TOTAL ATMOSPHERIC OZONE CHARACTERISTICS OVER A TROPICAL REGION

BY

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DECLARATION

I hereby declare that this Thesis is my original work and has not been presented for a degree in any other university.

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This Thesis has been submitted for examination with our approval as University Supervisors.

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TABLE OF CONTENTS

ABSTRACT

In this study total atmospheric ozone records from chiromo station - University of Nairobi (1°S,36°E), Covering the period April 1984 to May 1989, were first subjected to some homogeneity tests in order to determine the quality of the observations. The homogeneity tests used included the residual mass curve and the run's test. The homogeneous ozone records were then subjected to time series analysis so as to determine their trend, Seasonal characteristics and Cyclical behavior. Linear correlation and cross-spectral analyses methods were finally used to determine whether the observed fluctuations in the ozone characteristics can be associated with some of the stratospheric and tropospheric general circulation activities.

The trend of the ozone over Nairobi was determined from two independent approaches, namely the graphical and statistical methods. Smoothed ozone series were displayed visually on a graph, while the Mann-kendall rank statistic and arithmetic mean method were used in the statistical approach. Spectral analysis fluctuation in ozone exhibited any significant periodic or quasi-periodic patterns,

The degree of relationship between ozone and some meteorological parameters, including temperature, rainfall, wind speed and direction, tropopause height, relative humidity and cloud cover was investigated using both linear correlation analysis and cross spectral

analysis. In the former method the correlation coefficients so obtained were tested for significance by use of the analysis of variance technique.

In the cross-spectral analysis, coherence function was used to confirm the results from the simple and cross correlation analysis which indicated some degree of relationship. The phase relationship between ozone and meteorological parameters was examined using the phase functions derived from the cross-spectral technique.

The results from the quality control tests indicated that no significant heterogeneity could be determined from the ozone data. Trend analysis results showed non-significant trend from both graphical and statistical methods. Seasonal variations were evident with maximum in September to October and minimum in January to February. Spectral analysis showed existence of two major cycles in the ozone data, namely: 21-25 months (QBO range) and 45 months.

Linear correlation analysis showed significant correlation between ozone and temperature at the lower troposphere and lower stratosphere. Ozone correlations with zonal wind were significant at the lower and higher troposphere together with the lower stratosphere. Tropopause heights were negatively correlated with ozone.

Cross-spectral analysis indicated general low phase function values. Significant phase correlations were therefore imperatively dominant for time lags less than one month. Most of these significant correlations are explained in terms of general circulation characteristics.

LIST OF TABLES

LIST OF FIGURES

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DEDICATION

To My Parents. They availed the Opportunity.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Ozone exists in very small amounts in the atmosphere. If expressed in units of the height of an equivalent column of ozone at standard temperature and pressure, the total amount varies from about o.16cm to o.4 cm. About 90 per cent of this gas is concentrated within the stratosphere, with the rest in the troposphere (Isaksen and Hov, 1986).

Above the tropopause, ozone is formed from photochemical dissociation of oxygen by ultra-violet radiation followed by recombination of the atomic oxygen. It is well known that the concentration of ozone in the lower stratosphere is far much higher than that predicted by photochemical equilibrium, although in the upper stratosphere the observed and predicted concentrations agree reasonable well. This situation is prevalent due to the fact that the photochemically produced ozone in the lower stratosphere or that carried there from above by mixing processes is partly shielded from the solar ultra-violet radiation that could dissociate it. When an ozone molecule there is dissociated, it quickly reforms another ozone molecule. It can therefore be transported both horizontally and vertically as a more or less stable constituent (Kellog, 1964).

The natural ozone content in the troposphere is mainly determined by the rate of supply from the stratosphere and the rate of its destruction on the

earth's surface (Van Dop, et al., 1977). Ozone can also be produced photochemically in the lower troposphere due to presence of oxides of nitrogen (NO_x) and reactive hydrocarbons in association with high levels of solar ultra-violet radiation (Kroon, D.J., 1978; Logan, J.A., 1985). Industrial activities together with motor vehicular emissions may also result in photochemically produced lower tropospheric ozone. This anthropogenic ozone production is however far much smaller compared to the stratospheric production.

The importance of ozone in the atmosphere include:

a) Its absorption of ultra-violet radiation, especially between 330 and 220 nanometres (nm), the strongest absorption being at a wavelength of about 250nm. The small amount of ozone in the upper atmosphere effectively shields the lower layers from the biologically harmful solar radiation. Thus any changes in the total atmospheric ozone would have significant impacts on the ecosystem (Biswas, 1979; Titus, , 1986).

b) Due to ozone's strong absorbing capability in the ultra violet region, the stratospheric temperature is largely maintained by a balance between absorption by ozone and emission of atmospheric infra-red radiation by ozone, carbon dioxide and water vapour. Thus any alterations in the vertical distribution of atmospheric ozone, together with changes in atmospheric concentrations of other infra-red active

gases, would contribute to changes in stratospheric heating rates which will directly influence the temperature distribution, general circulation and the climate of the globe (Reck, 1976).

c) Lower tropospheric ozone has been recognized as a pollutant of regional and global significance (Wolff, et al., 1977) since it can impair health and cause damage to vegetation and materials. An example of the adverse effects of the oxidant ozone is the study by National Crop Loss Assessment Programme of the United States which identified widespread crop yield reduction as a result of exposure to ozone and other pollutants (EPA, 1978). The costs associated with this damage were estimated at between $2 billion and $ 3 billion annually for the United States.

d) The long life of ozone, particularly in the lower stratosphere makes it an ideal tracer of atmospheric motions (Reiter, 1978). As a three atom gas, it leaves a marked imprint on the radiation flux travelling the atmosphere. This radiation flux in turn dictates the heat and energy budget in the atmosphere and thus the atmospheric motions.

(e) Ozone has received attention from aviation systems engineers and meteorologists due to the possible exposure of its adverse oxidizing effect on the people in high-flying supersonic transport aircrafts (Biswas, 1979). Crews and passengers may have to be shielded

against its high toxic qualities.

In the last two decades there has been increasing concern about the effects of the pollution of the stratosphere, and in particular the stratospheric ozone dèpletion due to photochemical reactions involving certain trace substances which include chlorofluorocarbons, halons, methane, nitrous oxide and carbon dioxide. The technologies responsible for the emissions of these gases include high altitude aviation activities, stratospheric nuclear testing, refrigeration, air conditioning, use of spray-cans, soil fertilization, etc. Considering that the ozone layer exists in its present form due to a sensitive balance between natural processes of its creation and destruction, it is then indicative that increase in anthropogenic factors would significantly reduce ozone concentrations, thus bringing about the associated severe impacts on the ecosystem and climate (Bruce, 1986).

In view of the above considerations, a lot of effort has been made to measure ozone characteristics under various conditions. These conditions include local (rural and urban), surface (snow and continental), geographical (polar, equatorial and mid-latitudes) and many others (Dobson , 1968; Coffey et al, 1978; Ogawa, and Miyata, 1984). These informations have proved helpful in understanding natural production and transport mechanisms as well as providing bench mark data for future comparisons. Most of these studies have been made possible due to the prevailing

international co-operation in tackling the ozone issues. The international concern has resulted in, among others:

i) a globally extensive ozone observational programme initiated in the International Geophysical Year (IGY) of 1957,

ii) the formation of Global ozone Research and Monitoring Programme, in 1976, for dissemination of ozone data globally,

iii) the Villach conference of 1985, and

iv) the March 1989 London Conference on 'Saving the Ozone Layer'.

Despite these considerable international efforts in obtaining atmospheric ozone measurements and ozone related aspects, no significant study about ozone characteristics has been performed in the East African region. This forms the basis of the present study.

1.2 OBJECTIVES

The objectives of this research were to investigate:

i) the temporal variations of total atmospheric ozone over Nairobi, Kenya, and

ii) the influence of meteorological factors on the observed variations.

These investigations are essential for providing bench mark information of ozone variations over East Africa, which is a vital initial step towards any future modelling of atmospheric ozone aspects over the tropical regions like East Africa. Additionally, the information forms a basis for future comparison in view of the prevailing international concern about the depletion of the ozone layer.

In order to fulfil these objectives, total atmospheric ozone data for Nairobi station, covering the period April 1984 to May 1989 was subjected to the following analyses:

i) Time series analyses: These were used in order to determine the seasonal and inter-annual variation of ozone over Nairobi. The time series analyses included trend, seasonal and cyclical analyses.

ii) Correlation analyses: The spatial and temporal variations of ozone depend on the space and time characteristics of meteorological elements. These meteorological elements determine both the physical processes involving transport and dispersion of atmospheric ozone and the chemical processes involving the reaction of ozone precursors in the atmosphere.

The physical processes bringing about transport and dispersion of ozone include the atmosperic mixing processes and wet deposition. In wet

deposition, rainfall deplets ozone by wash-out and cloudiness depletes it by rain-out. Atmospheric mixing processes, which are explained in details in the next chapter, are a function of wind speed and direction, temperature and pressure.

Some chemical processes influencing ozone amounts are a function of meteorological elements. An example of such is the photo-dissociation of ozone into atomic oxygen and molecular oxygen. The rate of reaction is depended on the intensity of light (which is proportional to temperature) and the spectral density of the Solar spectrum.

In view of the above, the last part of this study examined how total ozone is influenced by weather elememts at various heights of the atmosphere, using correlation analyses. The parameters correlated with ozone included temperature, relative humidity, wind speed and direction at various atmospheric levels together with the total solar radiation, rainfall and tropopause height.

CHAPTER 2

2.0 BACKGROUND REVIEW

2.1 CLIMATOLOGY OF OZONE

In this study the general climatology of total ozone is discussed by describing its spatial and temporal characteristics. The spatial components are divided into horizontal and vertical distributions.

2.1.1 Horizontal Distribution

Figure 1 gives some indication of the mean zonal and meridional distributions of ozone by London et al (1976). These patterns have been confirmed by recent Satellite observations (WMO, 1986; Fishman and Larson, 1987).

The general patterns indicate a peak value of ozone in the sub-polar latitudes in both hemispheres and minimum values Concentrated within the tropics. Although these patterns prevail throughout the year, in March and April the north hemisphere maximum tends to shift to the poles. The corresponding drift in the Southern hemisphere maximum is less emphatic, and is delayed until November and December (Biswas, 1979).

Other spatial ozone studies indicate that ozone variations in north temperate and north polar regions are positively and significantly correlated. In the Southern hemisphere, a negligible correlation between these climatic zones has been observed, suggesting a basic difference in circulation patterns (Angell and Korshover, 1973).

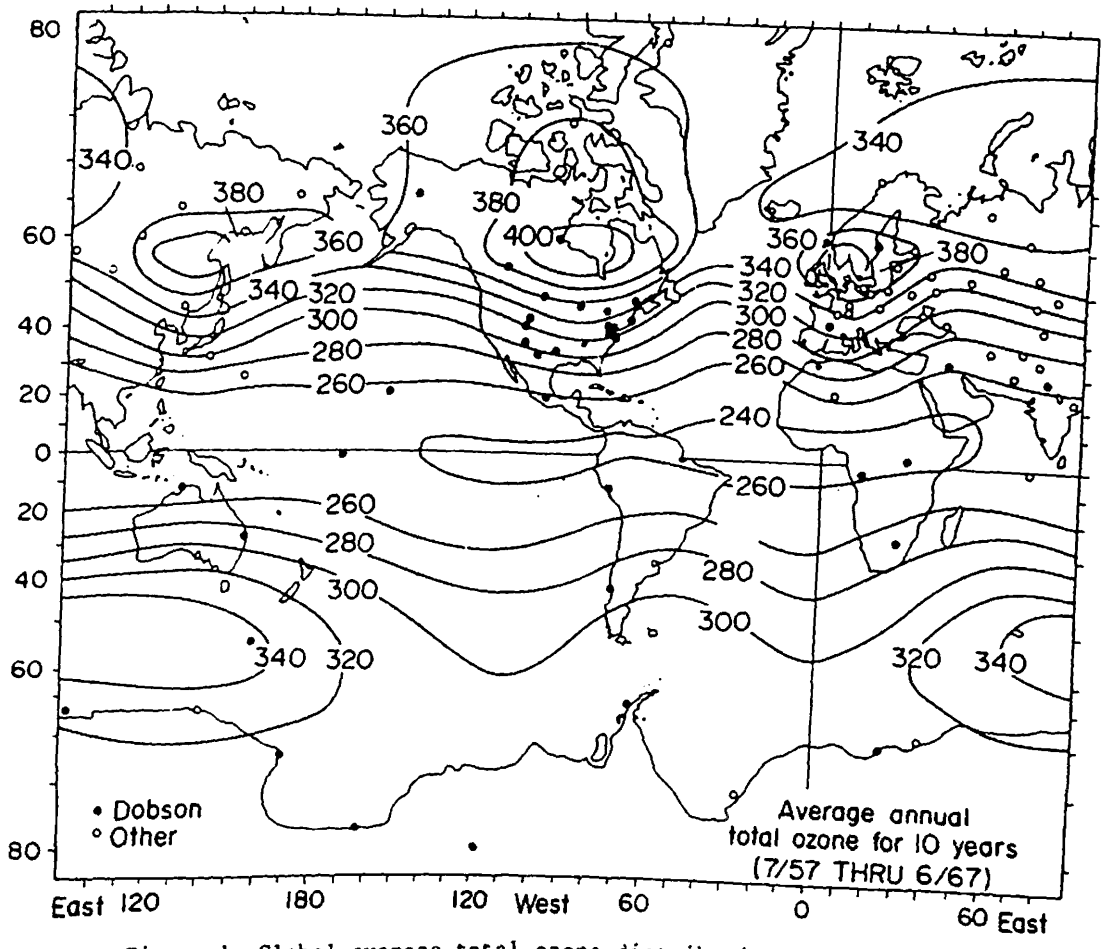


Fig. 1. Global average total ozone distribution for the years 1957-1967, expressed in m-atm-cm (Dobson units). The dots and small circles indicate station locations. (London et al., 1976).

2.1.2 Vertical Distribution

Under this section the mean distribution of ozone in both the stratosphere and troposphere are discussed separately.

2.1.2.1 Stratospheric distribution

Pioneering investigations of ozone's vertical distribution were done by use of umkehr techniques, an optical method of estimating ozone concentration at various levels of atmosphere (Craig, 1965). Various studies have shown that maximum ozone density is generally concentrated in the lower stratosphere. Variations in total ozone amount has been associated with the variation of the lower stratospheric ozone (Mateer and Godson, 1960; Reiter, 1975).

