

CHARACTERISTICS OF VERTICAL PROFILE OF OZONE NEAR THE EQUATOR.

BY

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ABSTRACT

Although ozone is rare in the atmosphere, it has several vital roles which depend on vertical distribution of the gas. Consequently, the major objectives of this study were to determine the vertical distribution and dynamics of ozone. An attempt was also made to determine the influence of meteorological parameters on the vertical profile of ozone.

Measurements of the primary data that were used to compute the vertical profiles of ozone were obtained by the use of Dobson ozone spectrophotometer No. 18. The instrument is stationed at Chiromo campus, University of Nairobi (1° S, 36° E) at an altitude of 1710 m above sea level. The data were collected for six months (November 1995-April 1996) that represented a hot and a cold season.

The primary data were subjected to the new Umkehr inversion algorithm to yield the vertical profiles of ozone. To investigate the general vertical distribution of ozone, arithmetic average of ozone quantity in each layer over the entire duration of the study was computed.

An investigation of the dynamics of ozone was realized by studying the monthly variation of ozone in

each layer. This investigation was further enhanced by analyzing the ozone standard deviations. The degree of relationship between ozone profiles and some meteorological parameters that included long-term mean tropopause height, tropopause temperature, temperature wind speed wind direction at various levels was carried out.

Subjection of raw data to the new Umkehr inversion algorithm yielded 34 ozone profiles out of 65 days of Umkehr observations. The average vertical profile of ozone indicated low and high ozone concentration in the troposphere and stratosphere respectively. About 10.4% of ozone was located below 12.5 km whereas the remaining amount (89.6%) was above this level.

Analysis of ozone variability in each layer showed three distinct patterns. These patterns were associated with the three vertical cells (Lower, middle and upper cells).

Highest negative spearman rank correlation coefficients between ozone amount and tropopause height were obtained in layers 4 and 5. Ozone correlation with tropopause temperature indicated high coefficients in layers 3, 4, and 5 relative to other layers. Relationship between temperature and ozone in layers 1-2 and layers 3-5 depicted positive and negative

correlations respectively. Correlation between zonal wind speed and ozone quantity in layers 1-5 indicated variability which was associated with varying wind directions.

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CHAPTER ONE

1.0

INTRODUCTION

1.1 INTRODUCTION

Ozone occurs in small quantity in the atmosphere, averaging about three molecules of ozone for every ten million air molecules. Nonetheless, atmospheric ozone plays vital roles that belie its low concentration.

Ozone is mainly found in two regions of the earth's atmospheric vertical profile. The largest ozone concentration (about 90%) resides in a layer between approximately 10 and 50 kilometers above the earth's surface, in the region of the atmosphere called the stratosphere. The remaining ozone is in the lower region of the atmosphere, the troposphere, which extends from the earth's surface up to about 10 kilometers. Figure 1 shows ozone's vertical distribution in the atmosphere (IPCC, 1994).

Ozone (O_3) creation takes place above the tropopause with maximum formation at altitude of about 30 kilometers in the tropical stratosphere (Rowland, 1991).

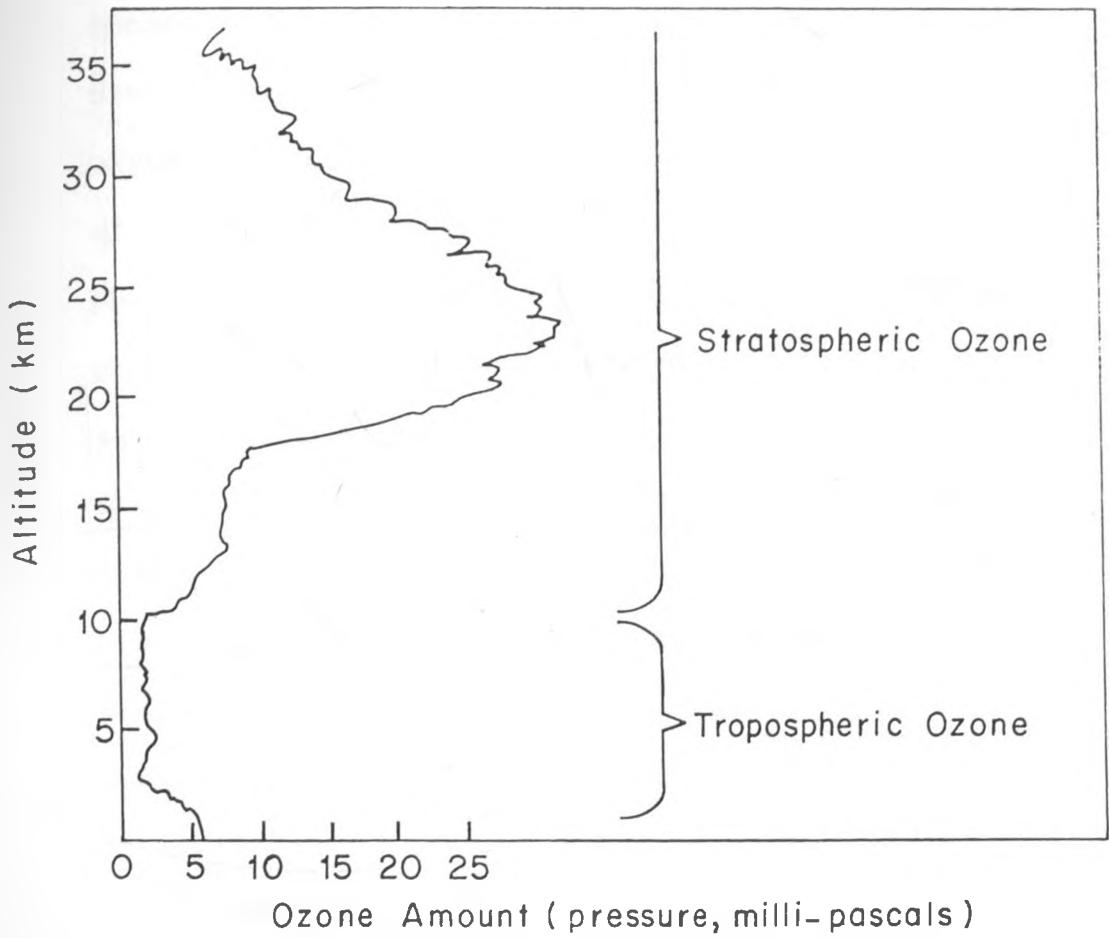


Fig. 1: Vertical distribution of ozone (IPCC, 1994)

This process of formation commences when photochemical dissociation of oxygen (O_2) into individual atoms (O) by ultraviolet (UV) radiation of wavelength shorter than 242 nanometers (nm) takes place. The free atoms consequently combine with oxygen molecules to form ozone. Ozone is naturally split into atomic oxygen and oxygen molecule when it absorbs ultraviolet radiation of wavelength ranging from 240-290 nm (UV-C). In the photochemical region of the upper atmosphere these processes of formation and decomposition go on at the same time and there is finally an equilibrium between the amount of ozone being formed and the amount being destroyed. These natural balanced processes of formation and destruction of ozone are shown in equations 1, 2, and 3 (Mathews, 1991). Where $h\nu$ represents UV-radiation and M is a third molecule (any molecule) which carries away the excess energy from the reaction.



Despite the small amount of ozone in the atmosphere, it has several vital roles. These include:

- (A) Ozone helps in maintaining the stratospheric temperature distribution. This warmth is due to absorption of solar UV radiation by the ozone. A reduction of ozone concentration in the stratosphere has the effect of lowering the temperature in this region (IPCC, 1994).
- (B) Tropospheric ozone acts as a greenhouse gas, thus modulating the earth's climate (Galbally and Roy, 1991). However, ozone in this altitude is a secondary product of complex photochemical processes involving amongst other substances, carbon monoxide (CO), methane (CH₄), reactive

nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHC). Tropospheric ozone is short-lived (lifetime: several weeks), and thus its distribution in space and time is rather non-uniform (IPCC, 1994).

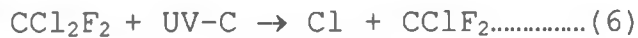
- (C) Ozone protects life at the earth's surface from damaging ultraviolet radiation from the sun. In UV spectrum, light of wavelength shorter than 180 nm does not reach the stratosphere. That of range between 180-242 nm is absorbed primarily by oxygen splitting it into atomic atoms and does not reach the lower stratosphere. UV-B (290-320 nm) radiation is partially absorbed by ozone and the portion which reaches the earth's surface is largely responsible for the various harmful effects on living organisms and materials (Ilyas, 1991). Longer wavelength UV-A (320-400 nm), which is relatively harmless to life on the earth's surface is entirely transmitted through the ozone layer to the ground.
- (D) Lower tropospheric ozone has been recognized as a

pollutant since it can impair health and cause damage to vegetation and materials. For Instance, in Netherlands, it was found out that in 1983, ambient air pollution reduced crop production by 5%, of which 70% was caused by ozone. The reduction in crops production was more dominant in horticultural crops (Tonneijck, 1989).

Stratospheric ozone depletion and its subsequent impacts on the biosphere has gained considerable attention within the international scientific community in the recent past. Scientific evidence has shown that human-made chemicals are responsible for the observed depletion of the ozone layer (WMO et al., 1994., IPCC, 1994). These chemicals contain various combinations of the chemical elements chlorine, fluorine, bromine, carbon and hydrogen (halocarbons).

The major depleters of ozone layer however, are the chlorofluorocarbons (CFCs) which are made of carbon (C), chlorine (Cl) and fluorine (F). CFCs have many

applications including refrigeration, air conditioning, cleaning of electronic components, and as solvents. The long residence times of these substances in the troposphere enable them to slowly drift up to the stratosphere, where intense UV-C radiation severs their chemical bonds, releasing chlorine, (equation 5 and 6) which strips an atom from ozone molecule, resulting into ordinary oxygen molecule (O_2) and chlorine oxide (ClO , equation 7). Because the usual reaction of atomic oxygen (O) involves the formation of ozone as shown in equation 2, the effect of equation 8 is equivalent to removal of two ozone molecules. The chlorine acts as catalyst, accomplishing this destruction without itself undergoing any permanent change (WMO et al., 1994), so it can go on to repeat the process (chain reaction).





The chain reaction can be temporarily diverted through alternate reactions such as shown in equations 10 and 11 which put Cl into other chemical molecules such as HCl or chlorine nitrate (ClONO₂).



While in these reservoir compounds, the Cl atoms do not destroy ozone. However, these reservoir molecules are temporary in the atmosphere (Rowland, 1991), and chlorine is soon set free again. The chain process therefore continues as long as the chlorine remains in the stratosphere, and the average number of ozone destroyed per individual chlorine atom is eventually

about 100,000.

Stratospheric ozone depletion leads to increased UV-B radiation on the earth's surface which is highly detrimental to plants, animals and materials.

The effect of UV-B exposure on man include skin cancer, eye cataracts, damage to genetic DNA, aging, wrinkling and suppression of the efficiency of the immune system. Under cloudless condition, each 1% reduction in ozone results in an increase of about 1.3% in the UV-B reaching the surface of the earth which affect skin tissues. The total ozone decline so far has resulted in a small increase in UV-B reaching the ground except over tropical belt. Further ozone decline could have considerable harmful consequences, not only to humans but also to other life forms (Bojkov, 1995).

The effects of UV-B radiation on animals have generally received little attention, as it is assumed that they are protected by their outer coverings. However a few experiments have shown that large doses of UV-B radiation given during the development stages of various animals could lead to abnormalities

(Tonneijck, 1989).

Physiological and developmental processes of plants are affected by VU-B radiation, even by the amount of UV-B in present day sunlight (UNEP, 1994). Tests carried out on 300 crops in Netherlands (Tonneijck, 1989) and other plants species have indicated that two thirds are sensitive to ultraviolet light. Among the most vulnerable are peas, melons, cabbages and related species. UV-B radiation may also reduce the quality of certain types of tomatoes, potatoes, sugar beets and soyabeans. Forests also appear to be vulnerable. About half of the species of canifer seedlings so far studied have been adversely affected by UV-B radiation. In addition, UV-B radiation is also known to break down polymers used in buildings, paints, packaging and many other products (D.O.E., 1995). Phytoplanktons and zooplanktons are critical components in typical aquatic food webs (nutritional pathways) that lead to larger animals, including those comprising commercial fisheries and therefore man himself (Damkaer and Calkins, 1982). However, solar

UV-B radiation has been found to cause damage to early developmental stages of fish, shrimp, crab, amphibians and other aquatic life. The most severe effects are decreased reproductive capacity and impaired larval development. Even at current levels, solar UV-B radiation is a limiting factor, and small increases in UV-B exposure could result in significant reduction in the size of the population of consumer organisms (UNEP, 1994).

Scientific evidence shows that ozone depletion caused by human-made chemicals is continuing and is expected to persist until chlorine and bromine levels are reduced.

On the international level, several agreements have been realized to save the declining ozone amount. These include among others the 1985 Vienna Convention for the Protection of Ozone Layer and the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer. However, worldwide compliance with current international agreements is rapidly reducing the yearly emission of the compounds that deplete ozone layer. As

these emissions cease, the ozone layer will gradually improve over next several decades. The recovery of ozone layer will be gradual because of the long times (table 1) required for the major ozone depleters (CFCs) to be removed from the atmosphere (WMO et al., 1994)

COMPOUNDS	LIFETIME (Yeas)
CFCl (CFC-11)	50 (+/-5)
CF ₂ Cl ₂ (CFC-12)	102
C ₂ F ₃ Cl ₃ (CFC-113)	85
C ₂ F ₂ Cl ₂ (CFC 114)	300
C ₂ F ₅ Cl (CFC-115)	1700

Table 1: Residence time of common CFCs

(WMO et al., 1994)

In view of the impacts of ozone depletion, a lot of effort has been made to study the spatial and temporal ozone characteristics. The information has proved helpful in understanding natural production and transport mechanisms as well as producing bench mark data for future comparison (WMO, 1989). In spite of the international effort to investigate the ozone characteristics very limited work has been conducted in East Africa. One of such studies (Muthama, 1989) only

analyzed the characteristics of the total amount of ozone. However, the characteristics of the vertical profile of ozone, which enhances the understanding of the dynamics of ozone in the atmosphere, has not been conducted. This forms the basis of the present study.

1.2 OBJECTIVES

The objectives of this study are to:

- (A) Determine the vertical distribution and consequently the dynamics of ozone near the equator.
- (B) Determine the influence of meteorological parameters on the vertical profile of ozone.

This study, being the first of its kind in East Africa, would form a basis for future research of atmospheric ozone in this region. The results would further contribute to understanding of the dynamics of ozone near the equator and increase data on vertical profile of ozone in the equatorial region.

CHAPTER TWO

2.0 BACKGROUND REVIEW

2.1 DISTRIBUTION OF OZONE

In investigating spatial and temporal distribution of ozone, several techniques have been employed throughout the globe. These techniques include the use of ground-based instruments, ozonesondes, satellites and aircraft.

Spatial distribution of ozone, composed of horizontal and vertical distribution forms the subject of the next discussion.

2.1.1 HORIZONTAL DISTRIBUTION OF OZONE

Figure 2 indicates total ozone distribution over the globe. The equatorial belt is characterized by low ozone amounts whereas high amounts are pronounced in the middle and high latitudes. Ozone appears to be more abundant in northern hemisphere than in the southern hemisphere (Levy, 1988).

