of the intrusion of commercial fleets of supersonic jets (like today's Concorde) that would fly at higher altitudes than conventional aircraft and perturb the natural chemistry of the stratosphere. Later the greater threat of CFC’s and bromine-
related gases came into the limelight, in time resulting in the international agreements on production limits that now serve as an example of effective worldwide policy response to environmental threats. As a result of actions taken, ozone-depleting gases in the atmosphere are increasing less rapidly and the ozone layer is probably degrading less rapidly. In addition, many countries have in the recent years started to monitor the ground-level UV radiation. Behind all of these actions were perceived impacts on the biosphere, and on human health in particular. Yet we are still not very sure of what the effects would have been, had we not phased out the production of these compounds.

Surprisingly, little effort has been made in studies of any of the potential effects when compared to that given to the causes of the loss of ozone. There may be several reasons that may explain the imbalance, including the inherent difficulties in funding and accomplishing research that spans the chasms between physical, biological and medical science and of regulatory action as compared to longer-term monitoring and research.

Since India is a densely populated and rapidly developing country located in the tropical region, it is subjected to intense photochemical activity and trace gas emissions. The exchange of air between the tropical troposphere and stratosphere is very important and relevant to many key atmospheric chemistry problems. To investigate these aspects, regular accurate measurements of vertical distribution of ozone over different geographical locations covering remote areas of India are very essential. However at present, vertical ozone
profile measurements in India at regular short intervals of time up to about 50 km are very sparse, excepting the measurements made by IMD, Research laboratories in metro cities and those obtained from satellites. Although estimates of total tropospheric ozone amounts have been made by innovative methods like TOR and CCD, techniques for direct tropospheric measurements from satellite borne instruments are in the developing phase. Portable instruments like MICROTOPS II sun photometer are helpful in studying the diurnal variation of total ozone at remote places, but it requires regular calibration. It is also not very clear as to what fraction of the observed decrease in ozone concentration can be attributed to solar UV variability and what fraction to temperature of non-solar origin. (Mandal et al., 2004).

One of the central missions of the U.S. space agency is to understand and protect our planet. To advance this mission, NASA has developed the Earth Observing System (EOS) satellite Aura to study our planet's ozone, air quality and climate for a period of six years. Aura is part of a flotilla of satellites flying in formation in space, including Terra, Aqua, CloudSat, Parasol and Calipso. CloudSat, Calipso and Parasol have been launched in 2005. Together, their overlapping radars give a more comprehensive picture of weather and climate down on Earth. The formation of orbiting satellites is referred to as the A -Train. Flying at an altitude of 438 miles, Aura uses four science instruments to study Earth's atmosphere. Aura's Instruments incorporate advanced technologies developed specifically for environmental satellites. Each instrument complements the others, enabling daily observations of Earth's atmospheric ozone layer, air
quality, and key climate parameters. Each of the satellite's four science instruments is designed to monitor a different part of our global atmospheric system. They are:

**High Resolution Dynamics Limb Sounder (HIRDLS)** profiles ozone with the highest ever vertical resolution from space. The ozone measurements provide details on the lower stratosphere, where the largest ozone depletion has occurred.

**Microwave Limb Sounder (MLS)** focuses on the upper troposphere and stratosphere, measuring microwave radiation emitted by ozone, chlorine compounds and many other traces gases. It studies how water vapour and ozone destroying compounds like chlorine and bromine pass between the troposphere and stratosphere. MLS is a microwave sensor, which is able to measure trace gases inside the clouds.

**Ozone Monitoring Instrument (OMI)** monitors recovery of the stratospheric ozone layer. It measures both ultraviolet and visible radiation and provides daily high-resolution global maps and profiles of ozone.

**Tropospheric Emission Spectrometer (TES)** observes the heat emitted naturally from Earth's surface and atmosphere, as well as reflected sunlight. It provides night and day coverage of the atmosphere everywhere on the globe. TES is making the first direct global measurement of ozone in the lower atmosphere. It also will measure nitrates, water vapor and tropospheric ozone
precursors, such as carbon monoxide. TES provides data for use in atmospheric chemistry prediction models. It helps scientists distinguish between man-made and natural impacts on air quality.

<table>
<thead>
<tr>
<th>Satellite</th>
<th>Launch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aura</td>
<td>15/7/2004</td>
</tr>
<tr>
<td>Aqua</td>
<td>4/5/2002</td>
</tr>
<tr>
<td>Terra</td>
<td>18/12/1999</td>
</tr>
</tbody>
</table>

The Aura, Aqua and Terra are among a flotilla of six spacecrafts designed to fly in low polar orbits 438 miles above Earth. These satellites circle Earth 14 times a day. Aqua crosses the equator at approximately 1:30 AM and 1:30 PM, local time, about 3 hours behind Terra. Due to the instrument's narrow field of view, it takes about 16 days for Aqua to map the entire surface of the planet. Aqua's afternoon observations and Terra's morning observations will help scientists to understand the daily cycle of key science parameters such as precipitation and ocean circulation. The caravan of all the six spacecrafts resembles a train of satellites flying around Earth. The benefit of flying satellites in formation is that since the set of satellites are not very costly or complex, the risk of failure of one satellite does not kill an entire mission.
Bibliography.


19273, 1997.


[16] Dasgupta R and Bhaumik D K., *Upper and Lower tolerance limits of


properties in relation to tropical convection and El Niño-southern oscillation

collection at Rajkot. Journal of Indian Geophysical Union, 9 (3), 189 –
196, 2005.

1993.


1972.


[29] Hasebe F., The global structure of the total ozone fluctuations observed on
the time scales of two to several years. Dynamics of the middle atmosphere,

[30] Helsenrath E, Heath D F and Schlesinger B M., Seasonal and
interannual variations in total ozone revealed by the Nimbus 4 BUV


[40] London J., *The observed distribution and variations of total ozone.*


Halogen from Halocarbons: Implications for Stratospheric Ozone Depletion.  
Science, 272, 1318, 1996.


atmosphere due to the October-November 2003 solar proton events. CAL midterm review meeting, Elounda, Crete, Greece, 2005.


[80] Ziemke J R, Chandra S and Bhartia P K., Two new methods for deriving
tropospheric column ozone from TOMS measurements: The assimilated
UARS MLS / HALOE and convective-cloud differential techniques.


[82] The Earth’s Atmosphere and ozone.


[83] Climate of Gujarat, Diu, Daman and Dadra Nagar Haveli. Govt. of India,