Variability of ozone partial pressure in terms of its standard deviation has been investigated by Several scientists including Biswas, (1979). These studies indicate largest variability in the low stratosphere over the middle and high latitudes, and decreases to relatively small values at all levels in the tropics.

Observations from distribution of the vertical ozone profiles have shown that in lower and middle stratosphere the fractional ozone content increases poleward from equator, while in the upper stratosphere it decreases

slightly towards the poles. Consequently, about 38% of total ozone in the tropics is concentrated above 28 km (where greatest photochemical activity takes place) while in the polar regions only about 18% is found above this level (Biswas, 1979).

2.1.2.2 Tropospheric ozone concentrations

Tropospheric ozone is an air pollutant especially in large urban areas and a lot of studies have been done to characterise its variation patterns. These variation patterns of ozone provide detailed description of the oxidant problem, which in turn serves to guide control efforts better. The patterns also help in explaining the physical and chemical mechanisms by which emissions of pollutants disperse, react and finally induce the observed oxidant problems (EPA, 1978).

Some of the recent studies on tropospheric ozone include one by Fishman et al (1979) who discussed the latitudinal variation of ozone in the troposphere with particular interest in the asymmetrical behaviour of this gas with respect to the two hemispheres. The results of the work showed the existence of significant latitudinal differences in the distribution of tropospheric ozone for the two hemisperes. A major primary inter-hemispheric difference observed was the existence of more tropospheric ozone in northern hemisphere than southern.

Tropospheric ozone characteristics over the tropics are not a adequately documented as in the mid and higher latitudes. However, som of the tropical ozone characteristics have been discussed by Ilyas (1987) an Sreedharam et al., (1974). Their studies indicated the existence of significant longitudinal differences. Frequently, varying local weather conditions seemed to influence ozone concentrations.

2.1.3 Temporal variations

In this study, temporal variations are discussed under two sections, namely;

i) Diurnal, inter-diurnal, seasonal variations and:

ii) inter-annual variations.

2.1.3.1 Diurnal, Inter-diurnal and Seasonal Variations

Some of the earliest scientists to investigate the temporal variation patterns of total ozone in the northern hemisphere include Kulkurani et al., (1959); and Godson (1960) among others. By utilizing the IGY data their studies showed that total ozone is a maximum in spring and minimum in autumn with largest amplitude of variation at high latitudes. Near the equator the results indicated very little seasonal variation with slight maximum in late spring and early summer.

Kulkurani (1962), and Funk and Garnham (1962) compared the seasonal variation of total ozone in southern and northern hemispheres. A close similarity was observed between 0 degrees and 55 degrees. However, for corresponding latitudes and seasons, the variations appeared to be smaller in southern than northern hemisphere.

As opposed to the above studies which indicated small seasonal variations over the tropics, more recent studies have shown significant seasonal total ozone variation over the tropics. However, basic patterns of the vertical distribution in the stratosphere remains practically unchanged throughout the year (Sreedharam et al., 1974; Ghazi and Barnett, 1980). Association between the seasonal characteristics of ozone and the general circulation will be discussed later in the text.

Diurnal variations in total ozone have been found to be insignificant by several authors including Sreedharam et al., (1974) and Biswas (1979). However, superimposed on the seasonal variations of ozone over extra-topics are short period fluctuations of the order of days. These variations are too large and rapid to be explained by photochemical processes. Some of the inter-diurnal variations have been related to:

a) Cold troposphere;

b) low troposphere;

c) warm stratosphere; and

d) a trough in the upper troposphere and lower stratosphere.

Studies over the tropics however indicate insignificant diurnal and inter-diurnal variations (Craig, 1965; Reiter, 1975).

2.1.3.2 Inter-annual variation

There exists undisputed observational evidence that the atmospheric concentration of the source gases important in controlling ozone levels continue to increase on the global scale due to anthropogenic activities. The ozone depleting gases include chloro-fluorocarbons, Halons, methane, nitrous oxide and carbon dioxide. Due to the possible anthropogenic influences on the ozone shield, several scientists have investigated ozone's inter-annual characteristics using its observed trend and cyclical fluctuations. Some of the results already documented indicate that:

i) When diurnal and seasonal variations are filtered out, the atmospheric ozone content undergoes an approximately 26 months oscillation in low latitude regions on both hemispheres. The ozone changes seem to be centred in the upper stratosphere above 25Km and appear to be intimately connected to the 26 months wind oscillation (Quasi-biennial oscillation, QBO) in the tropics (Rangarajan, 1964; Shah, 1967; Angell and Karshover, 1973; Hasebe, 1980). The amplitude of the 26 months oscillation has been observed to be greater in southern than northern hemisphere. The oscillation

has been clearly observable at least as far as latitude 38 degrees south in the southern hemisphere whereas in northern hemisphere it is hardly observable to the north of latitude 20 degrees (Rangarajan, 1964).

ii)` During the epoch when easterly stratospheric winds above 25Km weaken and change to westerlies, the ozone content is observed to increase in the northern hemisphere and decrease in the southern. In the epoch when the westerly winds weakens and change to easterly winds ozone content falls in the northern hemisphere and rises in the southern hemisphere (Rangarajan, 1964; Hasebe, 1980).

iii) Using global data for 15 years, Hasebe (1980) observed the existence of four year oscillation at high latitudes, particularly in the northern hemisphere. The maxima and minima of this oscillation were found to be in late winter and early spring of the even years in both hemispheres, while the phase in southern hemisphere was preceded by about 3/4 of pi to that in northern hemisphere (where pi = 3.142).

iv) Trend analysis using 1960s' records showed an increasing trend of total ozone (Angell and Korshover, 1973; London et al 1976). Analysis using more recent ozone data however indicate that the increase in total atmospheric ozone noted during 1960s'

appears to have ended, and a decreasing trend is evident. The reduction has been estimated to be upto 0.3% per year and most pronounced in the region where chlorine chemistry has its strongest effect on ozone (WMO, 1986; Reinsel, et al 1983; 1984).

Trend analysis based on Dobson Spectrophotometer data, after correcting for the effects of natural geophysical variability (quasi-biennial oscillation and solar cycle) however indicates a decrease of annual average total column ozone ranging from 1.7% to 3.0% for the period 1969 to 1986, at latitudes between 30 and 80 degrees in the northern hemisphere. The decreases are most pronounced during winter months averaged for December to March, ranging from 2.3 to 6.2% (WMO, 1988). Ground based Dobson data are not adequate to determine total column ozone inter-annual variations in the tropics, subtropics or southern hemisphere outside Antarctica.

In the next section one of the most unique features of the ozone characteristics (the ozone hole) is discussed.

2.1.3.3 The 'Ozone Hole'

In 1985 a British team reported that ozone in the antarctic atmosphere had shown a decrease since the commencement of observations there in the late 1950s, and that the decrease is observed during southern hemisphere

spring (WMO, 1987). This October diminishing of stratospheric ozone layer over the antarctic regions is usually termed as the 'ozone hole'. Extreme losses were for example reported in October 1987 when losses reached 50% of the total ozone within the hole. The loss within the hardest hit layer of the lower stratosphere went up to about 95%. Poleward of 60 degrees south, the total ozone fell to the lowest over recorded during the spring. The hole persisted upto November 1988, the latest disappearance since it was detected.

Another hole has been observed in the atmospheric ozone layer above the arctic from the U.S. Nimbus - weather Satellite records.

The causes of the ozone hole are not conclusively understood. Several hypotheses however have been advanced. The first group of hypotheses are based on the atmospheric ozone chemistry. The theories indicate that the unique meteorology during winter and spring over antarctica sets up the special conditions of an isolated airmass (polar vortex) with cold temperatures required for the observed perturbed chemical composition. This leads to unusual chlorine chemistry and subsequent ozone depletion due to anthropogenic halocarbon compounds. Other theories are based on the atmospheric circulation. The resumption of high solar activity after the polar night westerlies for example have been suggested to produce large amounts of ozone destroying nitric oxide (WMO, 1987).

A lot of international concern has arisen from the discovery of the 'ozone hole' especially due to some of the theories connecting the ozone

depletion with man's activities. (Farman, et al, 1985; WMO, 1987; WMO, 1988).

The next section discusses some of the meteorological processes which are connected to the ozone distribution.

2.2 OZONE AND METEOROLOGICAL PROCESSES

In this section various meteorological processes which have been associated with ozone distribution are discussed under two sub-sections, namely tropospheric and stratospheric circulations.

2.2.1 Tropospheric Circulation

The atmospheric exchange processes may be grouped into the vertical exchanges or convection, and the horizontal circulation or advection. Tropospheric circulation processes are therefore discussed here under two seperate sections.

2.2.1.1 Tropospheric Convection

Convection can generally be grouped into two types. The first type is termed as forced convection. It is created mechanically by interaction between moving wind and obstacles on the earth's surface, or between layers of air moving at different speeds. The second type, termed as free convection arises from the natural buoyancy of air that is less dense than the

surrounding. When warm air rises and cold air sinks, kinetic energy is created. This last principle embodies the process whereby the overall motion of the atmosphere is maintained against ceaseless braking action of friction. The net vertical transport of ozone, water vapour, carbon dioxide, methane and other substances through the planetary boundary layer is mainly achieved through these convective processes (Reiter, 1968).

The spatial scales of the atmospheric motions can be divided into three major divisions, namely micro-scale (or small scale), meso-scale and synoptic or macro scale motions. The micro-scale Convection includes the turbulence associated with winds near the ground and small scale cumulus clouds. The vertical scale of small scale motions is generally dominant in the low levels of the atmosphere.

Meso-scale convection generally consist of clusters (10 to 200 km across) of larger cumulus and cumulonimbus clouds which have strong updraft extending from the planetary boundary layer to the upper troposphere. Some of the highest cumulonimbus towers may reach above 20 kms, and at their crest may penetrate several kilometers into the stratosphere. Much of the water vapour they transport upwards is often precipitated as snow or hail. As clouds disperse, however, they leave behind little water vapour at high altitudes together with many other 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 are of larger geographical scale and are much slower (of the order of a few centimetres per second). They are vertically slanted at very low angles. One kilometre ascent of air may correspond to several hundred kilometres of horizontal motion of air (Reiter, 1968). Synoptic systems include cyclones, anticyclones, Jet - streams, atmospheric waves, Inter-tropical convergence zone, etc. They contribute a lot to some of the observed ozone variations (Sreedharam et al., 1974; WMO, 1986).

2.2.1.2 Tropospheric advection

Advection determines the horizontal air movements. The spatial scales of advection can also be grouped into three, namely; Micro, meso and macro (synoptic) scales. The micro-scale advections include the urban/rural winds and 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 large water bodies; topography and blocking systems.

Macro-scale advections generally consist of the horizontal component of the general circulation, example of which is given in figure (2).

2.2.2 Stratospheric Circulation

A major cause of the tropical stratospheric circulation is the reversal of zonal winds from westerlies to easterlies. The mean reversal period, as mentioned earlier in the text is about 26 months (i.e., QBO). Maximum activity is centred around 20-35 km. and progresses downwards with time. Another cycle superimposed on average zonal wind has also been evident. It is centred around 6 months. Its maximum effect is at about 40 km. Both the QBO and 6 months cycles have been observed to be variable from year to year (Wilcox, et al., 1977; Oltmans and London, 1982). These cycles have been shown to influence the periodic fluctuations of total column ozone.

In the extra-tropics, the dominant feature of the stratspheric flow is an immense, annually reversing system of circumpolar zonal winds, which are westerlies in the winter hemisphere 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 from year to year. They appear as strong westerlies as low as 20 km. in latitudes 55 degrees to 75 degrees of both hemispheres, where they are known as polar-night westerlies. They are subject to vigorous disturbances that produce strong uplift and subsidence through great depths. These give rise to strong temperature alterations. The associated subsidence creates dramatic "sudden warmings", sometimes of 20 degrees to 30 degrees in a day, which

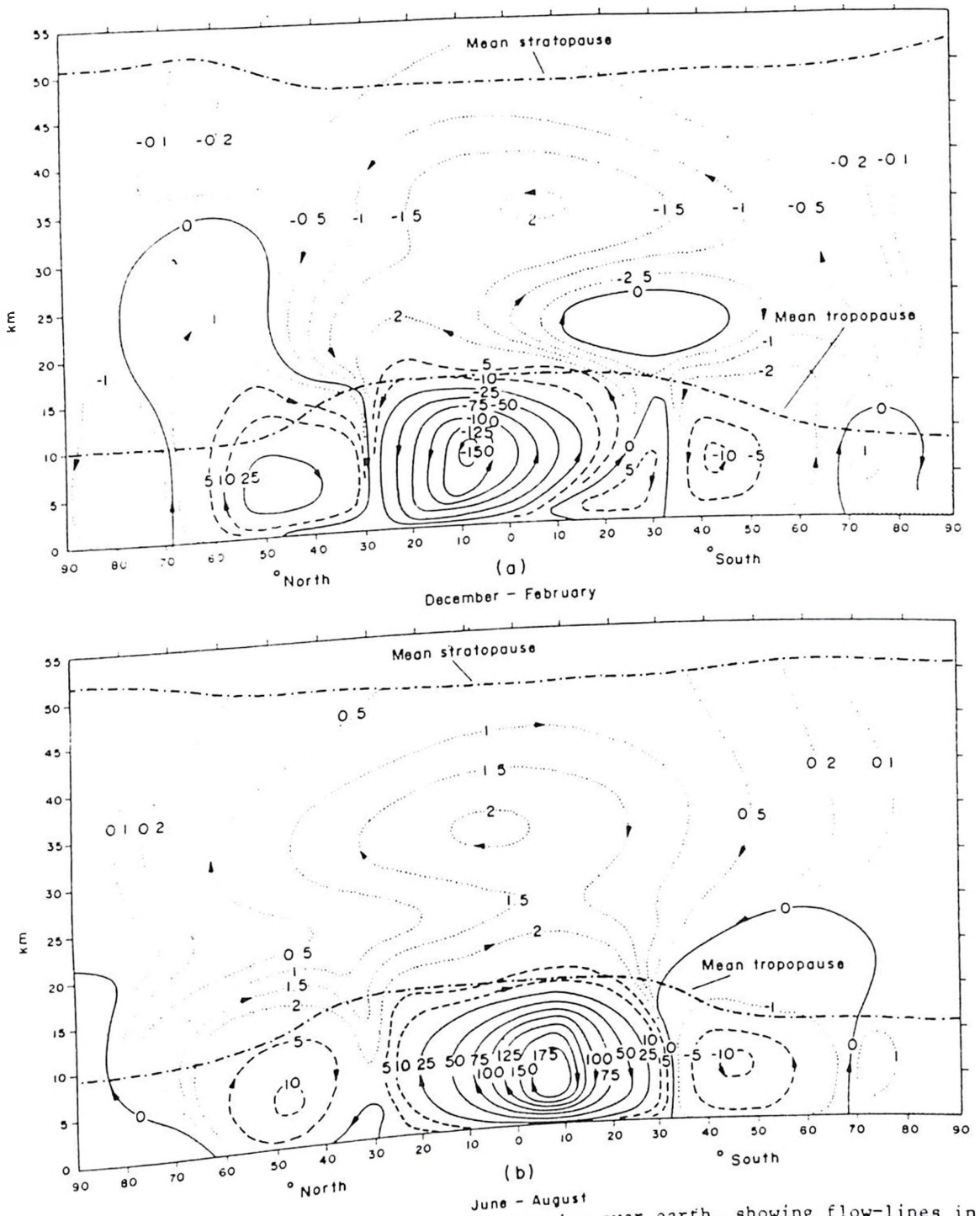


Fig. 2. Mean meridional circulation over earth, showing flow-lines in units of 10^{12} g s^{-1} mass transport. Diagram (a), for December-February, is more typical of the year than Diagram (b), June-August, where the Hadley cells are modified by the summer monsoons of the northern hemisphere.
CIAP Monograph 1 (Louis, 1974).

quickly destroy the westerly system. Large increases in total ozone occur with each warming, and there is no doubt that these systems account for the accumulation of much ozone in the lower polar stratosphere late in winter.