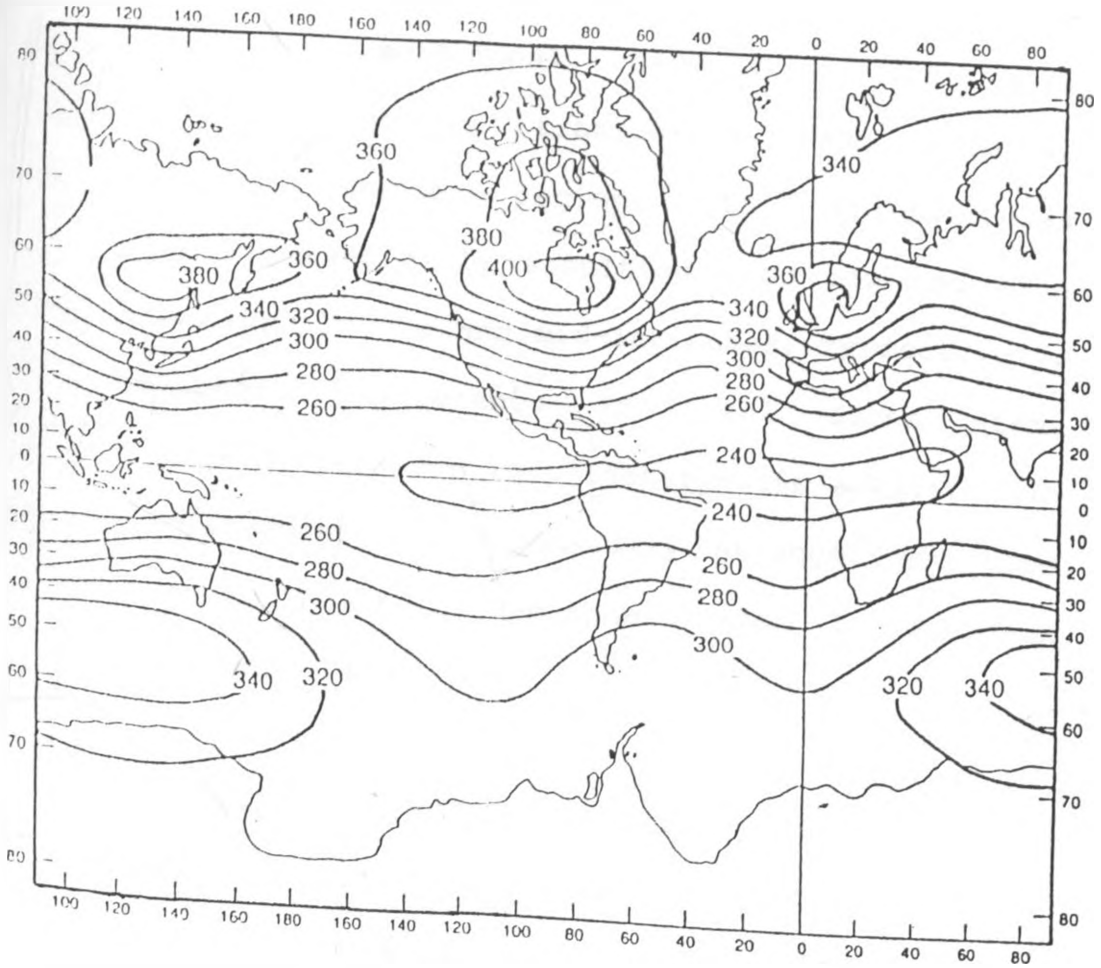


Fig. 2: Global average total ozone distribution for the years 1952-1975 expressed in Dobson units (WMO, 1986)

The latitudinal difference in ozone amount is attributed to meridional circulation of air. Subsequently ozone is transported from tropical stratosphere (source region) to mid-latitudes stratosphere consequently resulting into low and high ozone quantity, in low and mid-latitudes, respectively. Interhemispheric difference in total ozone stems largely from differences in planetary-wave activity. In winter, disturbances are generally stronger and more persistent in Northern Hemisphere than in Southern Hemisphere (WMO, 1989).

2.1.2. VERTICAL DISTRIBUTION OF OZONE

Vertical distribution of ozone in the stratosphere and troposphere are separately discussed below.

2.1.2.1 Stratospheric ozone distribution

The earliest study of vertical profile of ozone were conducted by use of Umkehr technique, an optical method of estimating ozone concentration at various levels of the atmosphere (Craig, 1965).

Various studies have indicated that maximum ozone density is concentrated in the lower stratosphere (WMO, 1986., Mathews, 1991). Total ozone variation has been associated with fluctuation of ozone in the lower stratosphere (Reiter, 1975).

Investigations of vertical distribution of ozone have shown that in the stratosphere, the level at which the maximum concentration of ozone occurs is much lower near the poles than near the equator, and shows a steady fall with latitude similar to the fall in the height of the tropopause (Biswas, 1979). Although there is always a general increase in the concentration of ozone with increasing height in the lower stratosphere, there are sometimes large irregularities, and layers of low ozone may be found above layers of higher ozone.

Variability of ozone using ozonesonde and satellite data has been investigated by several scientists including Subburaya et al., (1990). These studies indicate largest variability in low stratosphere over the middle and high latitudes, and decreases to relatively small values at all levels in

the tropics.

2.1.2.2 Tropospheric ozone distribution

Observations show that tropospheric ozone, which is formed by photochemical reactions involving pollutants, has increased over many locations (Mid and higher latitudes) in northern hemisphere over the last 30 years. Further investigations of latitudinal difference of ozone indicate that there is a major inter-hemispheric variation with more ozone in the northern hemisphere than southern (IPCC, 1994).

Logan (1994) analyzed the global ozonesondes records paying particular attention to heterogeneity in the data. The author concluded that upward trend over Europe was smaller since 1980 than before. This difference was attributed to better use of analysis methods than previously used.

Tropospheric ozone characteristics over the tropics are not as adequately documented as in the mid and higher latitudes. However, some of the tropical ozone variations have been discussed by Ilyas (1991)

and Fishman (1988). Their studies indicated the existence of significant longitudinal differences. Frequently varying local weather conditions seemed to alter ozone concentrations.

A recent investigation of ozone variation in the tropics (Natal) conducted by Logan (1994) indicated an increase in ozone concentration between 400 and 700 mb. The Melbourne record showed a decrease in tropospheric ozone between 600 and 800 mb and was largest in summer (WMO et al., 1994).

The following section describes the temporal variation of ozone.

2.1.3 TEMPORAL VARIATION OF OZONE

The temporal variations of ozone, which are categorized into diurnal, seasonal and spring-time ozone reduction in polar regions are discussed below.

2.1.3.1 Diurnal variation of ozone

Surface ozone concentration in the tropics begins to increase just after sunrise, attains its maximum

before noon, generally shows gradual decrease until sunset and remains almost constant after midnight. These conclusions were drawn from a study conducted in Indonesia by Komala and Ogawa, (1991) using ozone data for December 1986-March 1989. The variations of ozone were attributed to diurnal photochemical production and vertical mixing.

In India, Subbaraya et al., (1990) studied the vertical distribution of ozone at different times of the day and night using rockets. The study showed that ozone concentration was larger during the night-time at an altitude of about 50 km. A similar study conducted in Australia (Lean, 1982) examined the diurnal variation of ozone in the stratosphere and mesosphere. During the night, an enhancement in ozone densities occurred at altitudes above 50 km. At 70 km, for example, the night ozone was determined to be a factor of 6.4 greater than the sunset. In addition the author experiment suggested that near 40 km the magnitude of ozone density at noon could be greater by 10-15% than the night time concentration.

Insignificant diurnal variations of ozone in extra-tropics have been realized by several authors including Screeharam et al., (1974) and Biswas (1979). However, superimposed on the seasonal variations of ozone are short period fluctuations of the order of days. The variations are too large and rapid to be explained by photochemical processes.

Since largest of ozone concentrations are known to exist above the tropopause, it is only to be expected that these short-period variations would be closely related to the meteorological conditions in the upper atmosphere than to the surface conditions. There is a tendency of the following association (Dobson, 1968).

- (a) High ozone at the tropopause when winds are cyclonic.
- (b) High ozone in the stratosphere when temperatures are high at this region.
- (c) High total ozone when temperatures at the tropopause are low.

- (d) High total ozone with low level of tropopause.

High temperature in the stratosphere favours photochemical production of ozone resulting into high ozone quantities. Low level of tropopause height increases the depth of the lower stratosphere (reservoir of ozone). This increase subsequently results into high ozone content.

2.1.3.2 Seasonal variation of ozone

The earliest scientists to investigate the seasonal variation of ozone include Kulkurani et al., (1959), Godson (1960) and Khrgian (1973) among others. Their investigations showed that total ozone is maximum in spring and minimum in autumn with largest amplitude of variation at high latitudes. Near the equator, the results indicated very little seasonal variations with slight maximum in late spring and early summer. The above seasonal variations were associated mainly with stratospheric ozone fluctuations.

Recent studies of temporal variation of ozone in extra-tropics have drawn similar results. For instance in Japan, Tsumsum et al., (1991) using data obtained by ultraviolet absorption meter showed that ozone concentration was maximum and minimum in spring and autumn respectively. The author further indicated that ozone transportation from the upper troposphere to the surface was most active in the spring season.

In the tropics, Muthama (1989), by utilizing data obtained by Dobson spectrophotometer showed that minimum values of ozone occurred around January and February with the corresponding maximum values in September and October. The difference in ozone concentration was attributed to the height of the tropopause.

2.1.3.3 Ozone reduction in polar regions

The observation of substantial spring-time reduction in Antarctic ozone (about 60%), the Antarctic ozone "hole" focused world attention on the polar regions. Subsequently, a great deal of field data have

been gathered since the discovery of this phenomenon in 1985 (WMO et al., 1994).

Measurements of ozone and chlorine monoxides (a chemically reactive form of chlorine) taken by aircraft flying within highly depleted regions in south pole provided conclusive evidence that chlorine (alone and in combination with bromine) was primarily responsible for the Antarctic ozone hole (Anderson et al., 1989).

Recent observations from ozonesondes indicate that on 12 October 1993, total ozone at the South pole fell to a new level of 91 DU, well below the previous level of 105 DU measured there in October 1992 (WMO et al., 1994). Readings in the 90-105 DU range were measured on 8 consecutive soundings from September to 18th October, 1993.

Observations from both ozonesondes and satellites since 1991 revealed that spring-time ozone depletion at the South pole had worsened in the 12-16 Km region, with total ozone destruction at 15-16 Km in 1992 and 1993 (WMO et al., 1994). Similar observations were made in 1992 at Mcmurdo 78⁰S (Johnson et al., 1994)

indicating that depletion at lower altitudes was widespread.

Before the appearance of ozone hole, the naturally occurring spring-time ozone levels over Antarctica were about 30-40% lower than spring-time ozone levels over the Arctic (WMO et al., 1994). This natural difference stems from the exceptionally cold temperatures and different wind patterns within the Antarctic stratosphere as compared to the Arctic.

This difference in temperature and wind is associated with variations in land/ocean symmetry between the two regions. The South pole has a large land mass, (Antarctica) that is entirely surrounded by the ocean. These conditions produce very low stratospheric temperatures which in turn leads to formation of clouds (Polar stratospheric clouds). These clouds lead to chemical changes that promote rapid ozone loss during September and October of each year, resulting in the ozone hole (WMO et al., 1994).

In contrast, the Northern polar region lacks the land/ocean symmetry characteristic of Southern

polar area. As a consequence, Arctic stratospheric air is generally much warmer than in the Antarctic, and fewer clouds form there, subsequently resulting into low ozone depletion (WMO et al., 1994).

However, considerable episodic winter-time Arctic depletion associated with the presence of polar stratospheric clouds (PSC) has been measured. Confirmation of PSC processes in the Arctic vortex derived from measurements of chlorine monoxide (ClO). In 1991 and 1992, concentrations exceeding 1 ppbv were detected in the vortex. These were comparable in magnitude to concentrations observed in the Antarctic ozone hole (Waters et al., 1993). Furthermore, these concentrations were found in the air that had traveled through the coldest portion of the northern vortex. This implied activation by PSCs (Toohey et al., 1993). As temperatures rose in February, implying dissipation of PSCs, concentration of ClO fell.

Total column ozone losses of up to approximately 10 percent were measured by balloons over the Arctic during the winter of 1989-90 (Hofmann and Deshler,

1991). Further measurements made during the winter of 1991-92 showed total column ozone decrease of approximately 10 percent and losses of up to 25 percent at altitude between 15 and 20 km (NASA, 1992). Calculations indicated that this depletion was due to reaction involving both bromine and chlorine.

The distribution pattern of ozone is highly dependent on the atmospheric dynamics which are described below.

2.2 ATMOSPHERIC DYNAMICS THAT INFLUENCE OZONE

DISTRIBUTION

This section describes both tropospheric and stratospheric dynamics of ozone coupled with stratospheric-tropospheric ozone exchange.

2.2.1 DYNAMICS OF TROPOSPHERIC OZONE

Ozone distribution in the atmosphere may be associated with two circulation systems namely convective (vertical motion) and advective (horizontal motion).

There are two categories of convection. The

first one is produced mechanically by interaction between wind and obstacles on the earth's surface, or between layers of air moving at different speeds. The second category is as a result of free convection which arises from natural buoyancy of air due to differential heating (Reiter, 1975). The major vertical transport of ozone, carbon dioxide, methane, water vapour and other substances through the planetary boundary layer is achieved mainly through these convective processes.

There are three spatial scales of atmospheric motion. These are,

- (a) Micro-scale.
- (b) Meso-scale.
- (c) Macro-scale (synoptic).

In low levels of the atmosphere, vertical scale of small scale motions are dominant. These micro-scale convection includes the turbulence associated with winds near the ground and small scale cumulus clouds.

Larger cumulus and cumulonimbus clouds which have strong updraft extending from planetary boundary layer to the upper troposphere constitute meso-scale

convection (10-20 km). Huge cumulonimbus towers may reach above 20 km, and at their crest may penetrate several kilometers into the stratosphere. As clouds disperse, however, they leave behind little water vapour at high altitudes together with particles and gases brought up rapidly from below. Meso-scale convection is the most dominant upward transporting process in the troposphere over most humid, low latitude areas (Biswas, 1979).

Synoptic scale vertical motions, which are much slower (of the order of a few centimeter per second) are of larger geographical scale. One kilometer ascent of air may correspond to several hundred kilometers of horizontal motion of air (Reiter, 1975). Synoptic systems include among others jet-streams, cyclones, anticyclones and atmospheric waves. They contribute significantly to some of the observed ozone variations (WMO, 1986).

Advection of air is responsible for horizontal transport of ozone and other gases. While the mean flow is towards the east in mid-latitudes and towards the

west in the tropics and polar latitudes, the actual day to day winds are very variable (Levy, 1988).

The micro-scale advections include the urban/rural winds which are induced by small scale pressure gradients. Meso-scale advections like land/sea breeze and mountain/valley winds are induced by regional scale features like the larger water bodies, topography and blocking systems (Levy, 1988). Synoptic-scale advections generally consist of the horizontal component of the general circulation motion (Hadley, Ferrel and Polar cells).

2.2.2 DYNAMICS OF STRATOSPHERIC OZONE

The Quasi-biennial oscillation (QBO) of zonal winds is a tropical phenomenon situated in the lower and middle stratosphere. This phenomenon significantly determines stratospheric circulation in the tropics (Ogallo et al., 1993).

The QBO recurs after 28 months at all levels, although the phenomenon is by no means a periodic oscillation of zonal winds (Margarudt and Naujokat,

1997). Short and long cycles of less than two and about three years respectively have been realized. It has been established that above 30 hPa, easterly winds last longer than their westerly counterparts. However, below 30 hPa, the converse is evident. An investigation of the lengths of individual cycles further showed an increase with time. A least square estimate resulted in a positive trend of typically 1.8 months/decade in all levels. However, a convincing physical mechanism explaining the variability of cycles is still missing.

However, smaller systems that include gravity and tidal waves among others contribute to vertical motion in this region (Murgatroyd, 1969). These waves which have small amplitudes in lower stratosphere become increasingly major systems in the upper stratosphere and mesosphere.

The principal features of quasi-biennial oscillation are,

- (a) The zonal wind component in the equator varies between west and east with a recurrence of about

28 months (Marquardt and Naujokat, 1997).

- (b) The phase of the oscillation varies with height such that the easterly and the westerly currents descend at a rate of about 0.5 and 1 km per month respectively. However, while propagating downward, zonal wind speeds weaken (Marquardt and Naujokat, 1997).
- (c) The oscillation appears to have greatest amplitude at about 25 km and is nearly indistinguishable near the tropopause (Craig, 1965).
- (d) The oscillation occurs simultaneously in both hemispheres and at all longitudes, with largest amplitude near the equator (Craig, 1965).

These cycles have been shown to influence slightly the periodic fluctuation of the total column of ozone (WMO, 1986).

In the extra-tropics, the dominant feature of the stratospheric flow is an immense, annually reversing system of circumpolar zonal winds, which are westerlies

in the winter and easterlies in the summer, with maximum speeds in both cases at the stratopause or in the mesosphere.

The winter stratospheric westerlies are strong and variable. They are often called the polar-night westerlies because the strongest winds occur at relatively high latitudes near the boundary of the polar night. When the average winter circulation of the stratosphere and mesosphere is viewed as an entity, the strongest west winds are found at much higher levels (WMO, 1986).

In the summer stratosphere no such intense winds or violent changes occur. In the stratospheric easterlies above 20 km or so, the wind direction is surprisingly constant from day to day and latitude to latitude and seldom varies more than 10° or 20° from easterlies.

Nonetheless, there is evidence of rather small-scale, small-amplitude fluctuations in the stratospheric easterlies. Flohn et al., (1959) discovered oscillations with wavelength of about 100 km

from the trajectories of constant-level balloons and Mantis (1963), also from the study of constant-level balloon trajectories, showed that much of the variability of the winds near 30 km were associated with systems that were much smaller in scale than those found in the troposphere or indeed than could be revealed by conventional winds observations. Stratosphere-troposphere exchange of ozone forms the subject of the next discussion.

2.2.3 STRATOSPHERIC-TROPOSPHERIC OZONE EXCHANGE

At least six possibilities of stratosphere-troposphere mixing processes have been recognized (Biswas, 1979., Whitten and Gerry, 1986)

These include,

- (a) Motion associated with vertical arms of the general circulation cells which include Hadley, Ferrel and polar cells.
- (b) Penetration of the tropopause by cumulonimbus clouds as indicated in section 2.2.1.

- (c) Quasi-horizontal transfer through the tropopause discontinuity in the mid latitudes.
- (d) Downfolding of the tropopause in strong frontal zones especially when cyclonic disturbances are active.
- (e) Fall-out probably with scavenging.
- (f) Upward moving gravity waves, which are thought to play a rather special role in the winds of the lower stratosphere (Biswas, 1979).

The standard model for the exchange of air between stratosphere and troposphere was first proposed by Brewer (1949), based on observations of extremely low stratospheric humidity. The model calls for an extension of the Hadley circulation through the high, cold tropical tropopause, followed by poleward and downward motion in the subtropical extra-tropical stratosphere. The circulation is completed by subsidence in the extra-tropical stratosphere (particularly in the winter hemisphere) and outflow of stratospheric air into the extra-tropical troposphere

(figure 3). On the basis of this model, the outflow of stratospheric ozone into the troposphere should be greatest during winter and spring seasons, when the reservoir of ozone in the lower stratosphere is greatest (Bourman and Krueger, 1985). Confirmation of the basic pattern has come from general circulation model (GCM) studies (Levy et al., 1985).

The different heights of tropical and polar tropopause create a media for quasi-horizontal mixing of atmospheric constituents. For instance, a polar moving current from tropical zone at 16 km will move from the tropical tropopause into the polar stratosphere. Strong waves in the westerly jets stream, which are 2 to 5 km below this level, often induce such transfers. Such air is dry (temperature less than -75°C) and thus contains hardly no moisture, but particles and trace gases may be carried through the gap (Biswas, 1979).

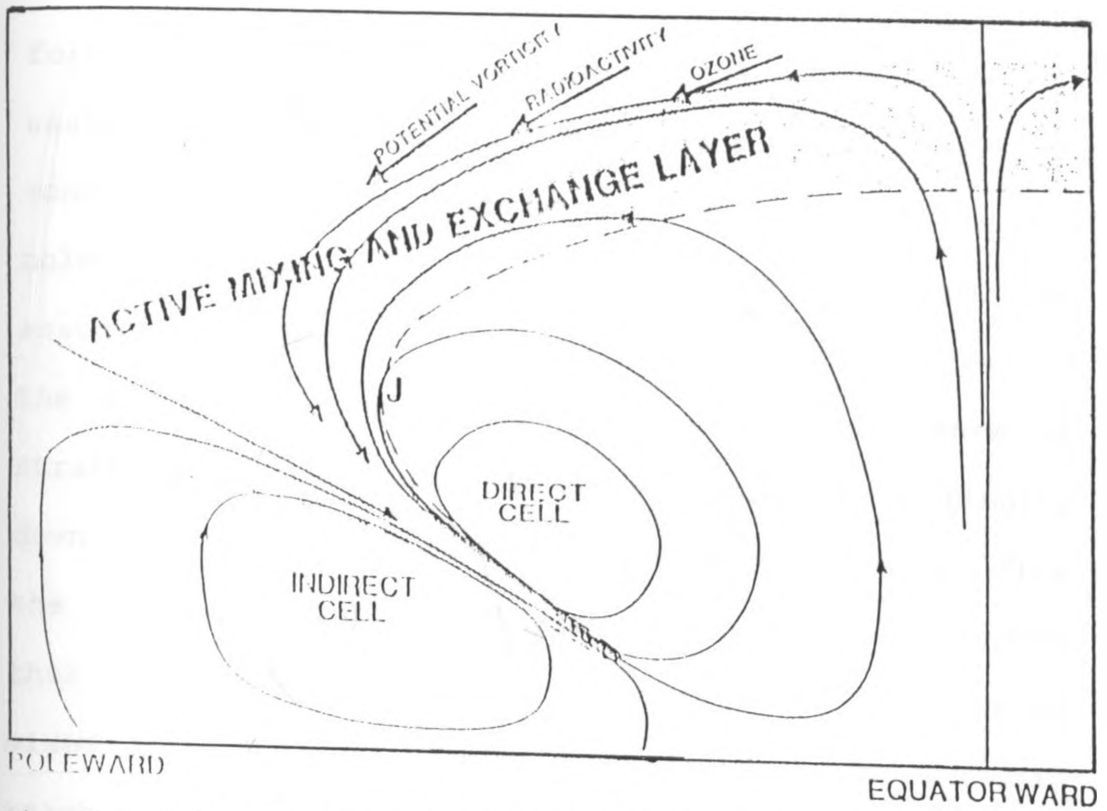


Fig. 3: Schematic view of stratospheric-tropospheric ozone exchange (Redrawn from Danielsen, 1968)

There is a similar mechanism in the tropopause folding. Immediately below the jet stream cores of the westerlies, there are found strong, sloping frontal zones. These are boundaries between cool air on the poleward side and warmer on the tropical. In association with the eastward moving cyclone waves of the westerly current, strong, slanting subsidence of stratospheric air occurs in the frontal zones, bringing down low humidity, radioactive tracers and ozone from the lower stratosphere (Biswas, 1979). The substances thus removed from the stratosphere are subsequently mixed into the troposphere, and in the long run may reach the earth's surface.

Fall out is not significant although it play some role in the mixing processes, since the lower stratosphere aerosol particles are generally too small to precipitate rapidly. Some meteoric dust does however gravitate downwards across the tropopause. Such dust may enter into various physical and chemical processes in the stratosphere and may hence carry some non-meteoric molecules or atoms along with it (Biswas,

1979).

The greatest obstacle to an accurate assessment of the flux of ozone from the stratosphere to troposphere lies in the episodic nature of the exchange processes. Attention has been drawn to cut-off cyclones in the upper troposphere as possible agents of stratosphere-troposphere exchange (Hoskins et al., 1985), and there have also been suggestions that the subtropical jet streams may play a part (Allam and Tuck, 1984). Quantitative estimates of ozone flux associated with these mechanisms have not been reported as yet, and it is not known as whether they are as important as tropopause folding (Vaughan, 1988)

Until recently, stratospheric-tropospheric exchange (STE) of mass and chemical species was regarded as a problem on mesoscale phenomenology of strong mixing events such as midlatitude tropopause folds and deep tropical convection. However, over the last few years, it has been explicitly recognized that STE is an aspect of a global picture of transport and mixing of mass and chemical species, which is constrained by the

dynamics of the whole stratosphere (Gettelman et al., 1997., Shepperd, 1997).

CHAPTER THREE

3.0 DATA COLLECTION AND ANALYSIS

There are several methods of measuring vertical distribution of ozone. These methods include among others the use of ground-based instruments, balloons and aircraft. Use of ground-based instruments is one of the most economical and convenient method of measurements of ozone vertical profile. These advantages coupled with availability of Dobson spectrophotometer led to the utilization of this instrument to obtain vertical ozone profiles.

The instrument is stationed at Chiromo campus, University of Nairobi, Kenya ($1^{\circ} 16' S$, $36^{\circ} 48' W$) at an altitude of 1710 m above sea level. The primary data were collected for six months ranging from November 1995 to April 1996. This period represented two seasons, namely , hot (December 1995, January 1996 and February 1996) and cold (November 1995, March 1996 and April 1996). Consequently, this duration was assumed to

be fair representation of the entire seasons of the year.

Since no upper air observations were available at Chiromo station, long term mean values of meteorological parameters that included tropopause height, tropopause temperature, zonal wind speed, wind direction and temperature at levels 700 mb, 300 mb, 200 mb, 100 mb and 50 mb were obtained from Dagoretti meteorological station, situated in Nairobi at 6.2 km from the station.

Detailed observational procedure forms the subject of the next discussion. However, the working principle of the Dobson ozone spectrophotometer is first described.

3.1 PRINCIPLE OF OPERATION OF DOBSON OZONE SPECTROPHOTOMETER

Light enters the instrument through a window in the top of the instrument and, after reflection in a right-angled prism, falls on a slit S_1 of a spectroscopy (Figure 4). This spectroscopy consists of a quartz lens

which renders the light parallel, a prism which breaks up the light into its spectral colours, and a mirror which reflects the light back through the prism and lens to form a spectrum in the focal plane of the instrument (Komhyr, 1980). The required wavelengths are isolated by means of slit S_2 , S_3 , and S_4 located at the instrument's focal plane.

Two shutter rods are mounted at the base of the spectrophotometer. The left-hand S_4 shutter is used only when the spectrophotometer tests are conducted, and should be pushed all the way into the instrument when ozone observations are made. The right-hand selector rod blocks out the light passing either through slit S_2 or S_4 . When this rod is set to position SHORT, only slits S_2 and S_3 are open so that observations can be made on A, B, C, or D wavelength pairs (table 2). With the wavelength selector rod in the LONG position, only slits S_3 and S_4 are open and observations can be made on the C' wavelengths.

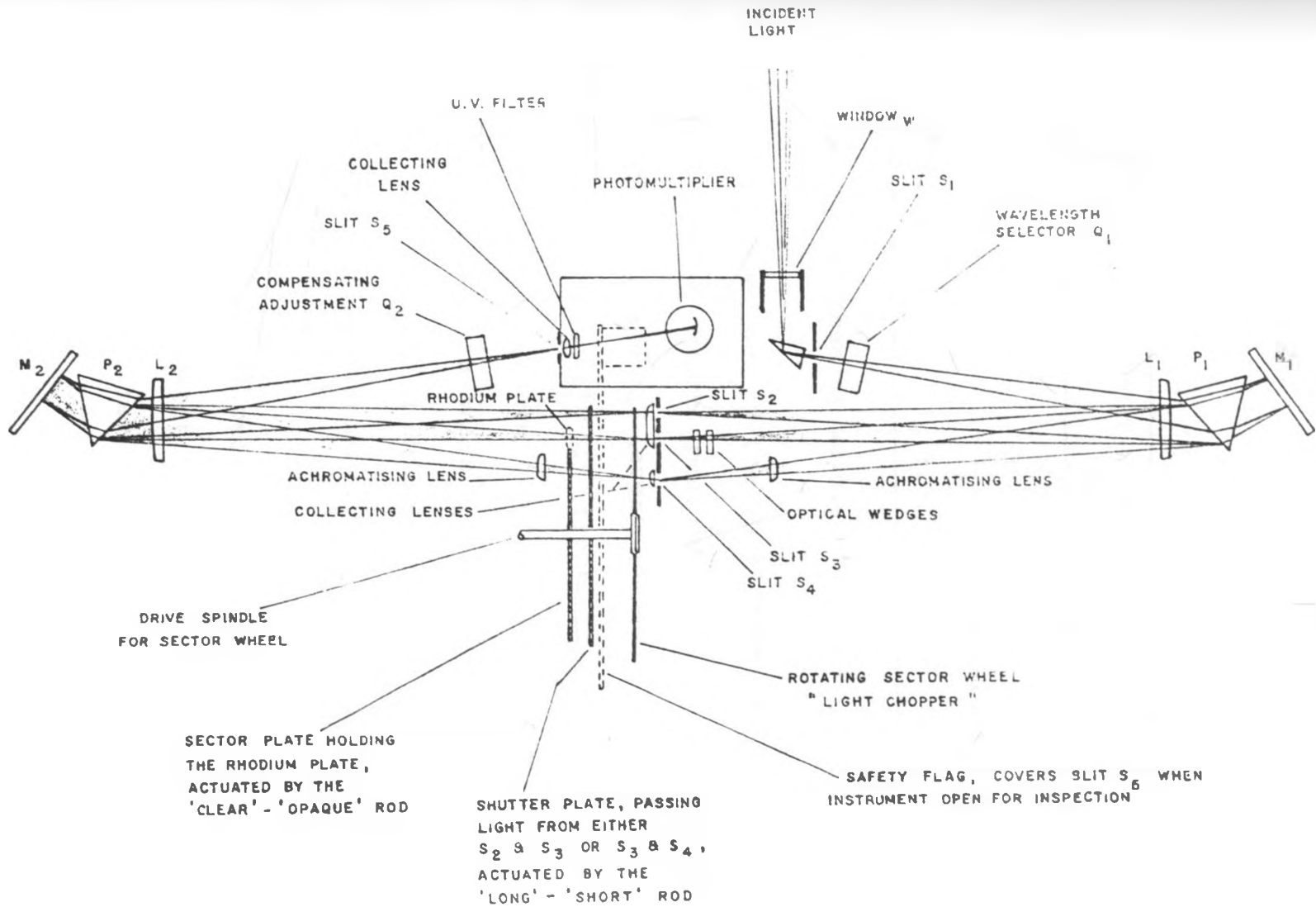


Fig. 4: Optical system of the Dobson spectrophotometer (after Komhyr, 1980).

WAVELENGTH PAIR	SHORT WAVELENGTH (nm)	LONG WAVELENGTH (nm)
A	305.5	325.4
B	308.8	329.1
C	311.5	332.4
C'	332.4	343.6
D	317.6	339.8

Table 2: Ranges of wavelength pairs

Selection of the wavelengths A, B, C, C', or D when making ozone measurements is accomplished by rotating Q_1 and Q_2 levers. Thick, flat quartz plates mounted immediately in front of the first and last slits (S_1 and S_5) are fixed to the levers. Depending on the direction in which the quartz plates are rotated, the light beam passing through them is refracted upwards, or downwards, thereby providing for wavelength selection.

An optical wedge, consisting of two quartz flats is mounted in front of slit S_3 . The position of the wedge is controlled by turning a graduated dial (R-readings) located on top of the instrument. With the

dial set at 0° the thin portion of the optical wedge is positioned in front of S_3 so that light passes through the optical wedge and slit S_3 with practically no loss of intensity. With the dial set at 300° , however, the S_3 light beam is almost completely absorbed by the thick portion of the optical wedge. It follows that there exists a "balance" setting of the dial somewhere between 0° and 300° where the intensity of light beam passing through the optical wedge and slit S_3 will have been reduced to the level of the intensity of S_2 wavelength beam (or S_4 wavelength beam if observations on C' wavelengths are made). For any given position of the dial the intensity of the light passing through the optical wedge is reduced in a definite ratio which is determined during the original calibration of the spectrophotometer. In order to measure the relative intensity of the two wavelengths on which observation are made, then it is necessary only to be able to detect the balance position of the dial.

Indication of the balance position of the dial is effected in the following manner: assume that the dial

is initially set off-balance so that the two light beams leaving slit S_3 and slit S_2 (or slit S_4) are not of equal intensity. The light beams then pass through the rotating sector wheels, driven by a motor, which chops them and allows them to proceed alternately into a second monochromometer, and, finally, to fall on the photomultiplier located behind slit S_5 . Since the two light beams falling alternately on the photomultiplier are of unequal intensity, they give rise to a pulsating electron current flowing out of the photomultiplier. This current is amplified by an alternating current amplifier, and causes a deflection on an indicating direct current micrometer. If on the other hand the dial is turned to the balance position, the two light beams falling alternately on the photomultiplier become of equal intensity. They then give rise to a steady, direct current which cannot be amplified by an alternating current amplifier. Since there is no pulsating current to amplify, the micrometer reads zero. Thus, a null reading on the micrometer is an indication of the balance position of the dial. The

relative intensities of the two wavelengths on which observations are made may then be obtained from the balance position dial reading and calibration tables supplied with the instrument.

Umkehr observations which yield useful information on the vertical distribution of ozone are described below.

3.1.1 TYPES OF UMKEHR OBSERVATIONS

An optical effect is observed when the ratio of the measured intensities of scattered zenith skylight at two different wavelengths (one strongly absorbed by ozone whereas the other is weakly absorbed) is plotted against the increasing zenith angle of the sun between 60° and 90° . The ratio increases with the increasing zenith angle up to about 86° , then a reversal (Umkehr) occurs. The combination of absorption and scattering of the wavelengths by ozone and air respectively results into Umkehr effect from which the vertical profile of ozone is deduced (Craig, 1965).

Two types of Umkehr observations are possible. The

first involves a standard Umkehr observation procedure (Mateer and Dutch, 1964) that has been in use since late 1950's while the second is the short method (Mateer et al., 1979) which has a time saving advantage that allows for an increased frequency of such observations to be made during conditions of clear sky (Komhyr, 1980). The latter type of Umkehr observation was employed in the study.

Observation of total amount of ozone which forms part of Umkehr observations, was made before any Umkehr observation was conducted.

The following section describes the theory of Umkehr measurements and observing procedures utilized in the present work.

3.1.2 UMKEHR OBSERVING PROCEDURES

The Umkehr observations commenced a few minutes before sunrise and continued until the zenith angle of the sun was less than about 80° . The afternoon measurements started when the zenith angle of the sun was about 80° and continued until shortly after sunset.

Measurements were made on A, C, and D wavelength pairs. One dial reading (R-reading) was obtained for each wavelength every two minutes (Komhyr, 1980).

To ensure that the data collected were of good quality, the spectrophotometer was subjected to two tests on monthly basis which are briefly described below.