The summer stratospheric easterlies also descend to about 20 km, but are light and almost disturbance - free below 30 km. Slow moving waves with some vertical motion, occur at higher levels in middle and low latitudes.

As in the troposphere, substances injected in the stratosphere will be rapidly carried around the earth (Biswas, 1979). Poleward or equatorward dispersion however is much less rapid than in the troposphere since there are fewer disturbances at these high levels.

Troposphere - stratosphere mixing processes are discussed in details in the following section.

2.2.3 Troposphere - stratosphere mixing processes

There are several possibilities through which the stratospheric and tropospheric air can mix (Reiter, 1975; Biswas, 1979; Whitten et al., 1986). These include:

i) Quasi-horizontal transfers through the tropopause discontinuity in the mid-latitudes,

ii) Downfolding of the tropopause in strong frontal zones especially when cyclonic disturbances are active,

iii) Fall-out probably with scarvaging,

iv) Upward-moving gravity waves, which are thought to play a rather special role in the winds of the lower stratosphere,

v) Motions associated with the vertical arms of the general circulation cells which include Hadley, Ferrel and Polar cells, and

vi) Penetration of the tropopause by tall cumulonimbus clouds, as explained in the previous section (2.2.1.1).

The gap between the tropical and polar tropopause creates a clear media for quasi-horizontal mixing of atmospheric constituents. A current moving poleward from the tropical zone at, say 16 km will infact move from the tropical tropopause into the polar stratosphere. Strong waves in the westerly jet stream, which are 2 to 5 km below this level, often induce such transfers. Such air is dry since it can hardly contain enough moisture (temperatures are less than -75 degrees centigrade) Hence no appreciable water exchange may occur, though, particles and trace gases may well be carried through the gap.

A similar mechanism is 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 eastward moving cyclone waves of the westerly current, strong, slanting subsidence of stratospheric air occurs

in the frontal zones, bringing down low humidities, radioactive tracers and ozone from the lower stratosphere. 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 plays some role in the mixing processes, since the lower stratospheric 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 process in the stratosphere and may hence carry so[illegible] non-meteoric molecules or atoms along with it.

The vertical arms of the general circulation cells contribute to the stratosphere - troposphere mixing of atmospheric constituents. Figure 2 gives a clear picture of the motions.

The next section is devoted to the environmental aspects of ozone.

2.3 ENVIRONMENTAL ASPECTS OF OZONE

The current international concern on the stratospheric ozone diminution has generally resulted from anthropogenic influence on the natural composition of the atmosphere. This section is devoted to the man's influence on the atmospheric ozone together with possible biological and climatic impacts due to ozone depletion.

2.3.1 Man's impact on the ozone layer

Stratospheric ozone amounts can be disrupted by both natural and man-made factors. The natural factors include volcanic eruptions and extra - terrestrial events (like solar flares), which in the event of their occurence perturb the concentration fields of the oxides of nitrogen. The anthropogenic mechanisms include Aircraft emissions; emissions of N_2O from fertilizers and/or nitrogen fixing vegetations; industrial and vehicular emissions of halons, chlorofluorocarbons, methane and carbon dioxide; nuclear bomb, etc. (WMO, 1986). The anthropogenic mechanisms are briefly described below.

The manufacture of the supersonic aircrafts, whose high temperature combustion engines inject nitric oxide directly into the stratosphere, provided the start of major research programmes on the perturbed stratosphere. Some of these studies show that ozone reduction is related to the injection rate and to the injection altitude (closeness to ozone production zone). Hence supersonic aircraft injections in the troposphere are not expected to have a noticeable effect, nor are small numbers of concord - type aircraft operating at 17 km or lower. On the other hand, studies carried out using models indicate that a fleet of advanced supersonic transport planes, operating at 21 km with an injection rate of 1.8 megatonnes per year could result in a 12% steady state depletion. In such a situation permissible total emission levels would have to be defined by international agreement (Biswas, 1979).

Various studies have postulated that increased usage of agricultural fertilizers and/or of nitrogen fixing vegetation might affect the nitrogen cycle and result in an increase in the amounts of nitrous oxide released from the surface into the atmosphere. This would lead to an increase of NO_x in the stratosphere through the mixing processes and thus may lead to a decrease in ozone amount. (Titus , 1986).

Halons, chlorofluorocarbons and methane can destroy stratospheric ozone. When chlorine is released by action of ultra-violet radiation on e.g. a CFC molecule at a medium altitude of 30 km, it goes through catalytic cycles in which ozone is destroyed and moved back to molecular oxygen reservoirs.

The major uses of Halocarbons are as propellants in aerosol spray cans, as cooling agents in refrigeration and air conditioning, and as blowing agents in foams. The aerosol sprays can account for about 75% of the emissions in the atmosphere, and about 75% of their use is in personal care products - hair sprays, and deodorants (WMO, 1986).

Various studies of Halocarbons have shown an increasing trend for the last two decade. One of the most recent model studies was carried out by the European Fluorocarbon Technical Committe in 1984. It predicted an overall growth rate of about 1.5% per year of fluorocarbons (WMO, 1986).

An important feature of the predicted reduction in ozone due to CFM release is shown in Figure (3). This diagram presents the expected reduction in ozone, after Crutzen (1975), as a function of height, for the years 1972, 2000 and 2025. The reduction is a maximum near the height of 40 km, that is near the region where the CFMs dissociate most rapidly and where ozone is essentially formed. According to this diagram, the direct measurement of a reduction in ozone due to CFMs could be best carried out near a height of 40 km. This is too high for most of ozonesondes, but BUV Satellite data are good and umkehr measurments show only slight evidence of a recent ozone decrease at these heights.

Nitric oxide produced by high temperatures in a nuclear explosion should result in ozone depletion. Some ozone may be created locally by Ultra Violet radiation from the explosion. After a few days, however, this effect should die out and depletion from nitric oxide grow in importance. The magnitude of the depletion effect is mainly a function of the injection level, and of consequent atmospheric diffusion and transport of the nitric oxide. So far various studies have failed to reveal any noticeable effect subsequent to nuclear explosion (Biswas, 1979). Simultaneous measurements of ozone and NO_x may throw some light into the apparent discrepancy between theory and observations.

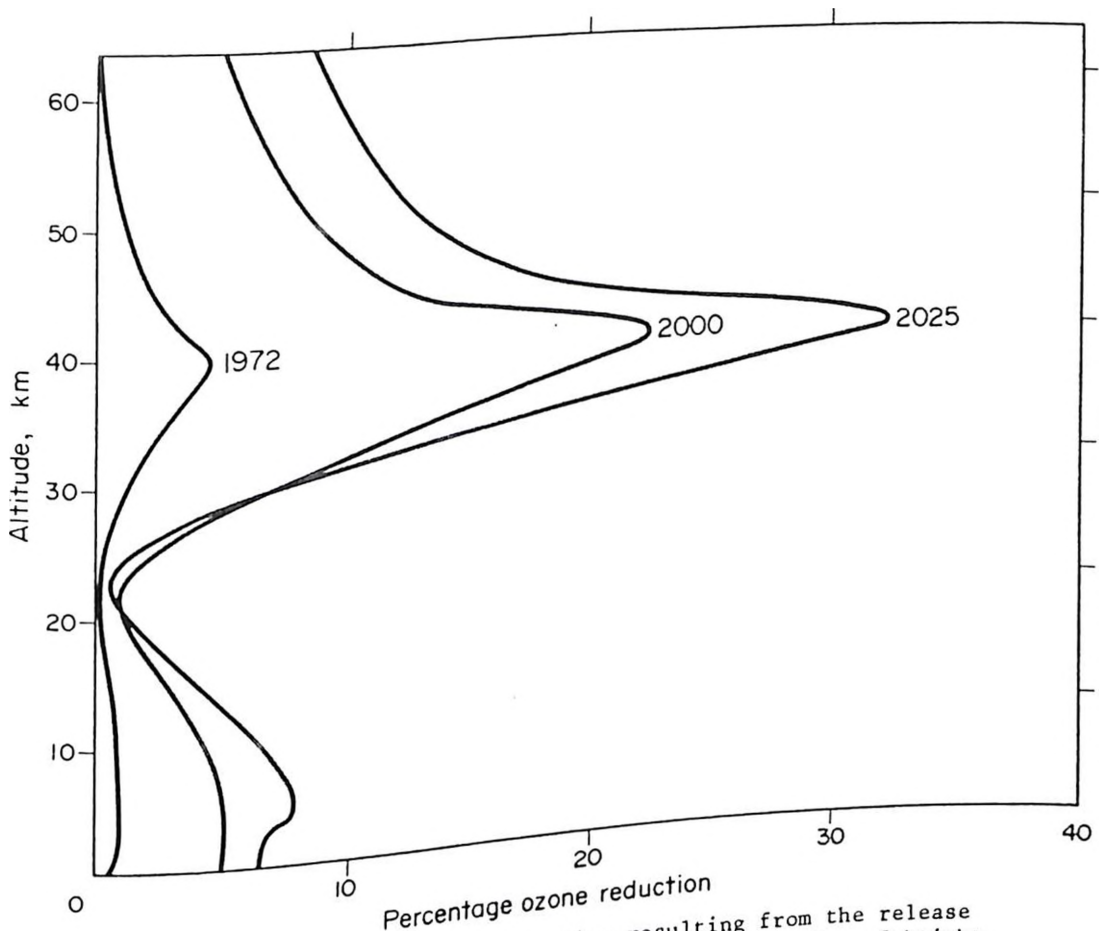


Fig. 3. Percentage ozone reduction resulting from the release of chlorofluoromethanes at the 1973 rate, as a function of height. Indicated are the model results for the years 1972, 2000 and 2025. (After Crutzen, 1975)

2.3.2 Man's impact on tropospheric ozone

Both man-made and natural factors contribute to the alteration of tropospheric ozone. The natural mechanisms mainly consist of:

i) the transport of ozone in the stratosphere to the troposphere due to mixing processes, and;

ii) the emission of N_2O from nitrogen fixing vegetation. Photochemical reaction of this N_2O with molecular oxygen produces ozone.

Surface ozone is produced artificially through emissions of hydrocarbons and N_2O from automobiles exhaust and fuel evaporations. It is also produced through oxygenated hydrocarbons and hydrocarbons emitted mainly from industrial activities. The photochemical reaction of the emitted hydrocarbons and oxides of nitrogen produce ozone (Aderson , 1979; Sterens , 1986).

Anthropogenic emissions are mainly concentrated in populated urban areas. Various studies have shown that anthropogenic factors are the major contributors of the observed increases in surface ozone over many large cities (EPA, 1978).

The next section dwells on the stratospheric residence time for gases.

2.3.3 Stratospheric residence time for gases

The time spent in the atmosphere by a gas before it irreversibly reacts with another substance is termed as its residence time.

The following observations have been made by Reck, 1976; Biswas, 1979; and Roy *et al.*, 1980, among others;

i) Residence time for chemically stable substances in the lower stratosphere increases with height from a week or two at north polar tropopause to several years at greater heights. The residence time generally depends on the level and on the slope of the tropopause, among others;

ii) Substances injected into the lower equatorial stratosphere (17-25km) tend to remain there for a period ranging from months to years;

iii) When tropical concentrations disperse to higher latitudes they do so along downward sloping paths. When they arrive in 60 degrees latitude they are often 5 to 10 km below their original level. Substances injected in the mid-latitudes tend to disperse upwards towards the equator and downwards towards the poles along similar sloping surfaces. Such processes require many months to complete.

iv) Chlorofluorocarbons have been observed to be present in the upper troposphere of northern hemisphere in substantial

quantities. They are engaged in slowly penetrating the upper stratosphere where they are dissociated by ultra-violet radiation. Due to the rapid increase of residence time with height it will take more than a century for the atmospheric processes to clean the atmosphere of the molecules which are already present, even if we cease manufacturing now.

These facts have serious implications on stratospheric pollution as described in the next section.

2.3.4 **Biological impacts of ozone alterations**

A reduction in stratospheric ozone would have severe impacts on man, animals, plants and indeed the entire ecosystem (Biswas, 1979; Titus, 1986). On the other hand, various studies have shown that surface ozone, being a pollutant, affect the constituents of the ecosystem (EPA, 1978).

Stratospheric ozone depletion would result in an increase in UV-B (290 - 320nm) radiation on earth's surface. The effects of increased UV-B radiation exposure to man include skin cancer, sun-burn, snow-blindness, eye damage, ageing and wrinkling of the skin. In man, tropospheric concentrations greater than 0.25 ppm have shown to produce the following effects; Nasal, eye and throat irritations, coughs, increase in airway resistance, changes in pulmonary functioning and even severe headaches, among others (EPA, 1978).

Various studies of increased UV-B radiation on animals (other than man) indicate that in latitudes where long periods of high natural solar ultra-violet radiations are prevalent, two effects have been noted. These are cancer eye, a form of ocular carcinoma; and pink-eye, a bacterial photosensitization. On the other hand various studies have shown that the exposure of animals to tropospheric ozone concentrations greater than 0.2 ppm may cause pulmonary malfunctioning and adverse effects on blood cells.

Increased UV-B radiation on plants has been shown to bring about depression of photosynthesis and the inhibition of leaf expansion. In plants, high surface ozone levels affect stomatal openings, respiration, photosynthesis and even biochemical pathways and enzyme system. These adverse effects on plants can cause a reduction in crop and timber yields, which could have a direct social and economic impact (Menzel, 1984, Moorman et al., 1973).