3.1.3 DOBSON SPECTROPHOTOMETER QUALITY CONTROL TESTS

It is possible that the spectral characteristics of a spectrophotometer may change with time in a number of ways so that the original calibration of the instrument will not apply. These changes include variation of wavelengths falling on slits S_2 , S_3 and S_4 due to slow deformation of the spectrophotometer main frame casting or a shift of some of the optical components and alteration of relative transmission along the optical wedge (Komhyr, 1980). In order to detect such changes and make allowances for them by applying corrections to observational data, two tests, described below were performed on monthly basis.

3.1.3.1 Mercury lamp tests

A correctly calibrated spectrophotometer that is permanently located at a station has associated with it a table of setting of Q. In this table are listed Q lever setting (in degree of arc) for A, B, C, D, and Hg-312.9 nm wavelengths versus instrument temperature (in degree Celsius). To ensure that ozone observations are being made at all times on correct wavelengths, routine mercury lamp tests are performed and the data obtained are compared with reference data presented in the table of setting of Q. Experimental and reference Q_1 values for the Hg-312.9 nm wavelengths should agree to within +/- 0.3 degrees (Komhyr, 1980).

If there should appear a persistent difference greater than about 0.3 degrees in the experimental and reference Q_1 values, all the wavelength settings of A, B, C, and D wavelengths should be corrected in the following proportions:

Hg=1.00°, A=0.67° B=0.87° C=0.99° D=0.97°

3.1.3.2 Standard lamp tests

Standard lamp tests are performed to confirm that the level of calibration of the spectrophotometer has remained constant. The test is conducted immediately after the mercury lamp test has been performed. After the test, a comparison of experimental mean data and reference data is performed for the same lamp given in the instrument's table entitled "Reference standard lamp data". Experimental values of R_a , R_b , R_c , and R_d should not differ from reference values by more than ± 1.0 degree and R_c values should agree to within ± 2.5 degrees. However, if the difference is larger than the maximum accepted value, it is subsequently added or subtracted to the corresponding N-value (Komhyr, 1980).

Processing of Umkehr data is discussed below.

3.2 PROCESSING OF UMKEHR DATA

In processing short Umkehr data for C wavelengths, the N_c (intensity of C wavelength ratio) values of interest are those corresponding to solar zenith angles Z of 80° , 83° , 84° , 85° , 86.5° , 88° , 89° , and 90° . To

extract the needed information from the entire body of observational data, plots of instrument dial readings R_c versus Greenwich Mean Time were drawn. Then, specific time for each solar zenith angle was computed. R_c values, corresponding to the computed times, were then extracted from the plotted data and converted to the required N_c values using the conversion tables (Komhyr, 1980). Short Umkehr N_a and N_d values were obtained in a similar manner from plots of R_a and R_d versus Greenwich Mean Time.

The N -values were subjected to the new Umkehr inversion algorithm for the computation of the vertical profiles of ozone. This algorithm is discussed below.

3.2.1 UMKEHR INVERSION ALGORITHM

Gotz (1931) discovered and named Umkehr effect. The author realized that observations of the Umkehr effect contained information about the vertical distribution of ozone in the atmosphere. The shape of the Umkehr curve and therefore the vertical distribution of ozone depends mainly on the total ozone

content. However, there is no strict mathematical method of finding the vertical distribution of ozone from a given Umkehr curve (Mitra, 1952). Hence, several algorithms have been advanced.

The first retrieval algorithm, which was highly subjective, was developed by Gotz et al., (1934), who described methods A and B. Walton (1957) and Ramanathan and Dave (1957) developed specific procedures for application of method A and B respectively. At about 1959, Dutch developed a computer algorithm for retrieval of profile information. His method was an elaboration of method B such that the subjective views of the individual analysis were eliminated. Mateer and Dutch (1964) proposed a standard algorithm to be used for evaluation of all Umkehr observations. More recently, improvements in understanding of retrieval techniques (Rodgers, 1990) and new values for ozone absorption coefficients and their temperature dependent (Bass and Paur, 1984., Paur and Bass, 1984) led to the development of a new Umkehr inversion algorithm by Mateer and Deluisi (1992). This algorithm, composed of

two models, is utilized in this study.

3.2.1.1 The forward model

This model describes how the measurement y (N -values) depends on the ozone profile x . The Dobson zenith sky measurements may be written as:

$$N(x, z) = 100 \log_{10} \frac{I(x, z, L_2) / F_0(L_2)}{I(x, z, L_1) / F_0(L_1)} + C_0 \dots (12)$$

where N is the relative logarithmic attenuation for the wavelength pair in 100 log-units: the ratio is taken so that N is always positive. The quantity x refers to the ozone profile, z is the solar zenith angle, $I(x, z, L_2)$ is the radiance for the weakly absorbed wavelength by ozone, $I(x, z, L_1)$ is the radiance for the strongly absorbed wavelength by ozone, F_0 is the extra-terrestrial solar flux, and C_0 is an instrumental constant.

In this model, N is broken down into four separate components:

$$N_p = N - N_{ms} - N_r - C_0 \dots (13)$$

where N_p is the primary scattering component of N , N_{ms} is the multiple scattering component, N_r is a refraction component. N_p is treated as the observation in the next model and the other N components as corrections to the observation. To eliminate the instrument constant C_o , observation at the smallest zenith angle is subtracted from the observations at each of the other angles.

3.2.1.2 The inverse model

This model describes the retrieval procedure. The atmosphere is divided into 16 layers as shown in table 3.

For publication and archiving, the profile is reported in 10 layers, with layer 10 including all ozone above layer 9, and layer 1 including the retrieval ozone amount for layers 0 and 1.

Layer Number	Layer-based Pressure (atm)	Layer-based Height (km)
0	1.00E+0	0.0
1	5.00E-1	5.5
2	2.50E-1	10.3
3	1.25E-1	14.7
4	6.25E-2	19.1
5	3.12E-2	23.5
6	1.56E-2	28.0
7	7.81E-3	32.6
8	3.91E-3	37.5
9	1.95E-3	42.6
10	9.77E-4	47.9
11	4.88E-4	53.2
12	2.44E-4	58.3
13	1.22E-4	63.1
14	6.10E-5	67.8
15	3.05E-5	72.2

Table 3: Layers used for Umkehr ozone profiles retrievals.

The first guess ozone profiles are first computed before the inverse procedure is applied. The computation of the first guess is obtained as follows.

For layers 6-12, the ozone amount in layer k is given by:

$$x_k = A_k + B_k \cos[(J - J_{ok}) 2\pi / 365] \dots \dots \dots (14)$$

where the constants A_k , B_k , and J_{ok} are known for each latitude. For these layers, the ozone amount has a seasonal dependence determined by the Julian day (J).

For layers 0-3, x_k is independent of Julian day and is given by a quadratic function of total ozone,

$$x_k = A_k + B_k(X-300) + C_k(X-300)^2 \dots \dots \dots (15)$$

where the constant A_k , B_k , and C_k are also known for each latitude and X is the observed total ozone. The amount of ozone in layers 4 and 5 are determined by assuming a cubic fit between $\ln(X_k)$ for layers 3, 4, 6, and 7 and the layer number, where X_k is the amount of ozone from the top of the atmosphere down to the base of layer k .

For layers 13, 14, and 15, X_k is given by:

$$X_{13} = (X_{12}/X_{11}) (X_{12}), \text{ etc} \dots \dots \dots (16)$$

The measurement vector y (N-value) is expanded about a linearization point x_n as follows:

$$y = y_n + \partial y / \partial x (x - x_n) = y_n + K_n (x - x_n) \dots \dots \dots (17)$$

where K_n is the matrix of weighting function, that is, the partial derivatives.

The ozone profile retrieval is obtained using the following iteration equation,

$$x_{n+1} = x^A [S_x^{-1} + K_n^T S_E^{-1} K_n]^{-1} [K_n^T S_E^{-1}] [(y - y_n) - K_n (x^A - x_n)] \dots \dots (18)$$

where x^A is the first guess ozone profile, S_x is the covariance uncertainty matrix for the first-guess profile, S_E is the error covariance matrix for the measurements, y_n is the vector of calculated observations for x_n , and the superscript T represents the matrix transposition.

Convergence is determined primarily by the size of the $x_{n+1} - x_n$, which must be less than 0.04 in all layers and the root mean square (r.m.s) value of the change

must be less than 0.01. Iteration is also terminated if the r.m.s value of the change in the last square bracket of the retrieval equation is no greater than 0.15 N-units. At most, five iterations are permitted. When more than five iterations are required for convergence, there is a poor fit and the observation is discarded.

The retrieved profiles were subjected to the following analysis.

3.2.2 PROFILES ANALYSES

To investigate the vertical distribution pattern of ozone, the arithmetic means of ozone quantity for each layer over the study period were computed and analyzed.

In order to assess the dynamics of ozone, monthly analysis of ozone concentration in each layer was conducted. This was realized by analyzing both the mean monthly variations of ozone and the subsequent standard deviations in each layer.

Spearman rank correlation technique was utilized in this study to determine the correlation coefficients between the ozone amount and the long-term mean of meteorological parameters.

This non-parametric method uses the rank of data rather than the actual data values. First each variable is ranked separately. The difference between the ranks of paired observations is then computed so as to measure the disagreement between the pairs. Finally, a relative measure of disagreement is calculated by summing the squared disagreements over all pairs.

Mathematically, Spearman rank correlation coefficient is given as:

$$r_s = 1 - \frac{6 \sum D_i^2}{N(N^2 - 1)} \dots\dots\dots (19)$$

Where r_s = Spearman rank coefficient.

N = Number of paired variables.

D = Difference between ranks of corresponding variables.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The discussion of the results is based on three major categories. The first describes the results obtained from the processing of raw data, the second is based on the analysis of the vertical profiles of ozone and the last one describes spearman rank correlation analysis between ozone amount and long-term mean of meteorological parameters.

4.1 PROCESSING OF UMKEHR RAW DATA

Results from the two lamp tests are shown in tables 4 and 5.

MONTHS	NOV. 199	DEC. 1995	JAN. 1996	FEB. 1996	MAR. 1996	APR. 1996
DIFFERENCE	-0.1	-0.08	-0.2	-0.04	-0.19	-0.13

Table 4: Results from mercury lamp tests.

MONTHS	NOV. 1995	DEC. 1995	JAN. 1996	FEB. 1996	MAR. 1996	APR. 1996
N _a	1.1	3.0	1.2	2.0	3.1	3.0
N _b	1.2	2.0	2.1	2.0	3.0	3.0
N _c	1.2	1.1	2.2	2.0	2.1	3.0

Table 5: Results from standard lamp tests.

The mercury lamp tests were within the acceptable limits (table 4). That is, the difference between the reference and experimental values were all less than ± 0.3 (Komhyr, 1980) and therefore, no adjustment were made on Q_1 values. This effectively showed that the ozone observations were made on the correct wavelengths.

However, for standard lamp tests, adjustment on N-values for each wavelength were performed by adding the values in table 5. This is because the difference between reference and experimental R-values for all wavelength pairs (A, C, and D) were greater than the maximum accepted value of ± 1.0 (Komhyr, 1980). Hence this test ensured that alterations of the

spectrophotometer calibration were accounted for.

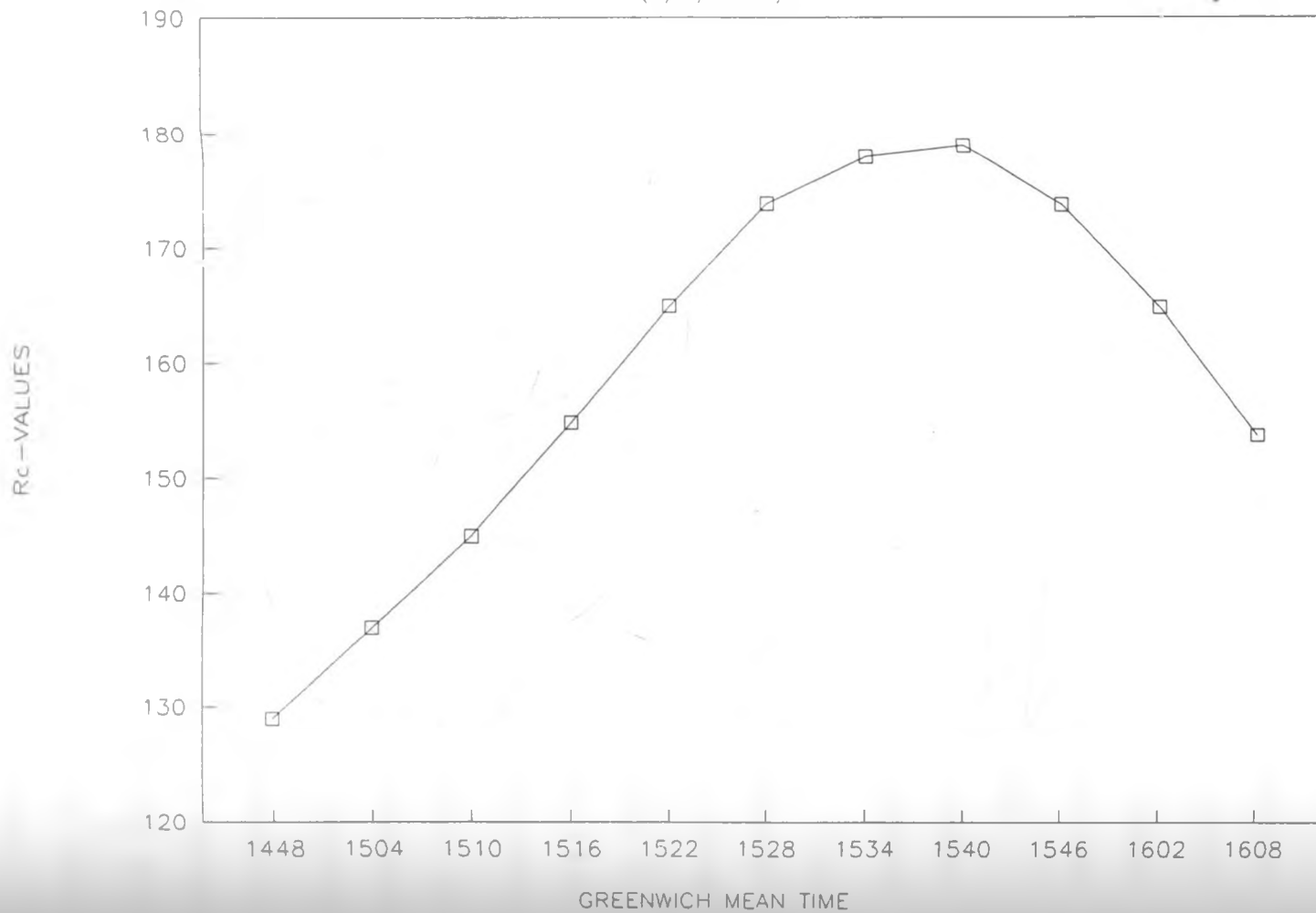
To extract the R-values corresponding to a specific time of a given zenith angle, plots of instrumental dial readings R versus Greenwich Mean Time were drawn. The graphs showed increase in R - values and eventual decrease (reversal or Umkehr) at about 86° zenith angle. This reversal in the plotted curve is related to the scattering height in the atmosphere of the wavelengths on which observations are made. A sample plot is shown in figure 5.

There were 65 days of Umkehr observations. However, only 34 days of retrieved profiles were obtained after subjection of the raw data to the new Umkehr inversion algorithm. This situation was attributed to erroneous raw data rejected by the algorithm which has a high quality data control.

Since the spectrophotometer was subjected to regular tests, the possible major sources of errors were associated with observations and clouds.

Fig. 5: SAMPLE PLOT OF UMKEHR DATA

(7/1/1996)



Umkehr observations are made when the zenith sky is free from clouds. At other times, it is desirable that the zenith sky be cloudless but permissible that clouds cross it periodically when measurements are temporarily terminated. With persistent clouds interference during Umkehr observations, the accuracy of the raw data is adversely reduced. This is because the Umkehr curves of such observations do not, in most cases meet the required smoothness standard due to non-continuity in R-values. In this study, clouds effects on the accuracy of the raw data were clearly evident. There were 20 days of Umkehr observations made with sporadic clouds passage over the zenith sky. Out of these observations, only 5 vertical profiles were realized. This essentially indicates that 23% of observed data was rejected due to clouds interference.

The rejection of the remaining 25% of observed data was attributed to mainly the inherent errors of the new Umkehr inversion algorithm (section 4.2.1) and to some small degree the observational errors. However, errors arising due to observation were minimized to the lowest

possible level by exercising precise observations.

4.2 ANALYSIS OF OZONE PROFILES

In an attempt to analyze the ozone profiles obtained, a brief look at some of the factors that have negative influence on the profiles are first highlighted below.

4.2.1 FACTORS THAT INFLUENCE THE OZONE PROFILES

Dobson spectrophotometer calibration and alignment errors produce bias errors in measurements and, hence, in the retrievals. For instance, optical calibration errors may produce a change in the retrieval profile shape which is somewhat dependent on total ozone amount (Rodgers, 1990). For these reasons, it is important to compare carefully Umkehr profiles obtained in the year proceeding and the year following any instrument change, namely, a new instrument in use, a re-alignment or a re-calibration. In the current study, none of these instrumental changes were effected.

Errors in the total ozone measurement may affect

the ozone profiles. For example when the total ozone measurement is 10 DU higher, this error causes the addition of ozone in all layers except 4, 5, and 6, where there may be a decrease. The percentage change is greatest in layers 0-3. When total ozone is too low, a similar result is obtained with reversed sign (Mateer and Deluisi, 1992). However, precise measurements of total ozone exercised in this work minimized this type of error.

Atmospheric aerosols, particularly stratospheric aerosols which were not accounted for in this study, produce changes in Umkehr observations which lead to significant errors in Umkehr retrievals. The changes in observation are due to scattering and absorption of radiation by aerosols, such as dust and sulphate particulates (haze effect). In general, haze affects the Umkehr measurements by producing an apparent decrease in ozone concentrations in the region of ozone maximum and an apparent increase in the ozone concentrations in the region below the ozone maximum (Deluisi, 1979). The magnitude of ozone error caused by

haze depends mainly on the aerosols vertical distribution of concentration and the optical scattering.

Inherent errors in the new Umkehr inversion algorithm may also influence the ozone profiles. For instance, the forward model does not include absorption by the tropospheric pollutant sulfur dioxide (SO_2). The effects on the Umkehr curve of SO_2 in the lower troposphere and subsequently on ozone profile were determined (Mateer and Deluisi, 1992). The study showed two separate effects. First, there was a change in the shape of the Umkehr curve. Second, the total ozone measurements were too high.

Another forward model error is the failure to include multiple scattering in the partial derivatives calculation. Mateer and Deluisi, (1992) examined this error by comparing results from an earlier experimental algorithm in which multiple scattering were included in or excluded from partial derivatives. The research showed that for layers 4-8, the average difference from the average Umkehr data for Arosa, Boulder, Perth, and

Tateno did not exceed 0.5% and the standard deviations were less than 1%. For layer 1, the standard deviations and biases were larger.

The multiple scattering corrections calculated for the annual average first guess ozone profile show that the maximum errors occur when layer six's ozone amounts are at maximum and minimum of their seasonal variation. However, these corrections were not accounted for in the Umkehr algorithm. At 45°N for example, the retrieval errors are within 1% in layer 1. For the other layers, the retrieval error does not exceed 0.6% (Mateer and Deluisi, 1992).

Despite the above errors that may negatively influence, to small extent the computed ozone profiles, the algorithm utilized have statistically been developed in such a way that the retrievals best respond to real ozone profile different from the first guess profile. Subsequently, the ozone profiles obtained would, to some high degree, be a reflection of physical variation of ozone.

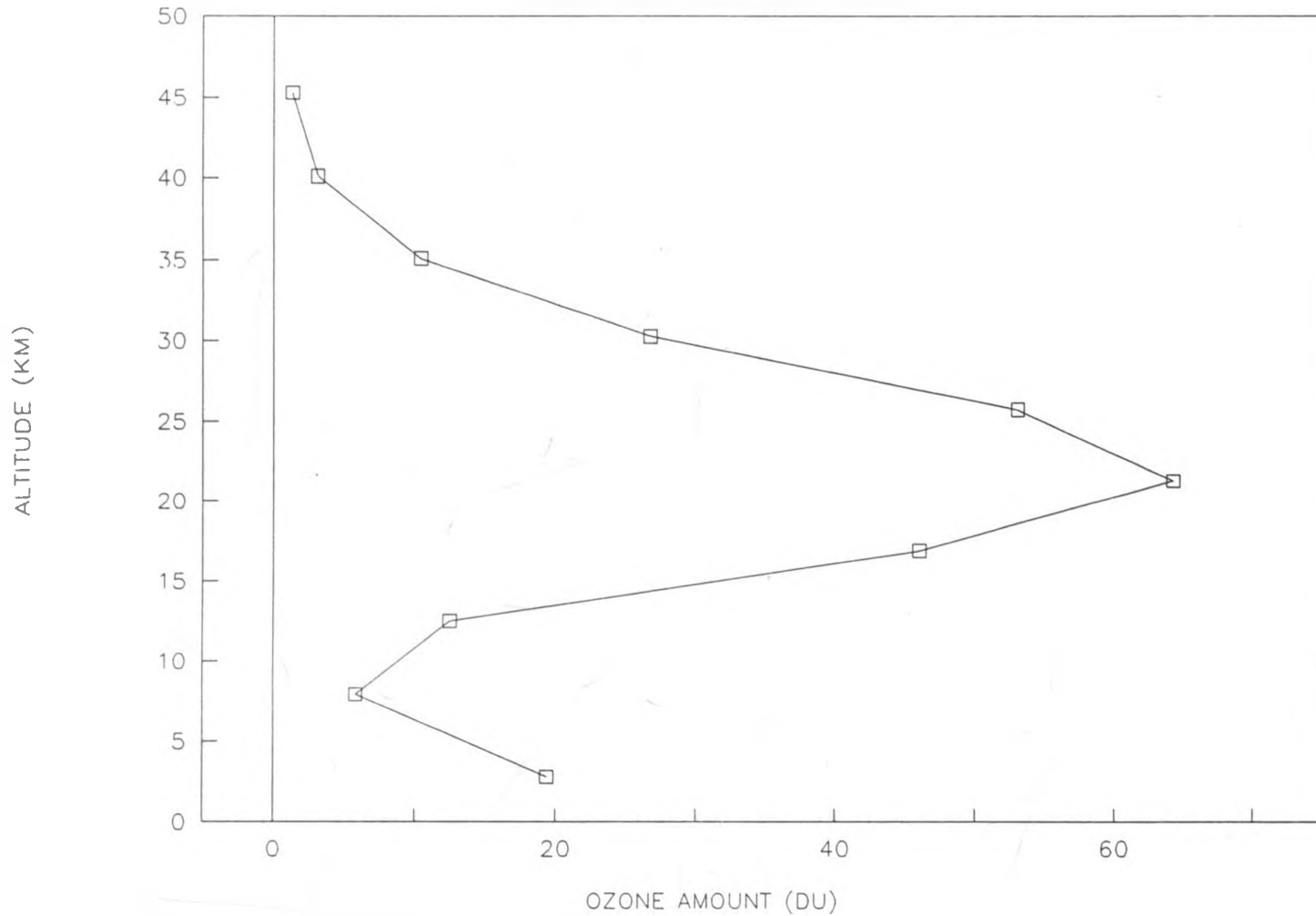
The following section describes the possible

physical factors responsible for the observed ozone variation.

4.2.2 MEAN VERTICAL DISTRIBUTION OF OZONE

Figure 6 shows the mean vertical distribution of ozone. It is evident from the figure that in this case, the largest concentration of ozone is approximately between 12.5 and 45 km which consists of about 89.6% of the total retrieved ozone. However, the peak ozone concentration (84.2%) is located in the region between 12.5 and 30 km. The figure further shows that the highest concentration is at approximate height of 21.5 km. The remaining ozone of about 10.4% is situated below 12.5 km.

Fig. 6: MEAN DISTRIBUTION OF
OZONE OVER THE STUDY PERIOD



Several studies in the tropics have drawn similar results of vertical distribution of ozone. These studies have shown that about 90% of ozone amount is located between 12 and 50 km with maximum concentration occurring between 19 and 23 km. Only 10% of total ozone is situated below 12 km (WMO et al., 1994., Subbaraya et al., 1990). This vertical distribution of ozone may be explained as follows.

A balanced natural production and destruction of ozone is most pronounced in the upper stratosphere (slightly above 30 km) as indicated in section 1.0. Due to the stability of the lower stratosphere (below 24 km and above the tropopause), ozone slowly drifts and diffuses to this region since it has high molecular weight (48 versus 29 of air). However, the tropopause inhibits further downward flow of ozone (Mathews, 1991). Hence, the lower stratosphere acts as a reservoir of ozone consequently resulting into the high observed concentration in this region (WMO, 1986).

Much of the tropospheric ozone originates from stratospheric-tropospheric exchange. This injection of

ozone occurs primarily at 30° to 40° latitude in both hemispheres and also at 50° to 60° latitude in the Northern Hemisphere. However, on infrequent occasions (Danielsen, 1980) this ozone-rich air can be carried into the tropical troposphere by the lower arm of the Hadley cell within a few days of leaving the stratosphere. Another source of ozone in the tropical troposphere is through downward mesoscale flow which balances the upward motion in convective systems. Ozone also takes part in an active photochemical cycle within the troposphere. This photochemical cycle can, depending on the concentration of nitric oxide, NO, and other ozone precursors such as methane, carbon monoxide among others lead to either production of more ozone or destruction of the ozone already present (Crutzen, 1974). Ozone is also destroyed in the troposphere by interaction with soil, plants and water surfaces (Galbally and Roy, 1991). However, the chemical processes that lead to this destruction are not well known. Due to lack of major sources of ozone in the troposphere coupled with significant destruction on the

earth's surface, low tropospheric ozone quantity is subsequently observed.

Details of quantitative variation of ozone in each layer and subsequently the dynamics of ozone are the subject of the next discussion.

4.2.3 VARIABILITY OF OZONE IN EACH LAYER

The monthly ozone variation in each layer over the study period is presented in figures 7 and 8. It is evident from these figures that layers 4, 5, 6, and 7 indicate the highest ozone fluctuations. In addition, these layers contain about 78.3% of the total amount of ozone. It therefore follows that total amount of ozone in this region is highly influenced by the fluctuation of ozone in these layers, situated between 15-33 km.

Fig. 7: MONTHLY OZONE VARIATION IN

LAYERS 1-5

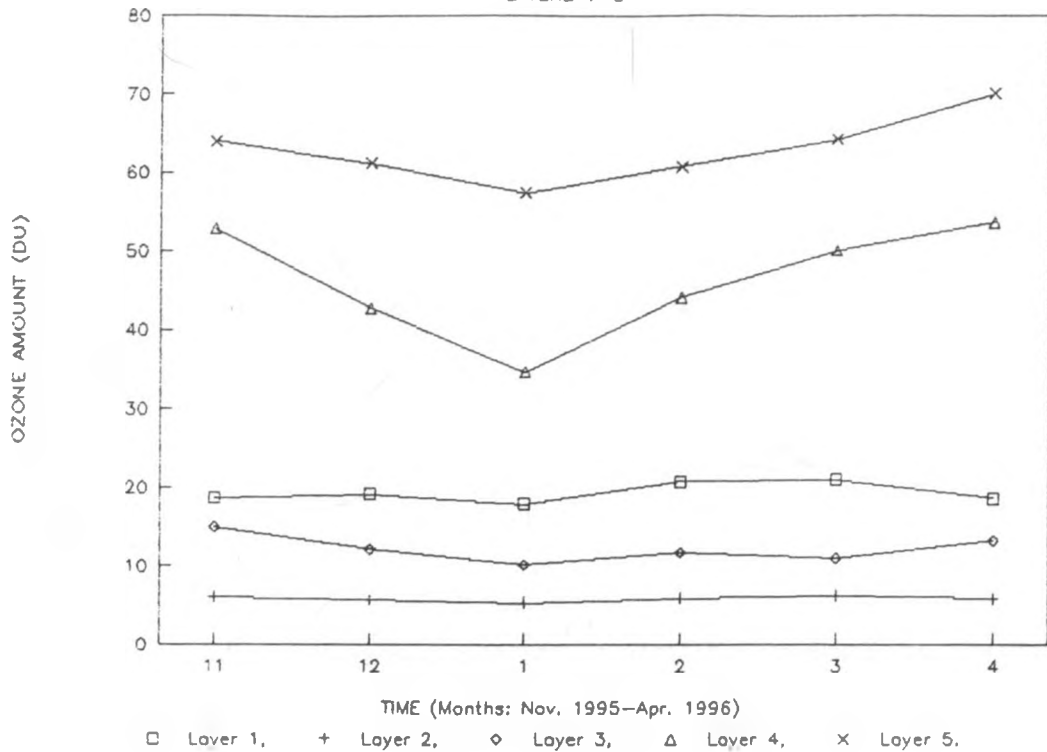
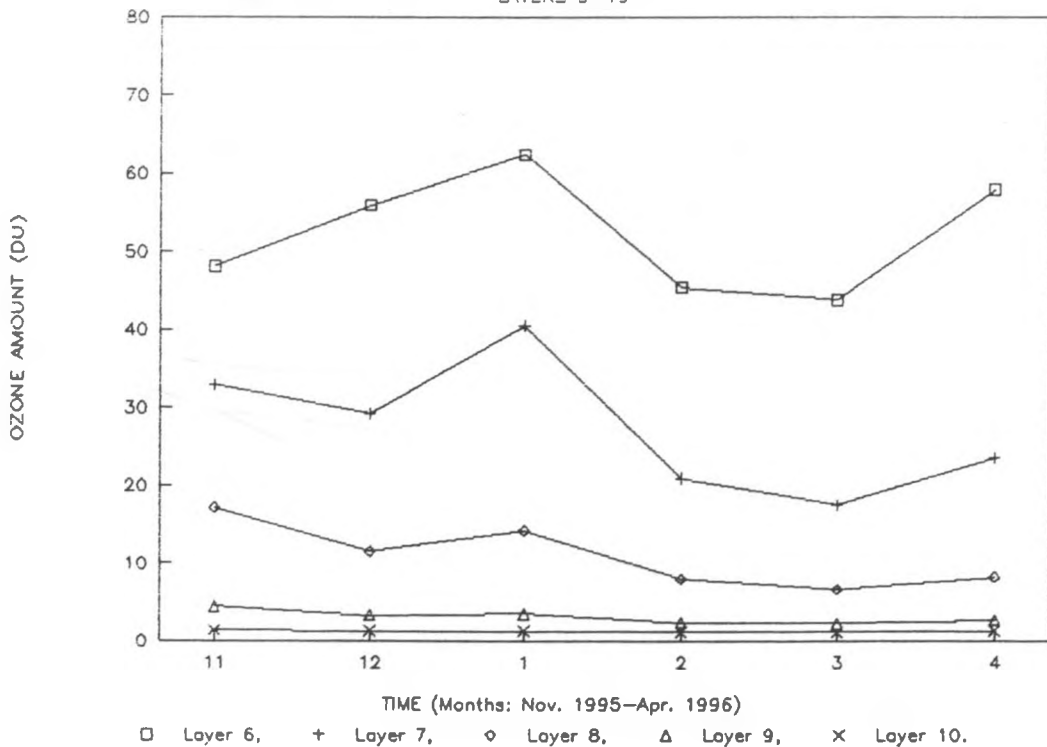


Fig. 8: MONTHLY OZONE VARIATION IN

LAYERS 6-10



Figures 9 to 18 show the mean monthly variation of ozone in each layer over the study period drawn on different scales. The figures exhibit three distinct patterns. These patterns may be grouped into layers 1-3, 4-5, and 6-10. Monthly standard deviations of ozone in each layer are shown in figures 19-21. The three patterns are further evident in these figures.

The observed patterns may be associated with the vertical circulation of air in the tropics. There are three vertical cells namely the lower cell (Hadley cell), the middle cell (indirect cell) and the upper cell (direct cell) as shown in figure 22. The lower cell is associated with the pattern exhibited in layers 1-3 , the middle cell with the pattern of layers 4-5 and the upper cell with that of layers 6-10.

The lower cell which is thermodynamically driven by the heat in troposphere has upward motion near the equator, poleward in the vicinity of the tropopause, downward motion in middle latitudes and equatorward near the ground. The reverse cell is driven by the upper and lower cells and has downward motion in the

stratosphere over the equator from about 24 km down to the tropopause and poleward motion near the tropopause.