High levels of surface ozone are known to be major contributors to deterioration of many types of organic materials such as elastomers (rubber), textile dyes, fibres and certain types of paints. (Mueller and Stickney, 1970)

Studies indicate that the likely impacts of increased UV-B radiation on aquatic ecosystems include a reduction in plankton production with negative effect on the aquatic food chain. There might be competitive ability

among organisms which could alter the entire ecosystem, although at present these are difficult to predict (Ilyas, 1986).

Therefore significant changes in ozone concentrations can have several ecological consequences which in turn can cause significant changes in the climate. Details of the impacts of ozone dimunition on climate is the subject of the next section.

2.3.5. **Impacts of ozone change on climate**

Ozone plays a major role in determining the radiative balance of the atmosphere, particularly in the stratosphere. A reduction and/or redistribution of ozone with altitude could alter the distribution of temperature and other weather elements. This is due to ultra-violet solar radiation which is very strongly absorbed by ozone. The temperature of the stratosphere is largely maintained by balance between absorption of solar radiation by ozone and emission of atmospheric infra-red radiation by ozone, carbon dioxide and water vapour. Any changes in stratospheric heating rates would have a direct influence on the temperature distribution in stratosphere and possibly in the troposphere. These temperature changes would have an effect on the patterns of atmospheric circulation and hence climate (WMO, 1986).

In addition to the possible climate impact of a decrease in stratospheric ozone there are other potential modifications by the ozone depleting substances. Greatest attention has been directed to the green-house

warming of the lower atmosphere by fluorocarbons, halocarbons and other trace gases (Ramanathan , 1976; WMO, 1987). The warming effects of these gases add to the warming by carbon dioxide. Atmospheric carbon dioxide concentrations are increasing due to man-made activities (Titus, 1986).

A reduction in the ozone column would result in an increase of the biologically harmful UV-B radiation reaching the earths surface. There is a possibility that the increase in UV-B radiation near the ground could increase the photochemical smog over large cities, and implicitly increase tropospheric ozone. However, it has been shown that the impact amounts to an increase in surface (urban) ozone of less than 1ppm (Biswas, 1979).

However, there are two difficulties in evaluating the effects of ozone change on climate. First, the climate simulations are in the primitive states, and no conclusive confidence can be assigned to the predictions. Second, climate has fluctuated on all time scales in the past and there is every reason to expect these natural fluctuations to continue (WMO, 1986).

On the other hand, there are overwhelming evidences of the general warming of the globe due to the increase of the greenhouse gases. The maginitude of the global warming has however varied from one model to another, but it ranges between 1.5 to 4.5 degrees centigrade (Villach, 1985).

The climatic changes at regional level are more realistic in the determination of the impacts of the regional anthropogenic processes. These

changes cannot however be accurately estimated with the existing climate models. This has been partly due to the inability of these models to parameterize the complex feedback processes between land - ocean - atmosphere and the natural response of the ecosystems to the expected changes. Knowledge of the past and present trend of ozone is therefore very useful in the understanding and planning for the future impacts of the greenhouse gases. The methods used to study the past and present ozone trend over Nairobi are discussed in the next chapter.

CHAPTER 3

DATA AND METHODOLOGY

3.1 DATA UTILIZED IN THE STUDY

This section is devoted to the basic measurements of ozone and the details of the data used in the study.

3.1.1 Sources of the data

Data on total atmospheric ozone amount was obtained by use of Dobson's ozone spectrophotometer No. 18 which is stationed at Chiromo Campus, University of Nairobi (1° 16'S, 36° 48' E), at an altitude of 1692 metres . The daily ozone data which is available from the station since April 1984 was utilized. Hourly measurements were however made within the period June 1988 to May 1989. The Nairobi observatory forms part of the global ozone network and is the only station near the equator. Thus the ozone data used in the study was solely from this station.

Meteorological records used in the study included cloudiness, total solar radiation, tropopause height, and rainfall. Temperature, relative humidity, wind speed and direction records used in this study were for the surface, 700 mb, 500 mb, 300 mb, 200 mb, 150 mb, 100 mb, 70 mb, 50 mb, 30 mb and 20 mb levels. Since no upper air observations were available for Chiromo station, all the upper air meteorological data were obtained from

Dagoretti meteorological station which is located 6.2 km away from the ozone station. The surface weather records were however obtained from Chiromo Campus observatory where the ozone Spectrophotometer is stationed. Ozone records were subjected to the analyses highlighted in the next section. The working principles of the ozone spectrophotometer are however discussed first.

3.1.2 Ozone measurements

Observations of total ozone amounts are made by use of either surface or satellite based techniques (Biswas, 1979). In the surface based method, the total ozone amount in the column above the observing station is measured by Dobson's ozone spectrophotometer which, although bulky and delicate, gives estimates of total ozone to with 2% if carefully operated and maintained.

Satellite based measurements are made by use of a Backscatter Ultraviolet (BUV) instrument carried by a polar orbiting satellite. These measurements have an advantage of quasi-global coverage by one and the same sensor, thus making the readings readily comparable. This method gives ozone values which are compatible to within 6% of those obtained by Dobson's spectrophotometer.

In the present work, the Dobson's ozone spectrophotometer was utilized to obtain total ozone data. A brief account of the instrument is

given below. Details of the instrument can be obtained from Komhyr (1980).

3.1.2.1 Operation principles of the spectrophotometer

Light enters the instrument through a window on top of the instrument (figure (4)). After reflection in the right angled prism, the light falls on slit S_1 of a spectroscope. This spectroscope consists of a quartz lens which renders the light parallel. The prism breaks up the light into its spectral colours. A mirror is then used to reflect the spectral colours back through the prism and lens onto the focal plane of the instrument. The required wavelengths are isolated by means of slits S_2, S_3 and S_4 located at the instrument's focal plane.

Two shutter rods are mounted in the base of the spectrophotometer. The left hand S_4 shutter rod is used only when spectrophotometer tests are conducted, and should be pushed all the way into the instrument when ozone observations are being made. The right hand wavelength selector rod blocks out 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 pair. 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.

Selection of the wavelengths A, B, C, C' or D when making ozone measurements is accomplished by rotating Q_1 and Q_2 levers to positions

specified in a table of settings of Q provided with the instrument. Thick flat quartz plates and last slits (S_1 and S_5) are fixed to the Q 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. Changes in refractive index of the spectrophotometer quartz prisms due to changes in the temperature of the instrument are allowed for by making slight adjustments to the settings of Q_1.

An optical wedge is mounted in the instrument in front of slit S_3. The position of the wedge is controlled by turning a graduated dial located on top of the instrument. For any given position of the dial the intensity of the light passing through the optical wedge is reduced in a definate ratio which is determined during the original calibration of the spectrophotometer. In order to measure the relative intensity of the two wavelengths on which observations are made, it is necessary to be able to detect the balance position of the dial.

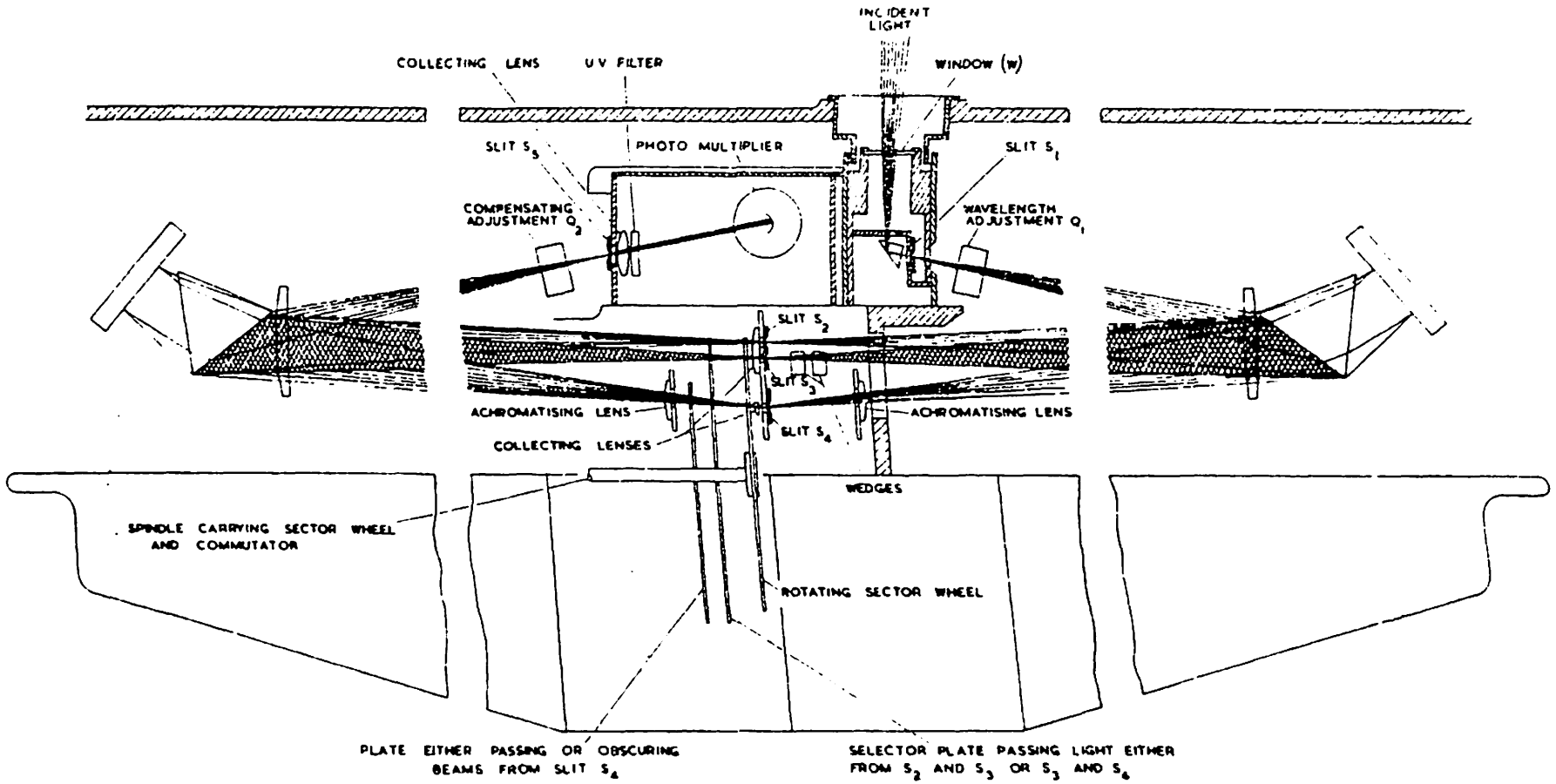


Figure 4. Optical system of the Dobson spectrophotometer (Komhyr , 1980)

Utilizing Dobson Spectrophometer, total ozone observations are made by measuring the relative intensities of selected pairs of ultra-violet wavelengths, called A, B, C, C^1 and D wavelength pairs, emanating from the sun, moon or zenith sky. The A wavelength pair, for instance, consists of 305.5 nm wavelength that is highly absorbed by ozone, and the more intense 325.4nm wavelength that is relatively unaffected by ozone. Outside earth's atmosphere the relative intensity of these two wavelengths remain fixed. In passing through the atmosphere to the instrument, however, both wavelengths become less intense due to scattering of light by air molecules and aerosols.

Additionally, the 305.5 nm wavelength is strongly attenuated while passing through the ozone layer whereas attenuation of 325.4 nm wavelength is relatively weak. The relative intensity of the A wavelengths as obtained from the instrument, therefore, varies with the amount of the ozone present in the atmosphere. This is due to the fact that as ozone amount increases, the observed intensity of the 305.5 nm wavelength decreases, whereas the intensity of the 325.4 nm wavelength remains practically unaltered. Thus, by measuring the relative intensities of the suitably selected pair wavelengths with the Dobson instrument, it is possible to determine the amount of ozone present in a vertical column of air extending from ground level to the top of the atmosphere in the neighbourhood of the instrument. The results are expressed in terms of a thickness of a layer of pure ozone at standard temperature and pressure.

The general data reduction equation for ozone observations made on single pair wavelengths such as A, B,C or D is of the form

$X = \{N-(\beta-\beta')mp/p_0-(\delta-\delta')Secz\}/(\alpha-\alpha')\mu$.....(1)

Where X = total ozone amount expressed in Dobson units (1D = 10^{-5}Metres of pure ozone at standard temperature and pressure).

$N = L_0 - L = Log\frac{I_0}{I_0'} - log\frac{I}{I'}$

I_0 and I_0' = intensity outside the atmospere of solar radiation at the short and long wavelengths respectively, of the wavelength pair;

I and I' = measured intensity at the ground of solar radiation at the short and long wavelengths, respectively.

β and β' = Rayleigh Scattering coefficients of air at the short and long wavelengths, respectively,

m = ratio of the actual and vertical paths of solar radiation through the atmosphere, taking into account refraction and the earth's curvature;

p = observed station pressure;

p_0 = mean sea level pressure;

δ and δ' = Scattering coefficients of aerosal particles at the short and long wavelengths, respectively;

Z = angular zenith distance of the sun;

α and α' = absorption coefficients of ozone at the short and long wavelengths, respectively;

μ= ratio of actual and vertical paths of the solar radiation through the ozone

layer, the main height of the ozone layer being 22Km.

The major problem of using equation (1) is related to the lack of a satisfactory method of estimating the aerosal scattering coefficients (δ and δ'). In practise, therefore, observations are normally made on double pair wavelegths, e.g, the AD wavelengths. Both the A and D wavelength pairs are approximately equally scattered by the atmosphere. The scattering effect is therefore nearly cancelled such that absorption by ozone becomes by far the major factor affecting the relative intensities of the double pair wavelengths on which observations are being made.

The general data reduction equation for observations made on double paid wavelenghths such as AD, BD, CD or AC pair is

$$X_{12} = \frac{N_1 - N_2 - [(B-B)_1 - (B-B)_2]mp/p_o - [(\delta - \delta')_1 - (\delta - \delta')_2]\sec(z)}{[(X - X)_1 - (X - X)_2]\mu} \quad \ldots(2)$$

where the subscripts 1 and 2 refer to the two wavelengths pairs and $(\sigma - \sigma)_1 - (\sigma - \sigma)_2$ is assumed to be zero. Here also, mean station pressure may be used for p without significant error.

The use of the spectrophotometer is not limited to that of measuring direct sunlight or moonlight. The measurement of zenith blue skylight can provide meaningful values of total atmospheric ozone. Skylight is scattered sunlight and ozone absorbs skylight just the same as sunlight. A graphical technique is employed to evaluate a measurement of skylight as opposed to the mathematical equation used to evaluate direct sunlight measurements.