Fig. 9: MONTHLY OZONE VARIATION IN

LAYER 1

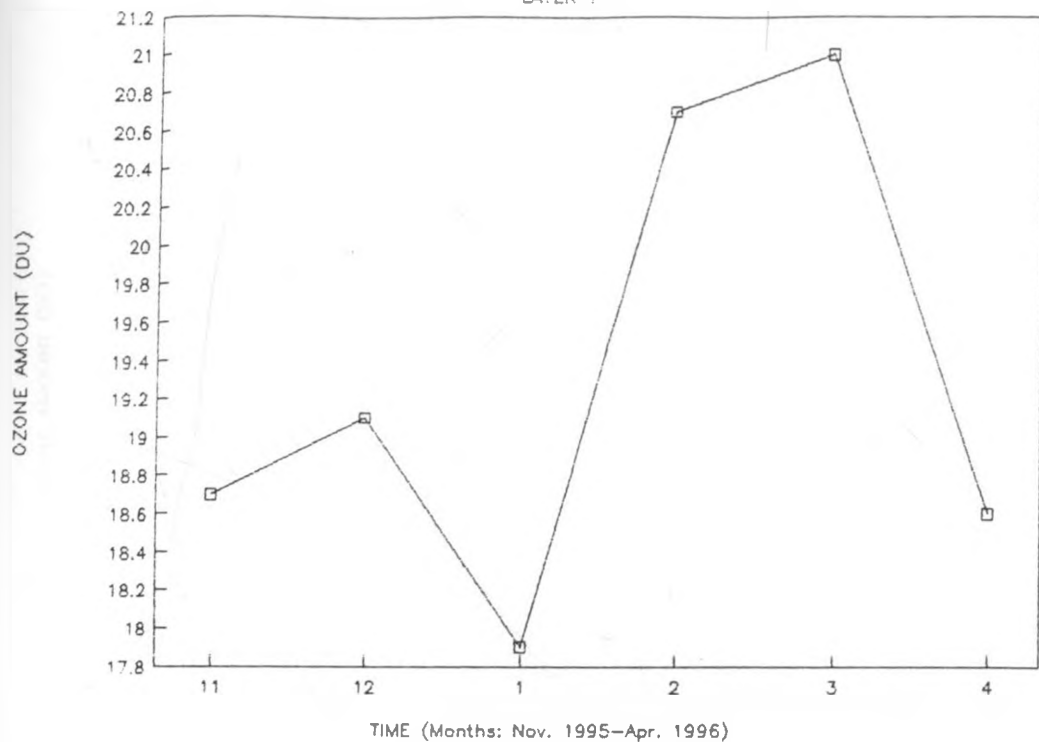


Fig. 10: MONTHLY OZONE VARIATION IN

LAYER 2

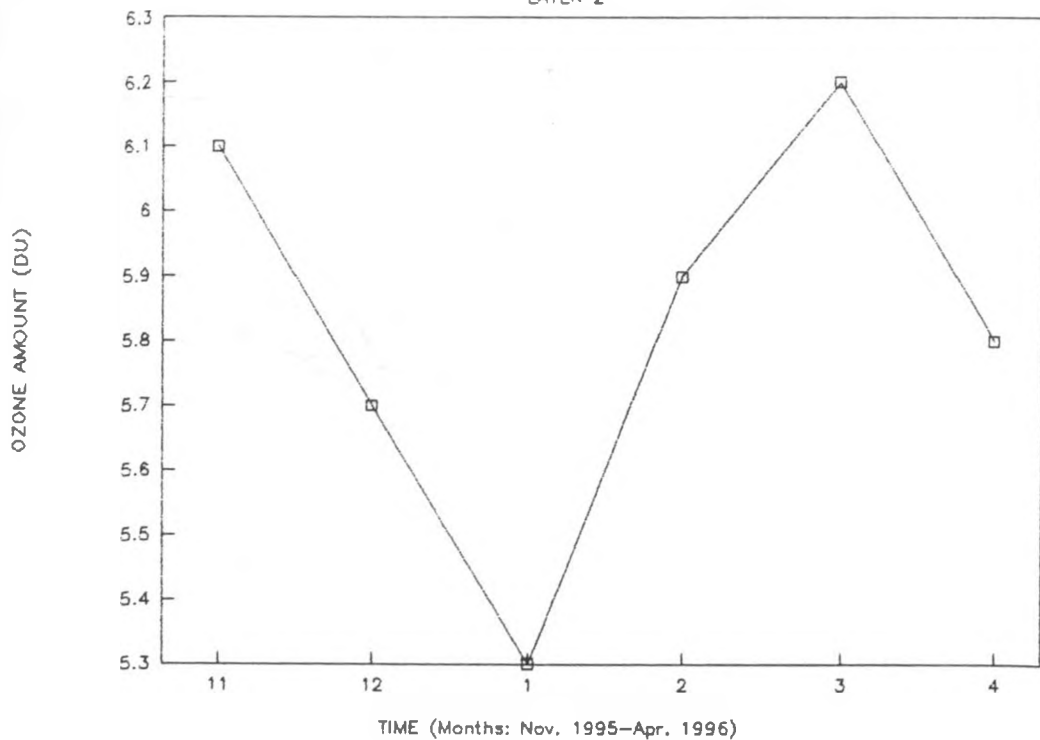


Fig. 11: MONTHLY OZONE VARIATION IN

LAYER 3

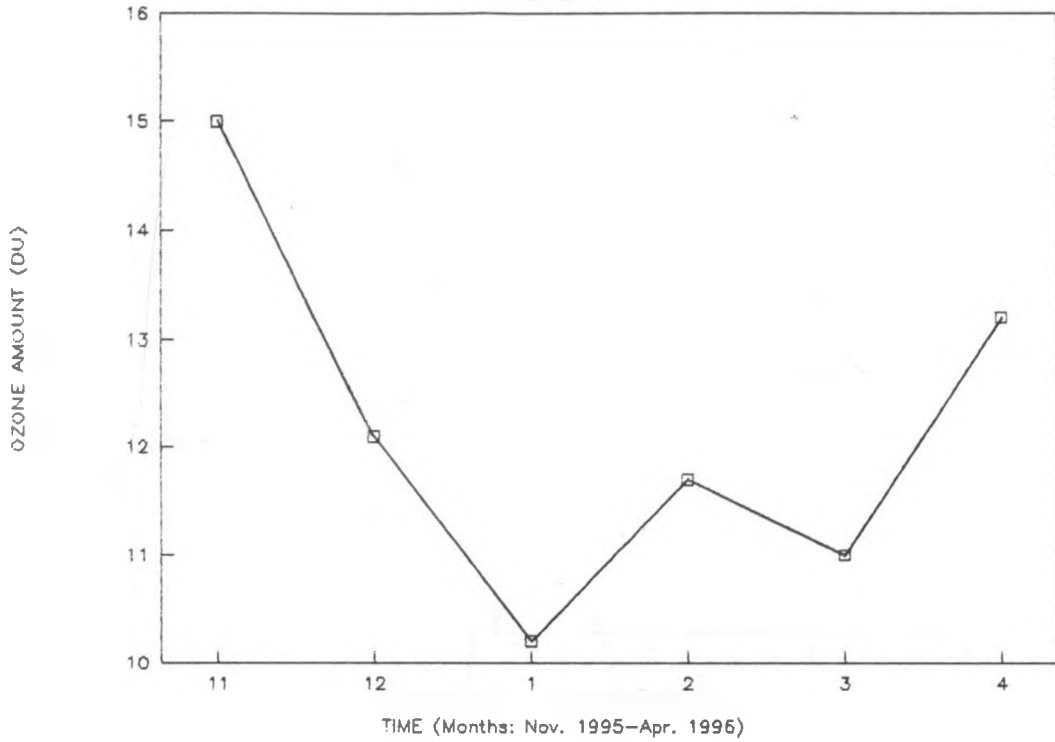


Fig. 12: MONTHLY OZONE VARIATION IN

LAYER 4

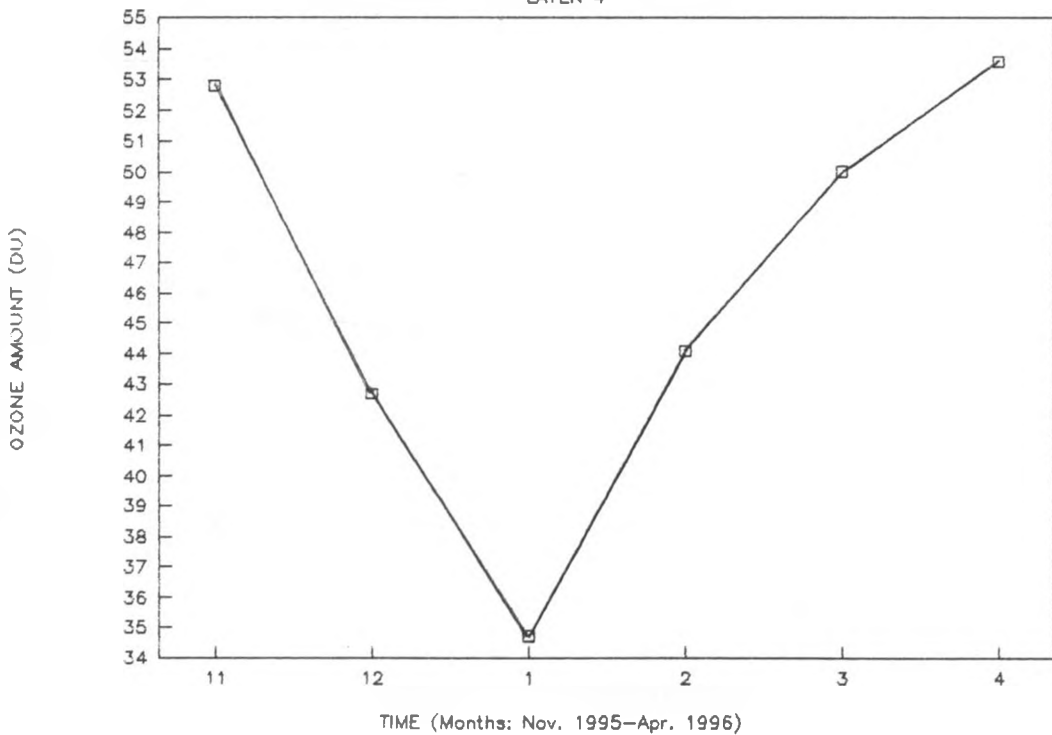


Fig. 13: MONTHLY OZONE VARIATION IN

LAYER 5

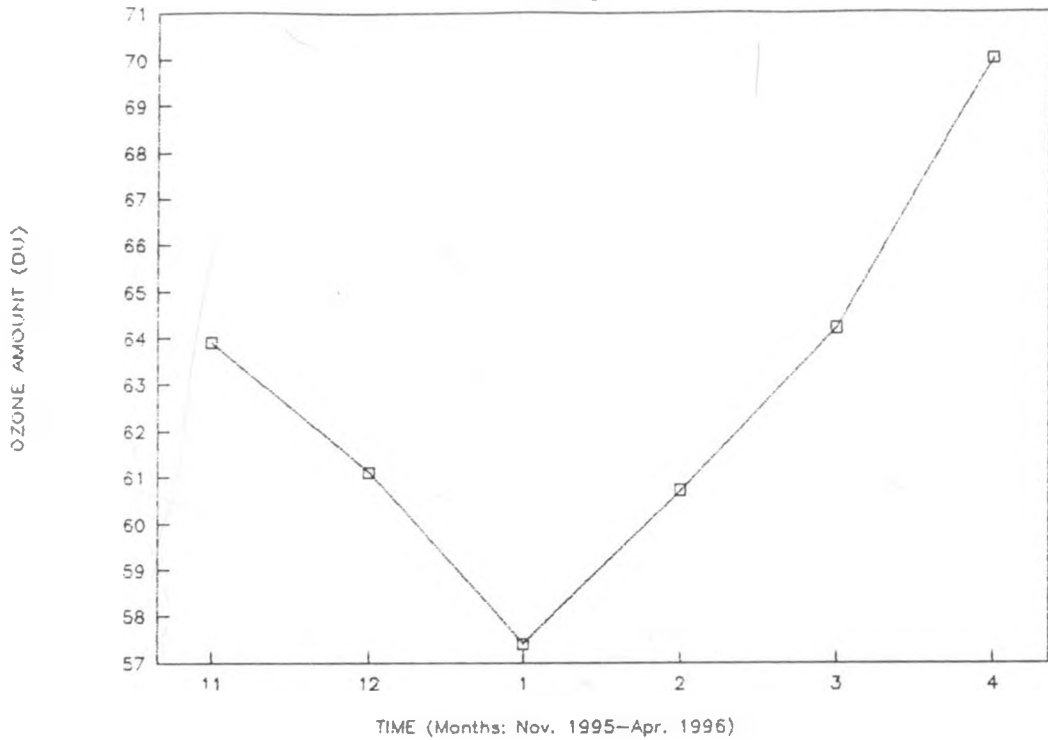


Fig. 14: MONTHLY OZONE VARIATION IN

LAYER 6

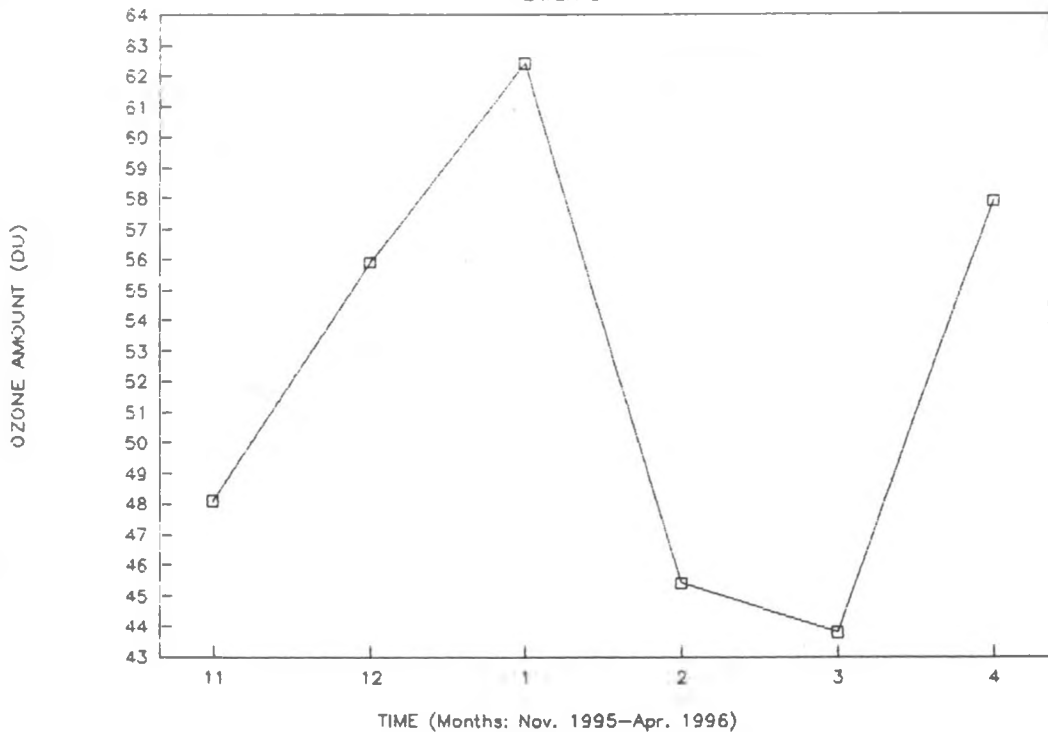


Fig. 15: MONTHLY OZONE VARIATION IN

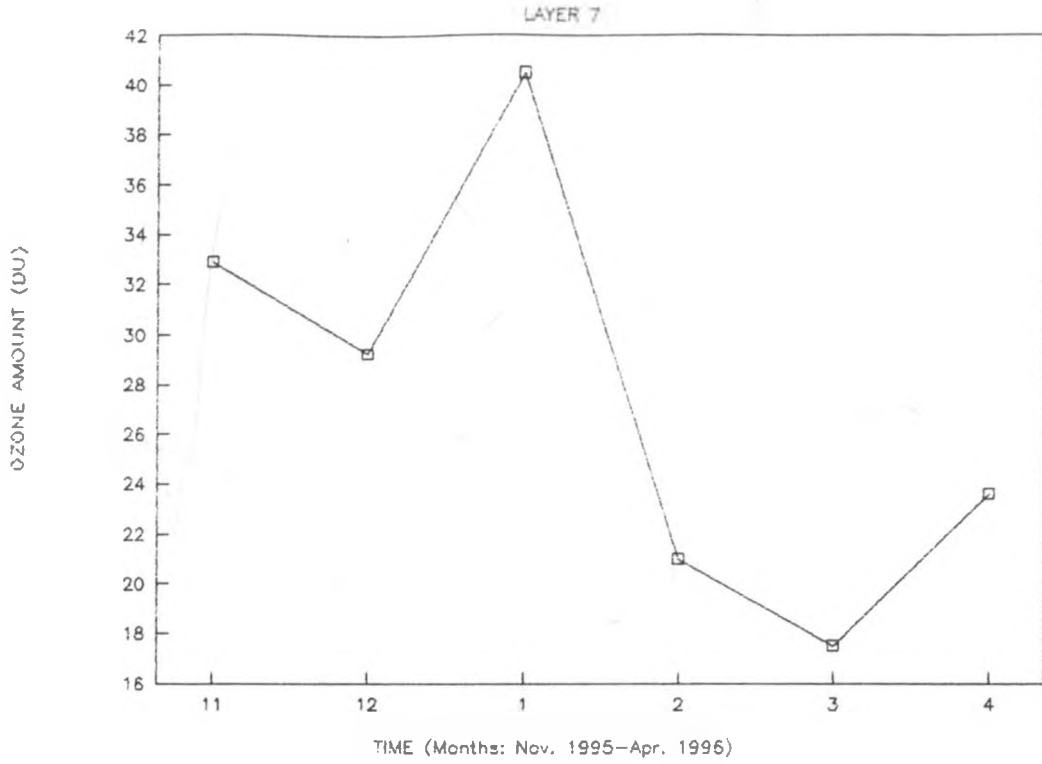


Fig. 16: MONTHLY OZONE VARIATION IN

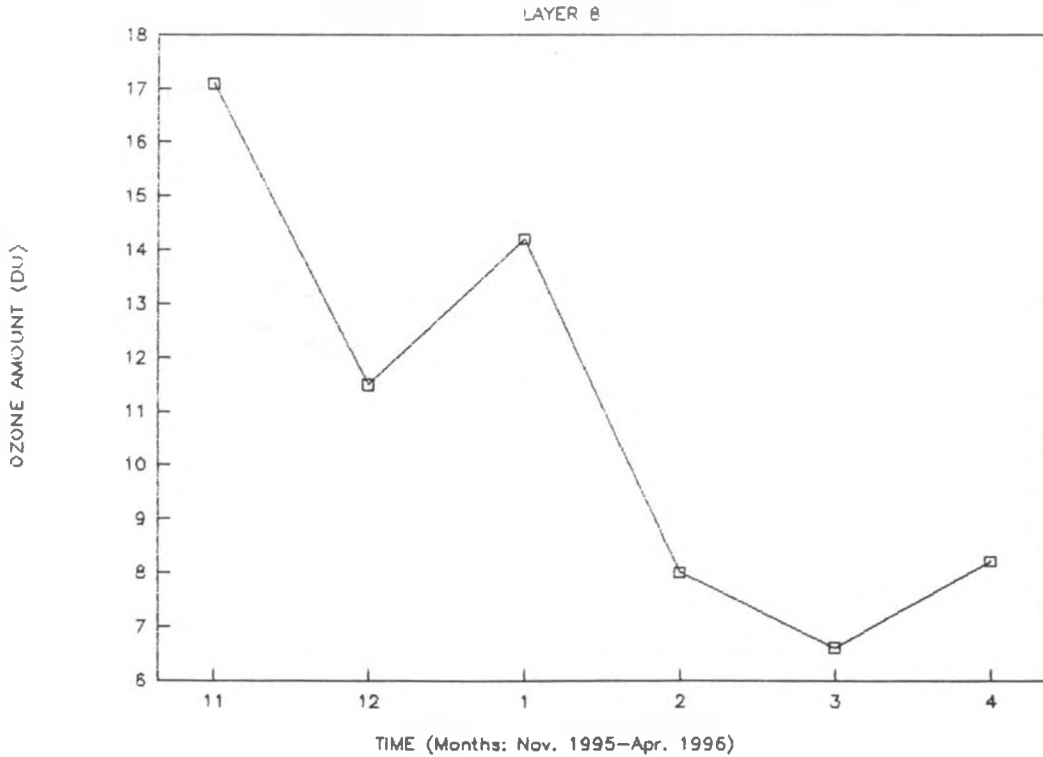


Fig. 17: MONTHLY OZONE VARIATION IN

LAYER 9

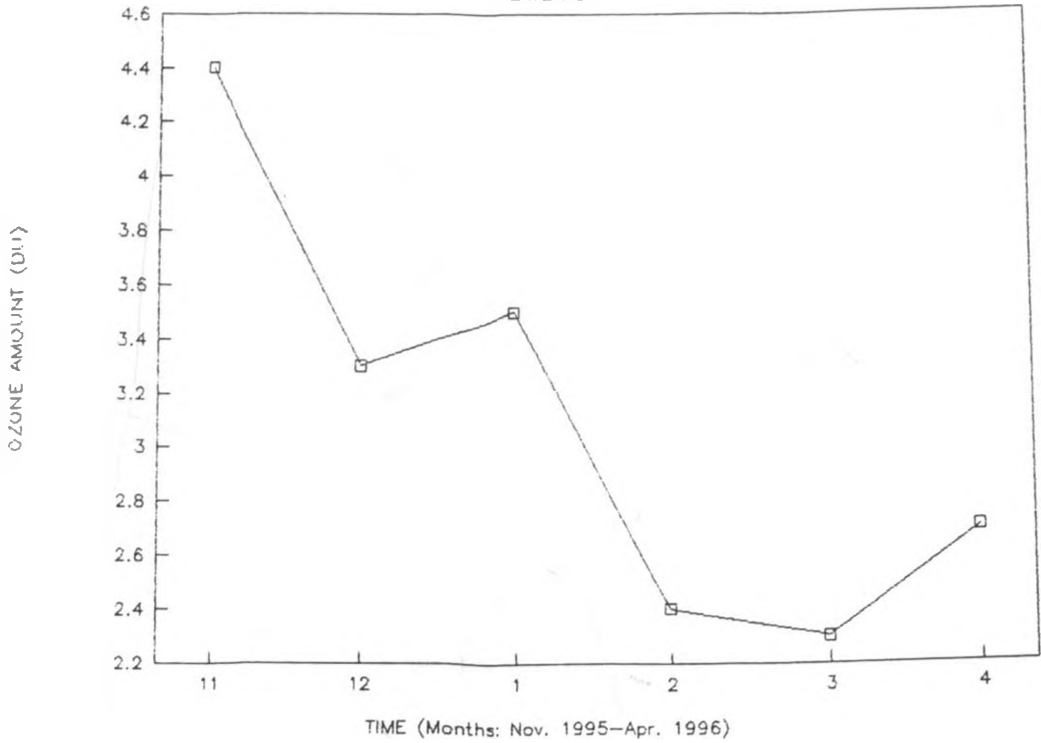


Fig. 18: MONTHLY OZONE VARIATION IN

LAYER 10

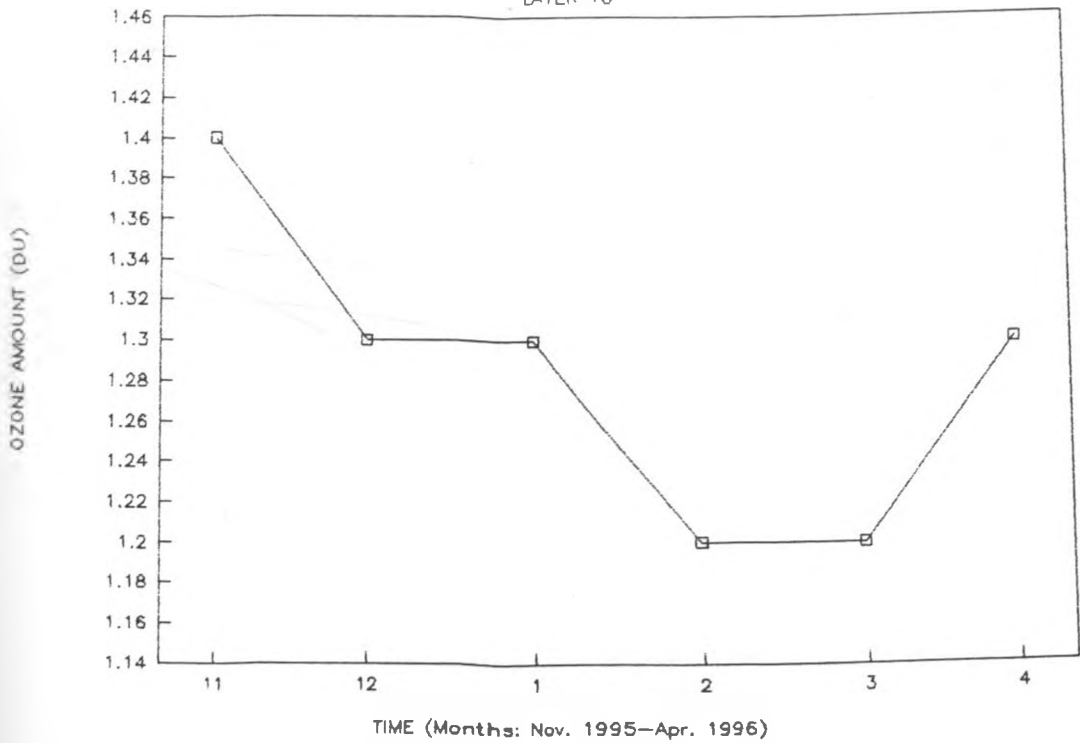


Fig. 19: MONTHLY STANDARD DEVIATION OF
OZONE IN THE TROPOSPHERE

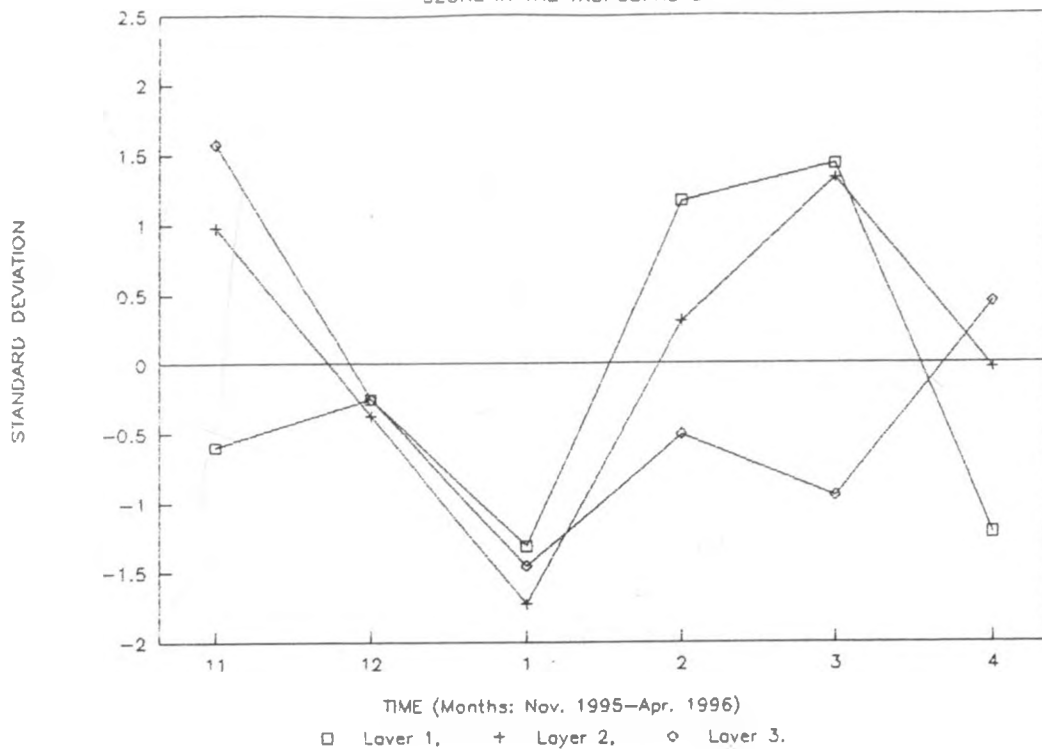


Fig. 20: MONTHLY STANDARD DEVIATION OF
OZONE IN THE LOWER STRATOSPHERE

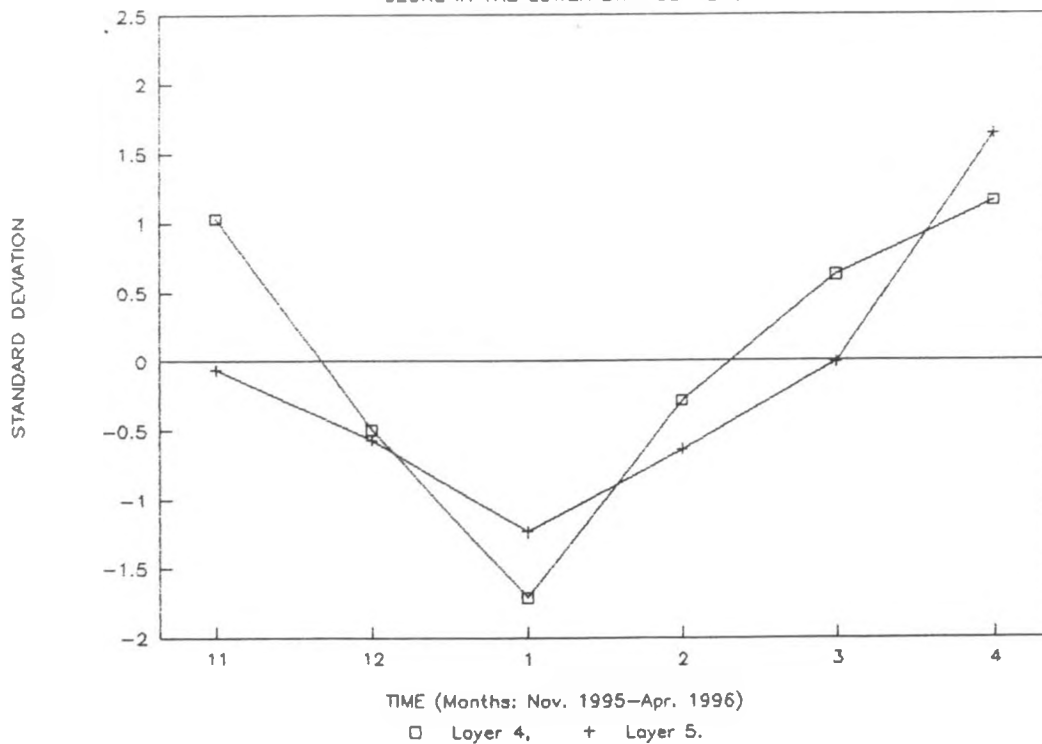


Fig. 19: MONTHLY STANDARD DEVIATION OF
OZONE IN THE TROPOSPHERE

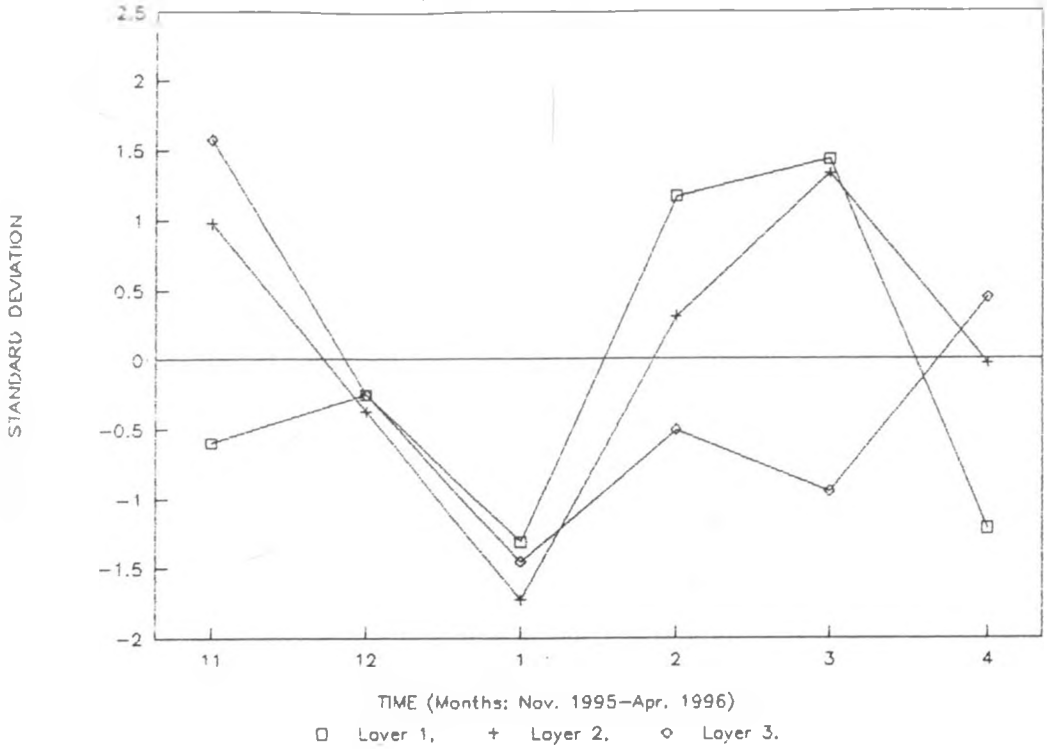


Fig. 20: MONTHLY STANDARD DEVIATION OF
OZONE IN THE LOWER STRATOSPHERE

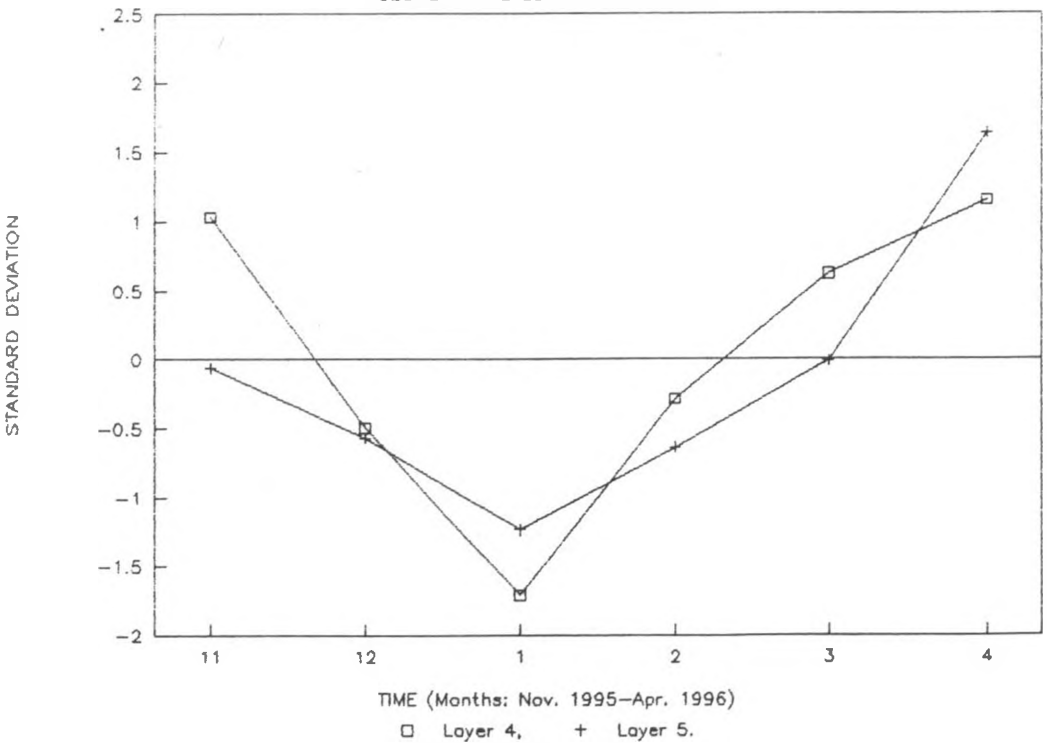
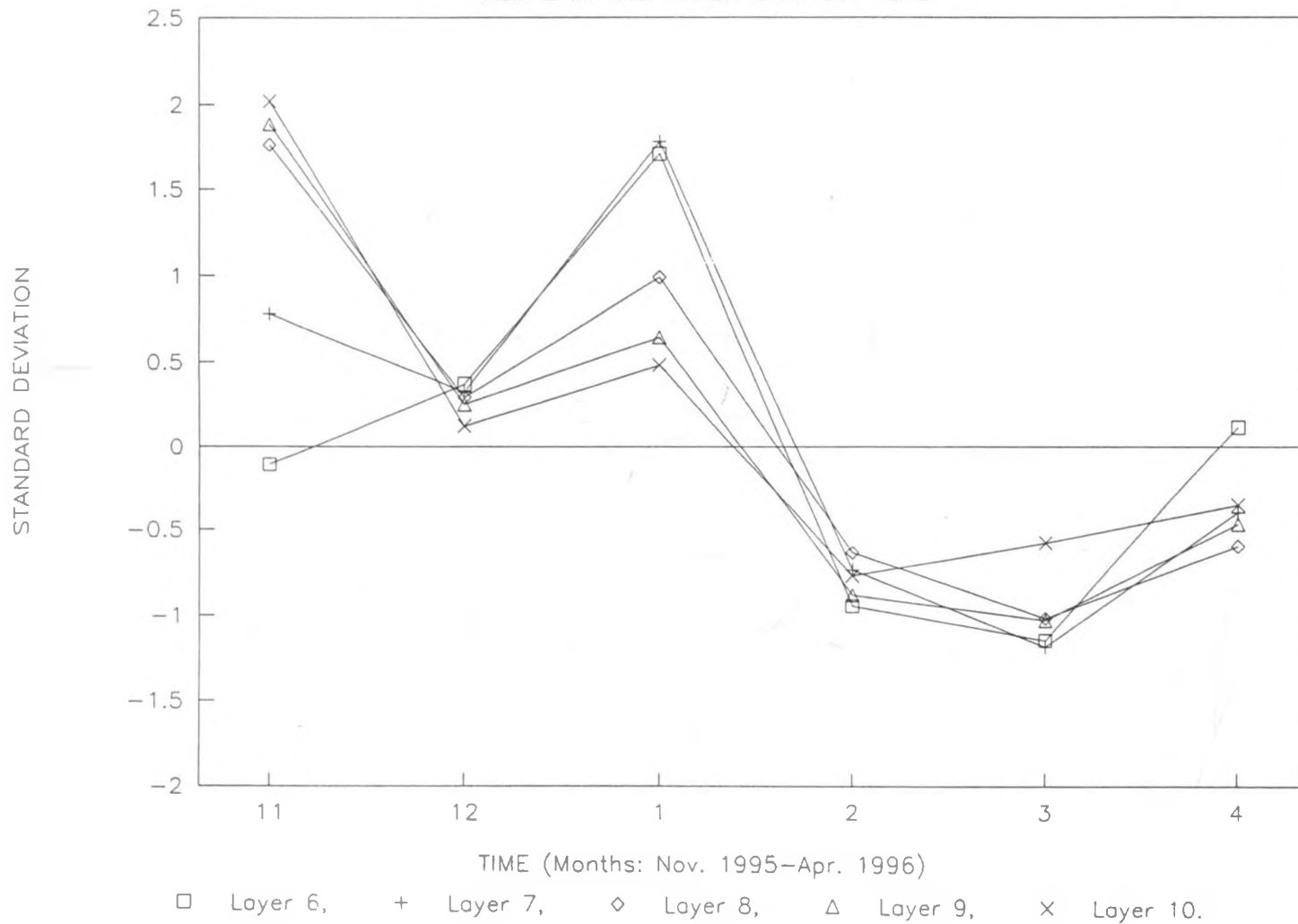


Fig. 21: MONTHLY STANDARD DEVIATION OF
OZONE IN THE UPPER STRATOSPHERE



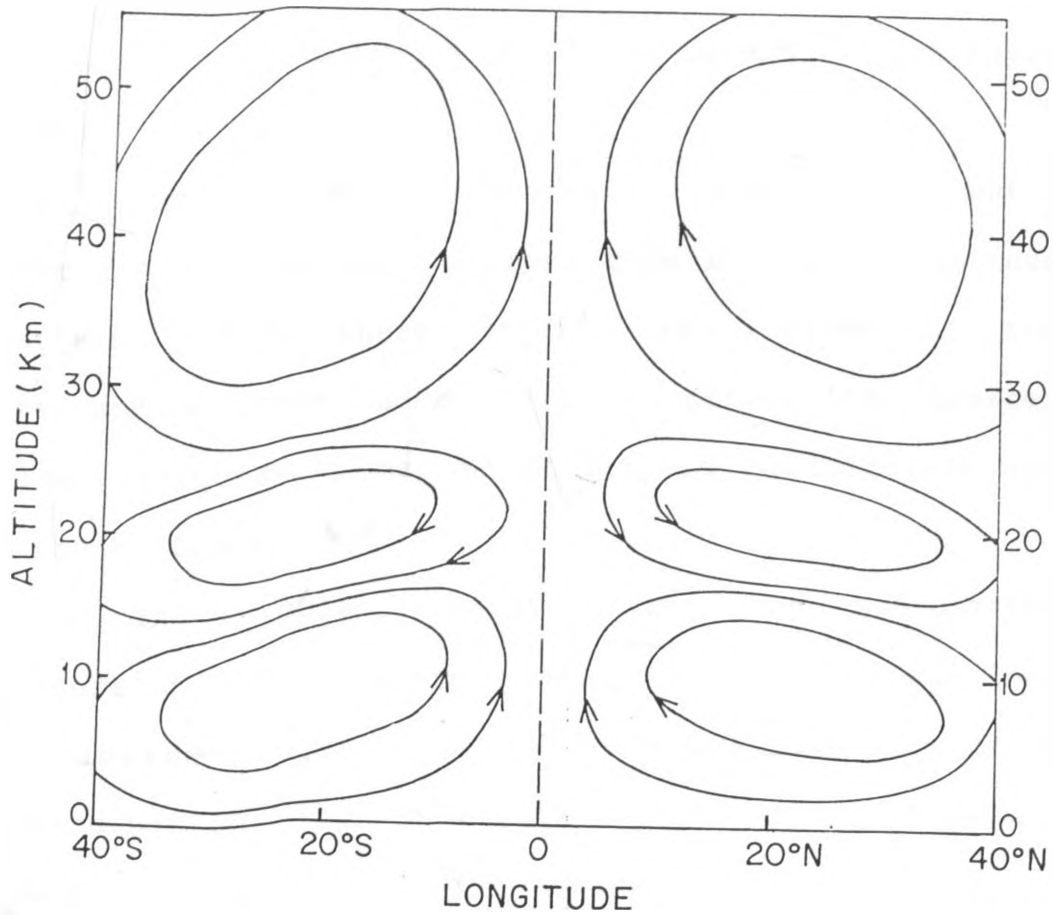


Fig. 22: Vertical meridional cells (Redrawn from Palmer, 1954)

The upper cell which is driven by heat absorbed by upper stratospheric ozone has the same direction as the lower cell with upward motion over the equator from 24 to 50 km and poleward at high levels (Murgatroyd, 1969).

The variations exhibited in layers 1, 2, and 3 over the hot and cold seasons show no clearly defined pattern. Since these layers are located in the troposphere where Hadley cell is active, the observed ozone irregularity may be attributed to turbulent air motions (Ilyas, 1991).

The turbulent motions promote the non-uniform mixture of ozone precursors which consequently may lead to irregular production or destruction of ozone depending on the concentration of the precursors (section 4.2.2). These motions may also promote irregular destruction of ozone at the ground.

Ozone variations in layers 4 and 5, which have effective altitudes at 16.9 and 21.3 km respectively, exhibit seasonal variation over the study period. The ozone amount on average is lower in hot season than in

cold season. The locations of the two layers coincide with that of the indirect cell which is pronounced in the lower stratosphere. The seasonal variation of ozone may be attributed to both the height of the tropopause and subsequent circulation strength of the indirect cell.

In hot season, the height of the tropopause rises due to intense heating from the earth's surface (Muthama, 1989). This effectively reduces the depth of the lower stratosphere since the upper limit of this layer (stratonull) depicts minimum seasonal fluctuations. Since the lower stratosphere acts as a reservoir of ozone, reduction in its depth consequently results into the observed low ozone concentration during hot season. This situation is evident in table 6 in which layers 4 and 5 indicate the highest negative rank correlations between ozone amount and tropopause height. The converse is evident during cold season.

Since the upper and the lower cells are thermally driven, their circulation speeds are expected to maximize in hot season due to high solar radiation

absorption. The speed of the reverse cell subsequently increases since it derives its energy from the direct cells. The increased speed of the indirect cell in turn reduces the rate of both diffusion and drifting of ozone from the upper stratosphere (source region) to the lower stratosphere. This process may to some small degree contribute to low ozone quantity in hot season. The reverse is true during cold season.

There is no defined ozone variation pattern in hot and cold seasons evident in layers 6-10 which are situated between 24-48 km. This may be associated with minimum temporal variation of meteorological parameters in upper stratosphere which diminish in intensity with increasing altitude (Holton, 1979). Ozone formation is most intense in this region and is proportional to solar radiation intensity (Craig, 1965). Layers 6-7 and 8-10 showed maximum ozone in January and November respectively. Hence, these two months may be associated with the highest temperature and consequently the strongest circulation of the direct cell. March was the coldest month since it depicted the lowest ozone

quantity in all the layers.

4.3 RESULTS FROM SPEARMAN RANK CORRELATION

Spearman rank correlation coefficients between the ozone amount in each layer and both long-term mean tropopause height and tropopause temperature are given in table 6.

LAYERS	TROPOPAUSE HEIGHT	TROPOPAUSE TEMP.
1	+0.17	+0.29
2	+0.08	-0.2
3	-0.08	-0.54
4	-0.54	-0.65
5	-0.89	-0.88
6	-0.2	-0.3
7	+0.09	-0.06
8	+0.11	-0.2
9	-0.2	-0.31
10	-0.09	-0.2

Table 6. Spearman rank correlation coefficients between ozone amount and both long-term mean tropopause height and temperature in each layer.

It can be noted from table 6 that the two

highest correlation coefficients between ozone amount and tropopause height are found in layers 4 and 5. These coefficients between ozone and tropopause height are negative indicating an inverse relationship.

The high negative coefficients may be explained as follows. Layers 4 and 5 are located in the lower stratosphere. This region acts as a reservoir of ozone. Lowering of the tropopause corresponds to more ozone being stored in this region as explained in section 4.2.3 and therefore a high negative correlation results.

Table 6 also shows that the three highest coefficients between ozone amount and tropopause temperature are in layers 3, 4, and 5. These layers are situated in upper troposphere (layer 3) and lower stratosphere (layers 4-5).

Low temperature in the tropopause corresponds to low level of tropopause height (Dobson, 1968). This in effect increases the depth of the ozone reservoir area above the tropopause. As a result, ozone increases in layers 4 and 5 resulting into the observed high

The relationship between temperature and ozone amount indicates positive correlation in layers 1 and 2 and negative correlation in layers 3, 4 and 5.

The positive/negative correlation can be explained in terms of corresponding location of each layer. Layers 1 and 2 are situated in the lower troposphere where ozone precursors are dominant. As such, high temperatures may favour the chemical formation of ozone resulting into high positive correlation coefficients. On the other hand, layers 3, and 4-5 are located in the upper troposphere and lower stratosphere respectively. Low temperature in upper troposphere is associated with low tropopause (Dobson 1968). This is because the convective activities which increases the tropopause height are suppressed. As a result, the level of the tropopause may fall increasing the ozone quantity in lower stratosphere. This subsequently increases ozone amount in layer 3 as explained earlier in this section. Similarly, low temperature in the lower stratosphere is associated with lowering of tropopause height. Subsequently, this also increases

the reservoir depth of ozone resulting into high negative coefficients indicated in table 7.

Table 7 also shows a positive coefficient in layer 1 whereas layers 2-5 depict negative coefficients between ozone amount and zonal wind speed.

It seems that the North-easterlies which have been found to be dominant over Nairobi (Ng'ang'a, 1979) could be associated with poorer ozone concentration as compared to South easterlies. However, further analysis on this would bring a better understanding of the problem.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

The conclusions which may be derived from the study are summarized below. Future improvements on the study are also suggested.

5.1 CONCLUSION

The raw data utilized in the study were fairly accurate. This is due to regular lamp tests conducted which led to the correction of observational data.