The graphs, which are constructed from simultaneous sunlight and skylight measurements, relate the intensity of zenith blue measurements to path length of total column ozone.

The total ozone measurements can also be made using light from the zenith cloudy sky. Light reaching the instrument from zenith cloudy sky is a mixture of sunlight and skylight and there is no reason to believe that one wavelength of a pair will be absorbed or scattered more than the other. Therefore, under cloudy conditions the relative proportions of sunlight and skylight entering the instrument are unimportant and useful observations can be made by utilizing the criteria for wavelength pairs and pathlength, e.g, an observation of double wavelength pair AD is best observed when m is equal to or less than about 2.4, while an observation of CD is desirable in the range of m, from about 2.0 to 6.0, etc (see equation (1)).

The ozone data were subjected to the analysis discussed in the next section.

3.2 METHODOLOGY

The various methods which were used to study the spatial and temporal characteristics of ozone over Nairobi are discussed in this section. The methods which were used to estimate the few missing ozone records and the quality control measures for the ozone records used in the study are however discussed first.

3.2.1 Estimation of missing data

It was observed from the ozone data archives that few records were missing within the period April 1984 to May 1988. An attempt was thus made to estimate the missing data with a statistical method as shown in equation (3).

The equation expresses the estimated ozone amount (E_x) as;

$$E_x=A_x(M_{i-2}/A_{i-2}+M_{i-1}/A_{i-1}+M_{i+1}/A_{i+1}+M_{i+2}/A_{i+2})/4....(3)$$

Where A_x = average ozone amount for the month with missing data

A_{i-2}, A_{i-1}, A_{i+1}, A_{i+2} = long term average ozone amount for two preceding and two following months, respectively;

M_i= ozone amount for the month (i) of the year under consideration.

Equation (3) is a more generalised form of the arithmetic average method of the estimation of missing records (Rainbird , 1967).

The quality of the estimated records were tested before they were included in the study. Details of the quality control tests are discussed in the next section.

3.2.2 Data quality control

Quality control deals with the detection of errors in data and ensuring that the data sets are near error free. In order to detect errors in the data, it is important to have some idea of the common types and causes of the errors so as to design suitable methods for detection and minimisation.

The major sources of errors in the ozone data are generally associated to:

(a) Instrumentation

(b) Station condition

(c) Observation and recording

(d) Coding and decoding, and

(e) estimated ozone records, among others.

The instrumentation errors are generally due to the conditions and intrinsic accuracy of the instrument. These errors are systematic, persistent and generally increase with time. The alteration of the station conditions like the exposure may change the microclimate of the station. Such changes induce persistent errors.

Observation and recording errors are associated with misreading of the scales, mis-interpretation of the units, wrong computations of the ozone amounts, etc, while coding errors originate from mistakes arising from the coding and decoding of records.

The other major errors in the ozone records which were used in the study could be associated with the estimated ozone records. One must therefore determine whether all of the ozone records are homogeneous (i.e. samples from the same statistical distribution).

In this study, internal consistency checks were done by testing calibration level of the Dobson's ozone spectrophotometer. Standard lamp tests were performed to check whether the level of calibration of the spectrophotometer had remained constant. When a permanent change occurs in the spectral characteristics of the instrument the lamp test data may be used to determine corrections to be applied to the ozone data.

Other sources of error were minimised by observing a strict observational and recording procedure of the data.

The quality of the ozone records was examined using homogeneity tests. Details of these tests are discussed in the next section.

3.2.2.1 Homogeneity of ozone data

Homogeneity tests are concerned with the detection of bias or drifts which may have taken place in the archieved observations after a long period of recording, i.e checking whether archived data are samples from the same statistical population. Heterogeneity in records may be due to changes in the instrument types, methods of measurements, instrument errors, change of exposure conditions, estimation of records, etc.

Many statistical methods have been used to test homogeneity in climatic records. They include Residual mass curve, Runs tests, Double mass curves, Correlation methods, Marrona and Yohai method, etc. The methods used in this study, namely, Residual mass curve and one sample run's test are discussed in details.

3.2.2.1.1 Residual mass curve

Cummulative deviation of observations from the mean are plotted against time (Residual mass curve). A straight line indicates homogeneity in the observations. Significant deviations of some points from the straight line are indicative of heterogeneity. If all observations do not lie on a straight line, two lines may be drawn on the graph. To test if the slopes of the two lines are significantly different from each other, the slope of the regression line (b), and the deviations from the regression line (D) are computed, where

$$b=(\overline{X_1 X_2}-\bar{X}_1 \bar{X}_2)/(\overline{X_1^2}-(\bar{X}_1)^2) \quad \ldots\ldots(4)$$

$$D=NR^2 \quad \ldots\ldots(5)$$

where $R = ((X_2 - X_2')/N)^{1/2}$

X_1 = Independent variable, X_2 = Dependent variable

X_2' denotes the values of X_2 given by the line of regression (X_2 being the actual observation of the dependent variable);

N = total number of observations; and

R = badness of fit, and the bar represents mean.

The ratio

$$t=(b_1-b_2)/[(N_1D_1^2+N_2D_2^2)(1/N_1+1/N_2)/(N_1+N_2-2)]^{1/2} \quad \ldots\ldots(6)$$

is then computed. A null hypothesis of 'b^1' is not significaly different from b^2 is assumed, which is rejected if $t>t_c$, where

t_c = limiting student t value at $N_1 + N_2 - 2$ degrees of freedom, at the desired percentage of confidence level.

3.2.2.1.2 One sample run's test

This non-parametric test is a method of testing a null hypothesis of 'homogeneity in records' against an alternative trend, slippage of mean, or some form of oscillations. It has been applied to many climatological time series(Ogallo, 1979; Ogallo,1981 a).

The number of runs above or below the median in a sample of observations can give an idea of the trend, cycles or random fluctuations in a time series. In the present study, a null hypothesis of 'no homogeneity in the records is assumed for the ozone series and the statistic Z is calculated from the formula,

$$Z = X/(\alpha/\beta)^{1/2} \quad \text{.....(7)}$$

Where $X = \tau - [2n_1n_2/(n_1+n_2) + 1]$

$\alpha = 2n_1n^2 (2n_1n_2 - n_1 - n_2)$ and

$B = (n_1 + n_2)^2 (n_1 + n_2 - 1)$

τ is the number of observed runs, n_1 and n_2 are number of runs above and below the median respectively, while n is the size of the sample. For large sample size (n>40) the Z approximates to a normal distribution with mean zero and unit variance. The significance of the assumed hypothesis is tested

by determining the significance of the calculated Z using a normal distribution table. For all cases where Z>1.96 the null hypothesis of 'no homogeneity in the ozone records' is accepted at 95% confidence level.

The major weaknesses with the non-parametric tests is that they are not based on the statistical distribution of the records. These tests are therefore generally weaker than the parametric tests. They are however the easiest to use.

The results from the residual mass curve and the one sample run's test were compared in this study. The homogeneous data samples were subjected to the analyses highlighted in the next sections.

3.2.3 Time series analyses

Any observations taken with respect to time are called a time series. The time series consists of the following components;

(i) Trend;

(ii) Seasonal variation;

(iii) Cyclical oscillation, and

(iv) Random element.

Some time series are of non-stationary nature (mean and variance not constant). Many times series analyses are however defined for stationary time series. The mean pattern of the time series can be detected from trend analysis.

3.2.3.1 Trend analysis

The trend component, which is defined as the long term movement of a time series, can indicate whether the series is stationary or non-stationary. This is particularly an essential factor to be examined prior to subjecting the time series to spectral and cross-spectral analyses.

Trend can be linear or no-linear. Three methods can be used to study the trend component. The most basic of them is the graphical approach. This method is however quite subjective since it depends on individual judgement of the patterns of the graph. Statistical analysis, using parametric methods, can also be utilized to examine the statistical significance of any trend observed from the graphical methods. The most commonly used of these is the arithmetic mean method. Alternatively, considering that the statistical distribution of many physical variables are not readily known and are quite complex at times, non-parametric (distribution free) tests have been widely used. The non-parametric tests include the Mann-Kendall rank statistic, T and Spearman rank statistic, among others (Ogallo, 1977). Three methods which are used in this study are discussed below.

3.2.3.1.1 Graphical methods

Smoothed and unsmoothed ozone time series were drawn under this method and the visual patterns examined. In the smoothed time series the trend at any given point in time is represented by a weighted average of the

observed values near that point. Various weighting functions have been used (Mitchel, 1966; Panofsky, 1968, Ogallo, 1977; Ogallo, 1981b , and many others).

In this study the ozone series was smoothed by binomial coefficients (Ogallo, 1977) and the resulting series was displayed graphically. The weights used were O.22 for the i^{th} month, o.20 for the i ±1 months, o.12 for the i ± 2 months. This low pass filter suppresses high frequency oscillations, and in this case all fluctuations of periods shorter than 10 months have been considerably suppressed.

3.2.3.1.2 Arithmetic mean method

Under this method, the ozone data is divided into two equal samples whose averages, $\overline{X}_1$ and $\overline{X}_2$, and standard deviations S_1 and S_2 are computed. Then the ratio

$$t = (\overline{X}_1 - \overline{X}_2)/[(N_1S_1^2+N_2S_2^2)(1/N_1+1/N_2)/(N_1+N_2-2)]^{1/2} \quad \ldots\ldots (8)$$

is computed, where N_1, N_2 = number of ozone observations in each sample. A null hypothesis of 'X_1 is not significantly different from X_2' is assumed. The hypothesis is rejected if $t>t_c$, where t_c is the value of t distribution with N_1 + N_2 - 2 degrees of freedom, at 95% confidence level (Panofsky, 1968).

3.2.3.1.3 Mann kendall rank statistic, τ

This is considered as a powerful test when the most probable alternative to randomness is linear or non-linear trend. In the test, considerations are made only on relative values of all terms in the time series X_i under consideration. Therefore prior to applying the test, X_i is replaced by ranks K_i such that each is assigned a number ranging from 1 to N that reflects the magnitude relative to the magnitudes of all other terms.

The statistic τ is computed by using the formula,

$$\tau = \left[\left(4\sum_{i=1}^{N-1} n_i\right)/(N(N-1))\right] - 1 \quad \ldots\ldots\ldots\ldots (9)$$

where n_i is the number of values larger than i^{th} value in the time series subsequent to its position in the time series of N values.

The statistic tends to a normal distribution with mean zero and variance equal to $(4N + 10) / 9N(N - 1)$ for N larger than 10. The value of τ can be used to assess the significance of trend by comparing it with the statistic τ_r defined by

$$\tau_r = \pm t_r \, [(4N + 10)\, 9N(N-1)]^{1/2} \quad \ldots\ldots\ldots\ldots (10)$$

Where t_r is the desired probability level of normal distribution for a two tailed test.

If the observed statistic τ is greater than theoretical statistic τ_r then the trend is significant.

The analysis of periodic and random components is made difficult by the presence of trend in a time series. Therefore the time series must first be made stationary.

A series is said to be stationary if there is no apparent trend in either the mean or the variance. That is when

$E(x_t) = \mu$, a constant, and

$Cov(x_t, x_{t+k}) = E\{(x_t - \mu)(x_{t+k} - \mu)\}$ remains

constant over time (Harvey, A.C., 1975).

The transformation of a non-stationary time series to a stationary one is through some form of filters, which are mathematical expressions capable of suppressing the undesired characteristics and bringing out only the required fluctuations. Several filters have been utilized in the analysis of time series. They include moving average filters, difference filters, band-pass filters, high pass filters and low pass filters. The difference filters which have been applied in this study are described below.

3.2.3.2 Difference filters

The difference filter of the first order may be defined as

$$Y_t = X_t - X_{t-1} \quad \text{.....(11)}$$

where Y_t and X_t represent the differenced and original records. Some characteristics of this filter are briefly discussed below.

(i) Suppose $X_t = a_0 + a_1 t + a_2 t^2$ (quadratic),

where t= time and a_0, a_1, a_2 are constants,

then $Y_t=X_t-X_{t-1}$

$= (a_0+a_1t+a_2t^2)-(a_0+a_1(t-1)+a_2(t-1)^2)$

$= C_0+C_1t$(linear)

A second differencing thus renders the series stationary.

(ii) If we now assume $X_t=e^{i\lambda t}$ where $i=\sqrt{-1}$ and λ= constant

then $Y_t=e^{i\lambda t}-e^{i\lambda(t-1)}$

$=A(\lambda)e^{i\lambda t}$

where $A(\lambda)= 1-e^{-i\lambda}$ is the transformation function

That is, $Y_t=[1-(\cos\lambda-i\sin\lambda)]e^{i\lambda t}(1-e^{-i\lambda})$

$=[(1-\cos\lambda)+i\sin\lambda]e^{i\lambda t}$

$=(1-\cos^2\lambda+\sin^2\lambda)^{1/2}(e^{i\theta}+e^{i\lambda})$.....(12)

where $\tan\theta=Y/X$

$=x+iy+(x^2+y^2)^{1/2}e^{i\theta}$.....(13)

In this case $\tan\theta=\sin\lambda/(1-\cos\lambda)=(2\sin\lambda/2\cos\lambda/2)/\sin^2\lambda/2$

$= 2\cot(\lambda/2)$.....(14)

This implies that $\theta=\tan^{-1}(2\cot x/2)$ and

$Y_t=(2\sin\lambda/2)e^{i(\lambda t+\theta)}$.....(15)

Therefore the effect of differencing is (a) to transform the amplitude from I to 2 sin $(\lambda/2)$ and (b) to alter the phase angle from 0 to θ. However

the wavelength or period of oscillation remains invariant = $2\pi/\lambda$. This implies that by using a difference filter the trend component is eliminated rendering the resulting series stationary.

The choice of the order of the filter depends on the flunctuations to be filtered out and the characteristics of the trend. The seasonal filter which was used here was of the form

$Y_t = x_t - x_{t-12}$.

This filter is capable of removing the annual component of the time series.

The differenced records were subjected to spectral and cross-spectral analyses. The mean seasonal characteristics were however examined without the difference filter.

3.2.3.3 Seasonal variations

The mean seasonal ozone patterns were examined by plotting the monthly mean ozone values. The mean values for any month j is given as

$$\overline{X}_j = (1/n)\sum_{i=1}^{n} x_{ij} \qquad \text{.........(16)}$$

Where i represents the year of record and n the total number of years. In this case n = 5 (i.e. from April 1984 to May 1989).

In order to compare the relative values between the months, a seasonal index (S_j) was defined as shown below.

$$S_j = 1/n\sum_{i=1}^{n} x_{ij}/m_i \quad \text{.....(17)}$$

where m_i is the mean total ozone value for the year i.