The vertical distribution of ozone in Nairobi indicated that about 89.6% of ozone was between 12.5 and 45 km whereas the remaining 10.4% was located below 12.5 km. The maximum concentration of ozone was located at about 21.5 km in this particular case.

Investigation of the variation of ozone in each layer on monthly basis indicated three patterns. These patterns were associated with vertical circulation cells (lower, middle and high cells) that were regarded

as determining both the dynamics and quantity of ozone over the equatorial region.

Layer 1-3 (lower cell) exhibited no defined pattern over the hot and cold seasons. This was attributed to turbulent mixing processes in lower troposphere where Hadley cell is active.

Variation of ozone in layers 4 and 5 (middle cell) showed low amount in hot season and high quantity in cold season. This variation was attributed to both the height of the tropopause and subsequent circulation intensity of the indirect cell (middle cell).

The quantity of ozone in layers 6-10 (high cell) showed poorly defined fluctuations in hot and cold seasons. This was connected to minimum variation of meteorological parameters in this region.

Spearman rank correlation coefficients between ozone amount and long-term mean tropopause height indicated higher negative values in layers 4 and 5 relative to other layers. This situation was related to the depth of the lower stratosphere (where layers 4 and 5 are located) which is inversely proportional to the

tropopause height.

There were higher negative coefficients between ozone quantity and long-term mean tropopause temperature in layers 3, 4 and 5 than in other layers. These high values were associated with the resultant tropopause height due to tropopause temperature variation.

Rank correlation coefficients between long-term mean temperature and ozone quantity indicated positive values in layers 1 and 2 and negative values in layers 3, 4, and 5. This difference was explained in terms of the photochemical formation of ozone in layers 1 and 2 and the tropopause height variation in layers 3, 4, and 5.

Results from spearman rank correlation coefficients between ozone amount and long-term mean zonal wind speed indicated variable values. This variability seemed to be influenced by changes in wind direction.

5.2 RECOMMENDATIONS

The results presented here were derived from a

study conducted for a short duration (6 months). As such, the conclusions drawn are by no means exhaustive.

Another major shortcoming emanated from lack of upper air observations during the duration of the study. Hence the long-term mean of the upper meteorological parameters utilized were not perfect substitutes. Furthermore, upper air data for layers 6-10 were entirely absent.

Lack of knowledge of aerosols quantity over the region of the study was another major drawback. This subsequently may have reduced the accuracy of the raw data.

To improve future studies of similar kind, the following suggestions may be advanced.

- (A) Several ozone measuring stations should be set up in this region. This in turn would enhance the inter-comparison of the profiles and thus improve the understanding of the dynamics of ozone.
- (B) Ozone precursors (such as NO_x, S₂O and hydrocarbons) over Nairobi need to be investigated in order to obtain a correlation

factor for the distribution of ozone in lower troposphere.

- (C) Upper air data should readily be available for future studies. These data would help explain the variation of the vertical distribution of ozone.
- (D) Studies on the influenced of wind direction on ozone should be conducted. This would further shed more light on the vertical distribution of ozone.
- (E) Aerosols quantity need to be known over Nairobi. If the quantity is large, correction on Umkehr observational data should be conducted.
- (F) There ought to be a continuous measurement of ozone vertical distribution in this region. This would further enhance the understanding of climatology of ozone over Nairobi and equatorial region at large.

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