Monthly values of $\bar{x}_j$ and S_j were plotted in this study.

3.2.3.4 Cyclical variations

After the removal of the trend and seasonal variation by difference filters, cyclical and random components of a time series remain. In this study, these two components were examined using two methods, namely the correlogram and the spectral analyses. These methods are discussed below.

3.2.3.4.1 Correlogram analysis

The autocorrelation function r(k) is defined as the ratio of the autocovariance R(K) to the variance R(o). For a time series of n observations,

$$r(k)=\{Cov(Y_t,Y_{t+k})\}/\{v(Y_t)v(Y_{t+k})\}^{1/2}$$

$$= \frac{\sum_{t=1}^{n-k} Y_t Y_{t+k} - (\sum_{t=1}^{n-k} Y_t)(\sum_{t=1}^{n-k} Y_{t+k})/(n-k)}{\{\sum_{t=1}^{n-k} Y_t^2 - (\sum_{t=1}^{n-k} Y_t)^2/(n-k)\}^{1/2}\{\sum_{t=1}^{n-k} Y_{t+k} - (\sum_{t=1}^{n-k} Y_{t+k})^2/(n-k)\}^{1/2}} \quad \text{.....18}$$

Assuming the time series to be sufficiently long, we may assume that

$$\sum_{t=1}^{n-k} Y_t^2 - (\sum_{t=1}^{n-k} Y_t)^2/(n-k) \simeq \sum_{t=1}^{n-k} Y_{t+k} - (\sum_{t=1}^{n-k} Y_{t+k})^2/(n-k)$$

Therefore,

$$r(K)=\frac{\sum_{t=1}^{n-k} Y_t Y_{t+k} - \{\sum_{t=1}^{n-k} Y_t\}(\sum_{t=1}^{n-k} Y_{t+k})/(n-k)}{\sum_{t=1}^{n-k} Y_t^2 - (\sum_{t=1}^{n-k} Y_t^2)/(n-k)} \qquad \text{.....(19)}$$

$$= R(K)/R(0)$$

A graph of r(k) versus K (the time lag) is called a correlogram. The analysis based on the correlogram is called correlogram analysis. This analysis essentially reveals the nature of the generating process. For a periodic process the shape of the correlogram is periodic, for a moving average process it vanishes, for a random process it is defined by the line r(k) = o, and for a first order markov process the correlograme decays exponentially.

The autocorrelations were calculated and correlogrames plotted for the ozone records.

3.2.3.4.2 Spectral analysis

Power spectrum is by far a more powerful and more useful variable to use in detecting periodic fluctuations. It involves the transformation of a time series into frequency domain.

Spectral analysis has undergone a lot of historical development. Currently, three most commonly used methods in computation of spectral

estimates include the Autocorrelation transform, Fast Fourier Transform and the maximum entropy method (Jenkins and Watts, 1968). The autocorrelation method was adopted in this study.

The power spectrum was expressed as a fourier transform of the autocorrelation function. The theoretical power spectrum can be expressed as:

$$f(\lambda)=(1/2\pi)\sum_{k=-\infty}^{\infty} r(k)e^{-ik\lambda} \quad \ldots\ldots\ldots(20)$$

Where λ is the frequency in radians per unit time.

The shape of the spetra depicts the nature of the process. The cycles show up as peaks in a frequency 'band'. The regular cycles have more sharp peaks.

For discrete observations equation (20) may be expressed as:

$$f(\lambda)=(1/2\pi)\sum_{k=-(m-1)}^{m-1} r(k)e^{ik\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(21)$$

$$=(1/2\pi)\,[r(o)+2\sum_{k=1}^{m-1} r(k)\mathrm{Cos}\,\lambda K] \quad \ldots\ldots\ldots\ldots(22)$$

The spectral estimate $f_m(\lambda)$ is inconsistent and cannot converge to a true value $f(\lambda)$ irrespective of the number of observations made. This inconsistency is solved by introducing weights to modify the estimates, which take the form:

$$f_m(\lambda)=(1/2\pi)\{r(0)w(0)+2\sum_{k=1}^{m-1} r(k)w(k)\mathrm{Cos}\lambda k\} \quad \ldots\ldots\ldots(23)$$

where w(k) is the weight which is known as a 'lag window'.

Since an ideal situation is hard to be achieved in the selection of a window to be used, a compromise has to be made between various factors. The most significant of these are (a) the side lobes of the spectral window, and (b) Band width of the spectral window (Jenkins and Watts, 1968).

The window length L determines the degree of smoothing. A shorter L implies a stronger smoothing effect, but a larger L gives a better resolution in the computed spectrum (Ogallo, 1977).

A desirable spectral window is that which is concentrated in its main lobe and only small side lobes. Negative side lobes lead to spectral leakage thus they preferably need to be as small as possible. An ideal window therefore has to have a narrow central lobe and unsignificant side lobes so as to minimise the spectral distortion such that the spectrum does not exhibit wide fluctuations within the range of the frequency considered.

Various researchers have investigated the weighting systems and have come up with several windows which include Hamming, Bartlett Daniell, Turkey, Parzen and Blackmann-Turkey (Jenkins and Watts, 1968). The Parzen window which was used in the study is of the form

$$K(K/T) = 1-6(K/T)^2+6(K/T)^3 \qquad \left|\frac{K}{T}\right| \leq 0.5 \quad .....(24)$$

$$=2\{1-\frac{K}{T}\}^3 \qquad 0.5 < \left|\frac{K}{T}\right| \leq 1.0.....(25)$$

$$=0 \qquad 1.0 \leq \left|\frac{K}{T}\right| .....(26)$$

where T is the truncation point and $K(\frac{k}{T})$ is the lag window.

The spectral window w(k) is given by

$$W(K) = (1/2\pi)\sum_{|K|\leq L} \exp(-ik\lambda)K(K/T).....(27)$$

Since the spectral window is non-negative thus leading to non-negative window spectra, then the Kernel in this case is 'positive definite'. This is a major advantage over most other windows (Kendall , 1976). The statistical significance of the observed spectral peak is usually tested using a number of methods as highlighted below.

3.2.3.4.3 Significance of peaks

Both white noise and red-noise hypotheses have been used in testing the statistical significance of the spectral peaks. The white noise hypothesis assumes pure randomness while non-randomness is assumed for the red noise.

The first order autocorrelation function, r_1, can be used to detect the degree of the 'white noise' in a time series. It can be shown that for a random series, r_1, is approximately normally distributed with mean -1/(N-1) and variance N - $2/(N-2)^2$ (Kendall, 1976). The significance of r_1 is tested by comparing with the tested value (rl)t defined by

$$(r_1)_t = [-1 + t_s \ (N-2)^{1/2}/ \ (N-1) \quad \text{..... (28)}$$

where t_1 is the standard normal variate corresponding to the desired level of significance S.

For large N, the probability distribution of r_1, is normal with mean zero and variance l/N. r_1 is significantly difference from zero if it falls outside the confidence limits of the test value (r_1) (Ogallo, 1977).

A series is termed as free from persistence if r_1 does not significantly differ from zero. A 'null' hypothesis assumed in this case is that of the 'white noise'. If r_1 differs significantly from zero then r_1 is checked if it approximates to an exponentical relation, $r_k \simeq r_1^k$.

This kind of analysis indicates the nature of the persistence. The 'red noise' hypothesis is then used. For a Markov linear type persistence $r_k \geq r_1^k$ while for a non-linear persistence, $r_k < r_1^k$.

In the case of the 'white noise' hypothesis the null continuum is that of a straight line whose value is everywhere equal to the average value of all the 'raw' spectral estimates in the computed spectrum. In the case of

persistence the shape of the line depends on the lag one correlation for the population. Details of the computation of the 'white noise' and 'red noise' spectral values can be obtained from Jenkins and Watts (1968).

3.2.4 Correlation analysis

Correlation analysis determines whether two or more variables are related. One of the simplest measures of the degree of the association used simple correlation coefficient (r) which can be expressed as

$$r = \frac{\overline{X_1 X_2} - \bar{X}_1 \bar{X}_2}{\sqrt{[\overline{X_1^2} - (\bar{X}_1)^2]}\ \sqrt{[\overline{X_2^2} - (\bar{X}_2)^2]}} \qquad \ldots\ldots\ldots\ldots (29)$$

where the bar represents mean. X_1 and X_2 are the independent and dependent variables respectively.

r lies between -1 and 1. A value of r close to zero indicates no relationship between the variables. Positive/negative r values indicate positive/negative relationship respectively between the pair of variables.

Significance of the computed r values can be tested using F test. Details of this test can be obtained from Panofsky (1968).

In this study r values were used to determine whether there was any significant relationship between total column ozone and the weather elements which were discussed under section 3.1.

3.2.5 Cross-spectral analysis

Time lag/lead relationship between variables can never be detected using simple correlation and all other analysis which were discussed in the previous sections. The most common method of studying the time lager relationship is by the use of cross-spectral analysis (Jenkins and Watts, 1968; Harvey , 1975).

In general, the theory of spectral analysis can be extended to multivariate time series. Thus the autocorrelation function (r_x) which was used in the spectral density function in equation (23) is replaced here by the cross-correlation function (r_{xy}) in order to obtain the cross-spectral density function F_{xy} (λ).

For bivariate time series [x_t] and [y_t] the cross-spectral density function F_{xy} (λ) can be expressed as:

$$F_{xy}(\lambda)=2\sum_{K=-\infty}^{\infty} r_{xy}(K)e^{-2i\pi\lambda k} \qquad ,0<\lambda<0.5 \qquad \text{.....(30)}$$

where r_{xy} is the sample cross-correlation function between the two series [x_t] and [y_t] at lag K.

Equation (30) may be divided into real and imaginary components as shown below:

$$F_{xy}(\lambda)=P(\lambda)-iQ(\lambda) \qquad \text{.....(31)}$$

The real P(λ) and the imaginary part Q(λ) are termed as the cospectrum and quadrature spectrum respectively. The phase angle $\theta_{xy}(\lambda)$ which can be expressed as:

$$\theta_{xy}(\lambda) = \tan^{-1} \frac{Q(\lambda)}{P(\lambda)} \quad \text{.....(32)}$$

The coherence function (H( )) is given by

$$[H(\lambda)]^2 = \frac{P(\lambda)^2 + Q(\lambda)^2}{f_x(\lambda)\, f_y(\lambda)} \quad \text{.....(33)}$$

where $f_x(\lambda)$ and $f_y(\lambda)$ are the spectral estimates of x and y at frequency .

The co-spectrum determines the in-phase covariance and the quadrature spectrum represents the out-of-phase covariance between [x_t] and [y_t] at a given frequency. The phase function indicates the lag or lead relationship between the two series.

The degree of relationship, over a range of frequencies, between the two series is obtained by use of the coherence function (H(λ)). Like simple correlation, r, H(λ) ranges between -l and l.

All these functions were computed in the present study in order to determine any lead/lag relationships between the meteorological parameters and the total ozone amounts. Details of the results obtained with the various analyses are discussed in the next chapter.

CHAPTER FOUR

RESULTS AND DISCUSSION

In this chapter, the results obtained from the various analyses are discussed independently under separate sections. The analyses included homogeneity tests, trend, correlation, spectral and cross-spectral analyses.

4.1 RESULTS FROM HOMOGENEITY TEST

Figure (5) gives an example of the patterns of the observed residual mass curves. It can be observed from this figure that a linear regression line can be fitted to the cumulative residual curve. There are however significant deviations at some points. These could be associated with the estimated ozone values. An attempt was therefore made to break the curve into two linear functions (Sections AB and CD). The details of the two linear functions are shown in table (l). A statistical test was then performed to determine whether there was any statistical difference between the slopes and the intercepts of the two lines. The tests indicated that there was no statistical differences between intercepts and slopes of the two lines (table (l)). It was therefore concluded that a single regression (line AD) table (l) could adequately be used to describe the pattern of the cumulative residuals, indicating that the data were a sample from the same statistical distribution (homogeneous).

Fig.5 RESIDUAL MASS CURVE

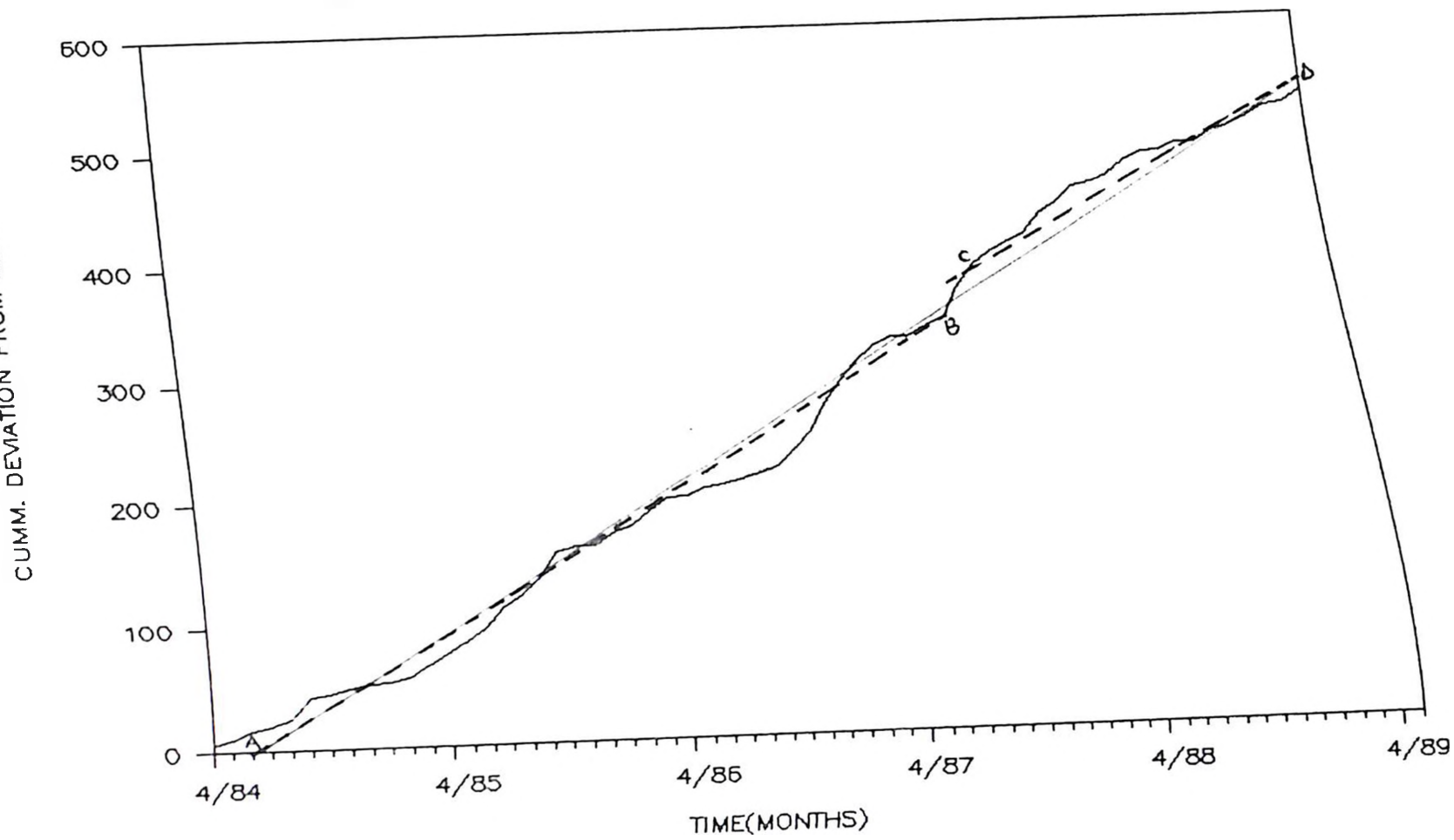


TABLE (1)

Observed values from homogeneity test of Residual mass curve.

	First sub-period (Line AB)	Second sub Period. (Line CD)	The whole Period. (Line AD)
Length of the period	April - 1984 to Aug. 1987	Sep. 1987 to May 1989	April 1984 to May 1989
Slope of regression line	8.35	8.76	8.54
Deviation from regression line	12.39	13.13	12.87

The results from the one sample run's test indicated that the value of Z (as given in equation (7)) was about 0.2. Thus the assumed hypothesis of 'no homogeneity' was rejected since the observed value of Z was less than 1.96. The one sample run's test therefore declared the ozone data samples, which included the estimated values, homogeneous.

It was therefore concluded from these tests that the estimated ozone records gave good estimates of the missing records. They were therefore included in the various analyses which are discussed in the following sections

4.2 RESULTS FROM TREND ANALYSIS

The smoothed and unsmoothed graphs of the ozone records during the period April 1984 to May 1989 are shown in figure (6). No clear trend is evident from the temporal patterns of ozone. Recurrences of large and low values are however evident.

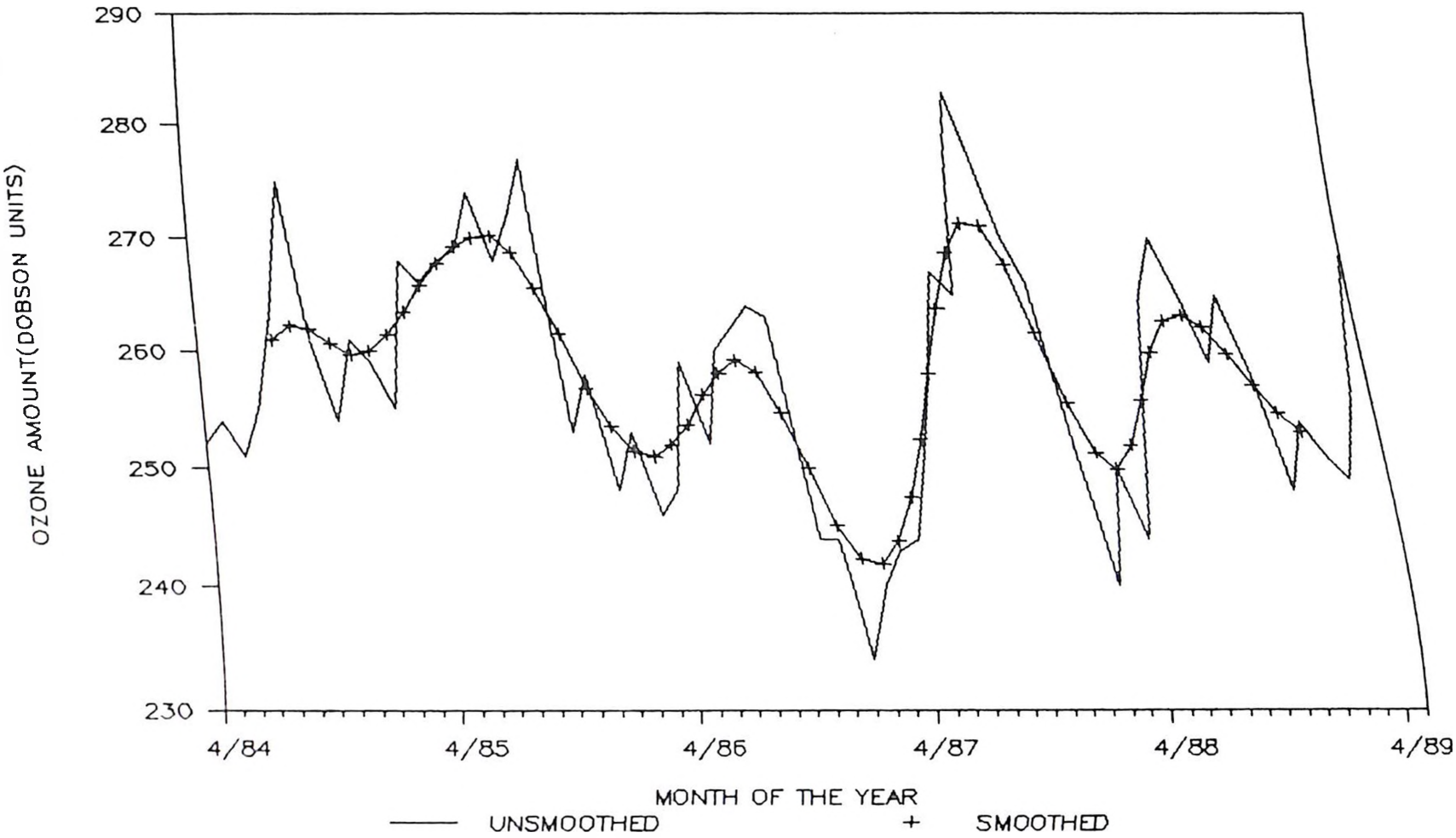
The values of the arithmetic averages for the various periods are given in table (2). Results from the test indicated no significant differences between the whole period and the sub-period averages. This significance further the non-existence of significant trend in the ozone records.

TABLE (2)

Arithmetic averages from arithmetic mean test.

Period	Mean Value Dobson Units
April 1984 - Oct 1986 (Sub-period 1)	260
Nov. 1986 to May 1989 (Sub-period 2)	256
April 1984 to May 1989 (whole period)	258

Fig.6 TREND OF TOTAL ATMOSPHERIC OZONE



Mann-Kendall rank statistic obtained with the ozone records was about 0.04. The value was not significant at 95% confidence level.

It was therefore concluded from the three methods that no significant changes in ozone trend has been recorded at the Nairobi observatory between April 1984 and May 1989.

Within latitudes 30 degrees North and 80 degrees North, Dobson spectrophotometer data have indicated a decrease in annual average of total atmospheric ozone between 1969 and 1986. The decrease ranges from 1.7 to 3.0%. (Farman et al., 1985; Renisel et al.,1981, Titus, 1986; WMO, 1988).

Other trend studies have used the solar and Backscattering ultra-violet spectrometer (SBUV) and Total ozone mapping system/ spectrometer (TOMS) satellite data. These were first normalised by comparison with nearly coincident ground based Dobson measurements in northern hemisphere. The resulting total ozone data, averaged between 53 degrees south and 53 degrees north indicated a decrease of about 2.5% from October 1978 to October 1985 (Bhartia et al, 1985; WMO, 1988).

Dobson spetrophotometer data are however not sufficient to determine total column ozone trends in the tropics, subtropics or southern hemisphere outside antarctica (WMO, 1988).

It may therefore not be possible to give a definite future trend of ozone over Nairobi from the five years of records used here. Details of the observed seasonal characteristics and quasi-periodic nature of ozone records

are the subjects of the next discussion.

4.3 SEASONAL VARIATIONS

The mean seasonal characteristics of ozone amounts over Nairobi is shown in figure (7). Maximum and minimum values are obtained during the months of September to October and January to February respectively. Similar characteristics are evident from the patterns of the seasonal index given in figure (8).

Similar studies outside the tropics have indicated the existence of maximum total ozone amount in spring and minimum in autumn. (Kulkurani, et al., 1959 ; and Godson, 1960, etc). Over the tropics, studies have indicated the same months of maximum and minimum ozone amounts as the ones observed in the present study (Ghazi and Barnett, 1980., Newell and Gould-Stewart, 1980).

The seasonal ozone characteristics have been explained by many authors in terms of the seasonal characteristics of the general circulation parameters (Kulkurani, 1962; Biswas, 1979; Newell and Gould-Stewart, 1981, Ghazi and Barnett, 1980; WMO, 1986).

The seasonal patterns of the tropopause height over Nairobi together with seasonal ozone fluctuations are given in figure (9). Close negative relationship between the tropopause height and ozone amounts are quite evident.

The seasonal patterns of total ozone and tropopause height can be explained by the following consideration. The lower stratosphere, termed as the reservoir of ozone, is a column which effectively shields ozone present there from photochemical destruction (WMO, 1986). The tropopause is termed as the boundary between the stratosphere and troposphere. Therefore the lowering of the tropopause height during the cold seasons together with the fact that ultra-violet radiation is low during these periods, implying less photodissociation of ozone, increases the ozone in the lower stratosphere. This could be associated with increased ozone values during August to October. The converse is also true during the hot seasons.

4.4 CYCLICAL VARIATIONS

4.4.1 Results from correlogram analysis

The patterns of the correlogram which was obtained using the ozone records is shown in figure (10). No purely periodic patterns can be observed from the correlogram since the fluctuations are not purely sinusoidal. This is indicative of the non-existence of purely periodic fluctuation in temporal ozone characteristics. The quasi-periodic fluctuations so observed were examined using spectral analysis.

Fig.7 SEASONAL VARIATION OF OZONE

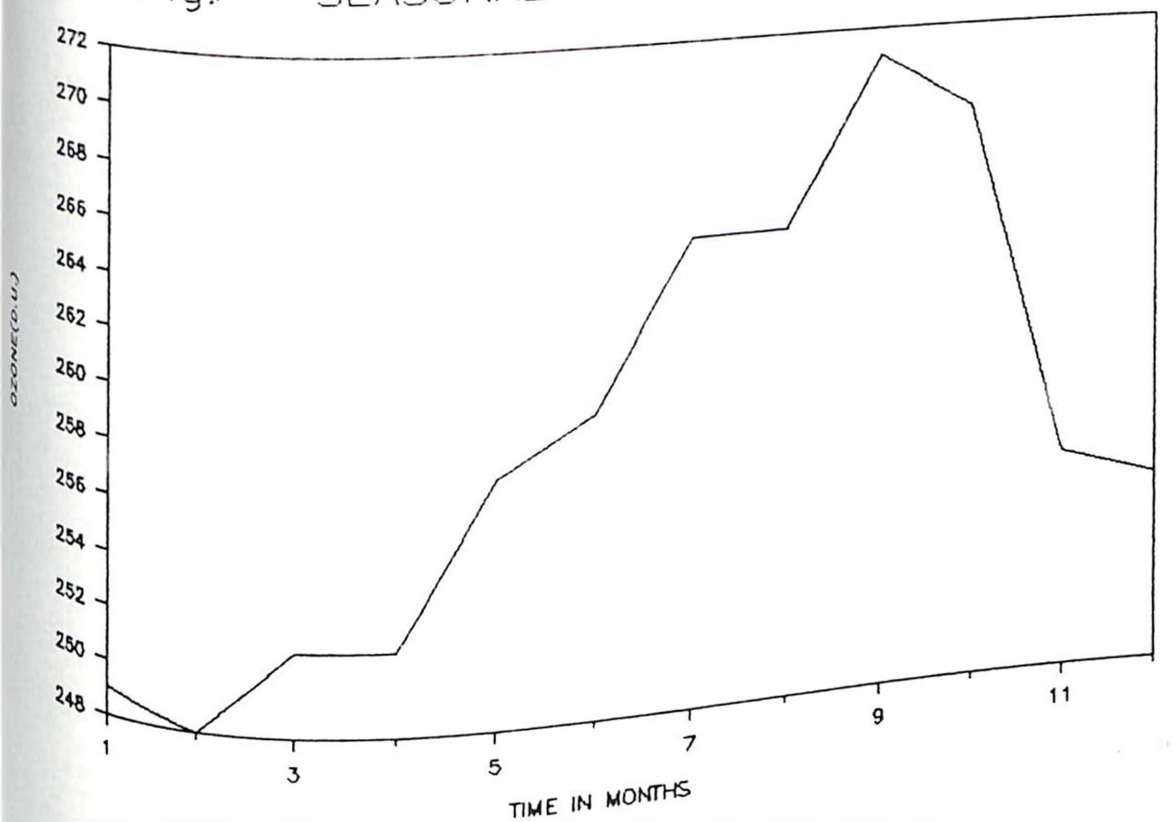


Fig.8 SEASONAL INDEX VERSUS TIME IN MONTHS

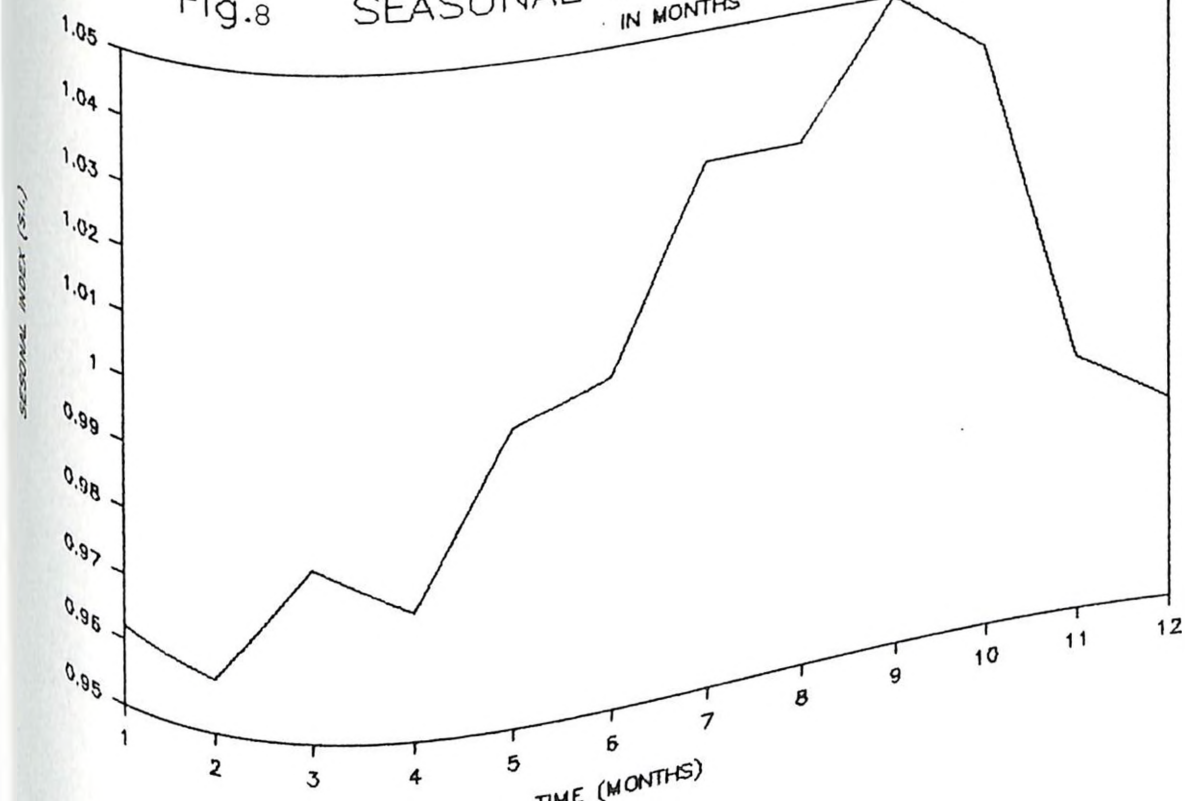


Fig. SEASONAL VARIATION OF OZONE AND TROPOPAUSE HEIGHT

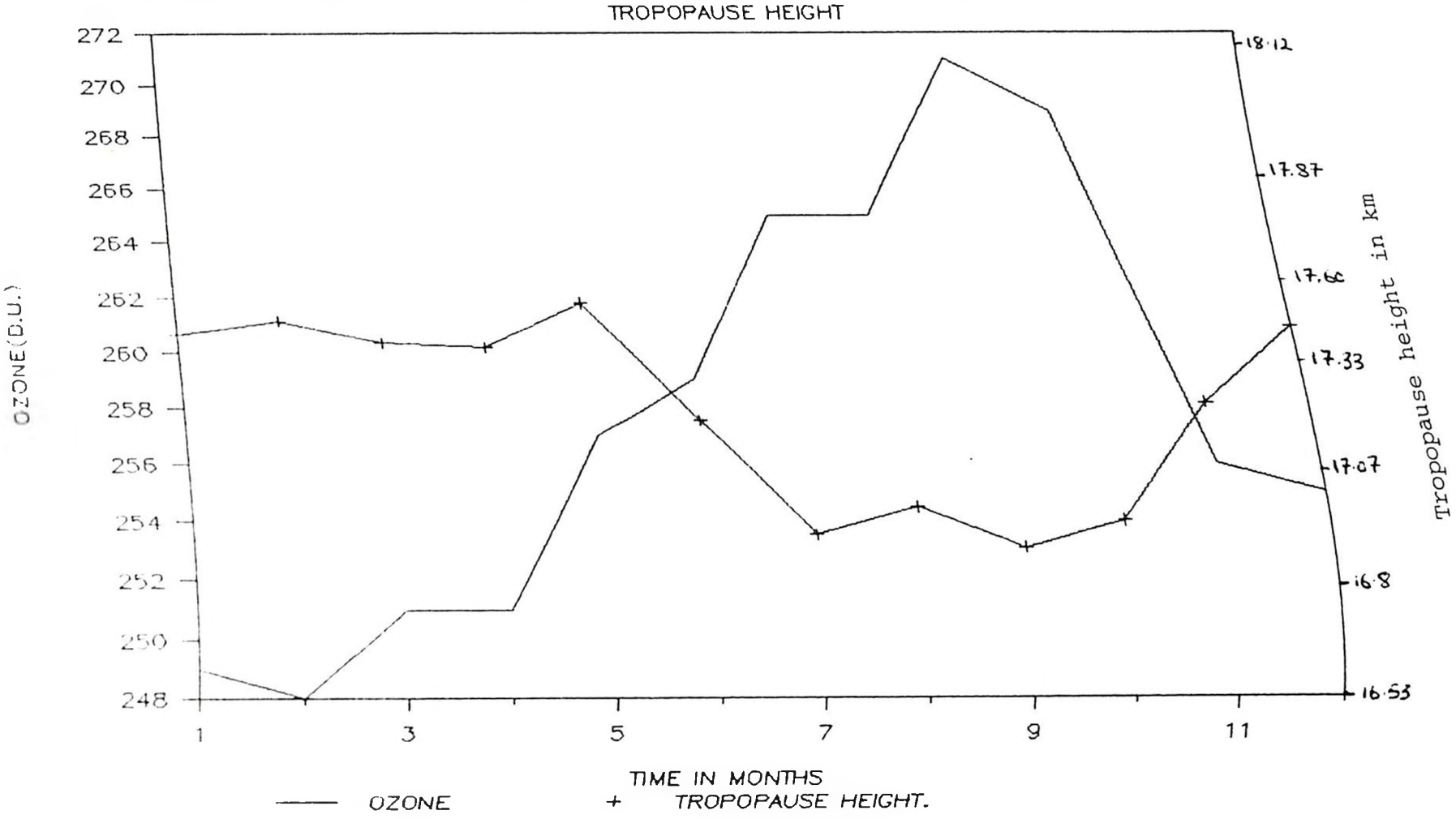
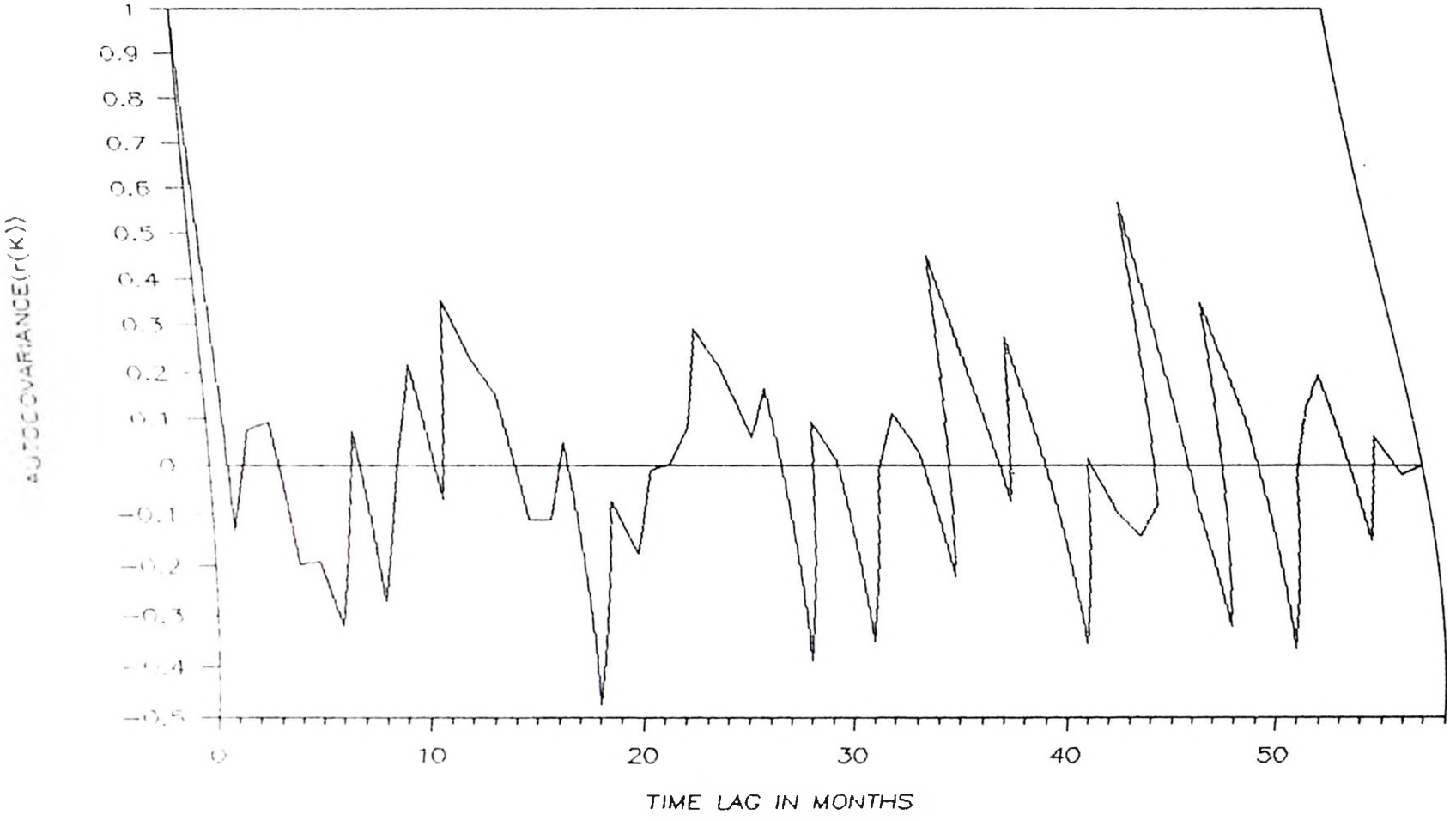


Fig.10 CORRELOGRAM



4.4.2 Results from spectral analysis

Examples of the spectral estimates which were obtained when the ozone records were subjected to spectral analysis is shown in figure (11). The 95% white noise spectrum is also indicated in the figure.

It is evident from the figure that six quasi-periods were present in the temporal ozone fluctuations. These fluctuations were centred around 21 to 25 months, 45 months, 6 months, 16 months and 40 months.

The 95% white noise spectrum indicates that the most dominant peak was the one centred around 21 - 25 months. The 45 months peak was also statistically significant.

Of necessity, the physical reality of the observed cycles require an examination. This has been done here by relating the observed fluctuations in ozone amounts to some physical processes in the atmosphere. The fluctuations of total ozone in a way is a general expression of certain characteristics in the general circulation of the atmosphere since ozone can be considered as a tracer of the atmospheric motions (Reiter, 1978). Thus variations in the total ozone at any location is largely depended on the structure of the large scale atmospheric circulation systems.

Several authors have investigated the physical reality of the cycles observed from ozone records, in view of the fact that ozone cycles may be statistically significant but have no physical reality. The processes which have been used to explain the ozone fluctuations include the general

circulation systems and man-induced activities (Ramanathan, 1963, Wilcox et al.,1977; Hansebe, 1980). The most dominant fluctuations patterns has been centred within the Quasi-Biennial Oscillation (QBO) range.

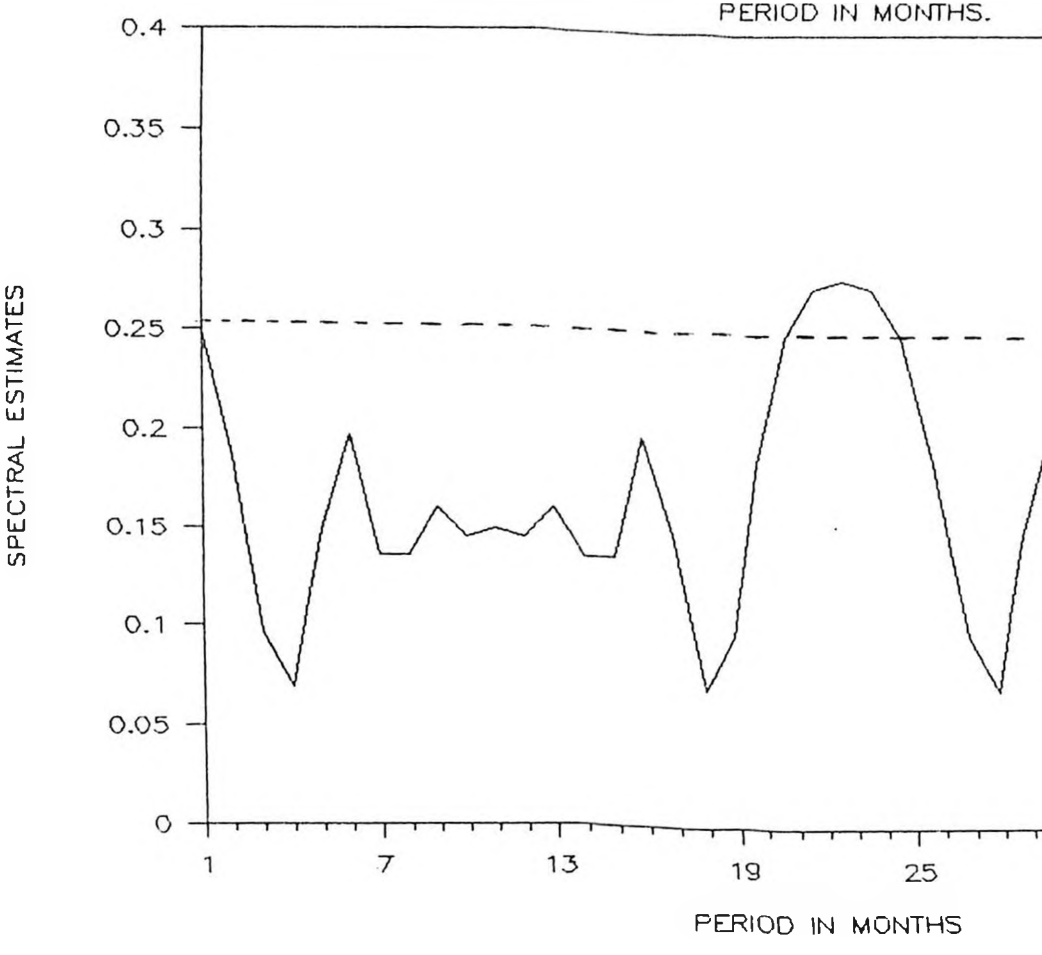
The QBO is a phenomenon where stratospheric winds change from easterlies to westerlies with a period of 24 - 26 months. It is concentrated within altitudes 20 to 35Km in the tropics. The system descends slowly, the wind direction successively being replaced from above by the opposite sign. This would significantly affect the patterns of the stratospheric advection (Angell and, Korshover, 1973; Wilcox et al.,1977; Oltmans and London, 1982).

The dominant 21 to 25 months period which was observed in this study (figure (11) may be associated with QBO effects. Results from the correlations with the stratospheric winds showed a close positive relationship between ozone and upper level zonal winds (table (4)). This implies that the easterly phase of the winds coincides with high ozone amounts, and the converse is true. This agrees well with other studies elsewhere over the tropics (Hasebe, 1980; WMO, 1986),.

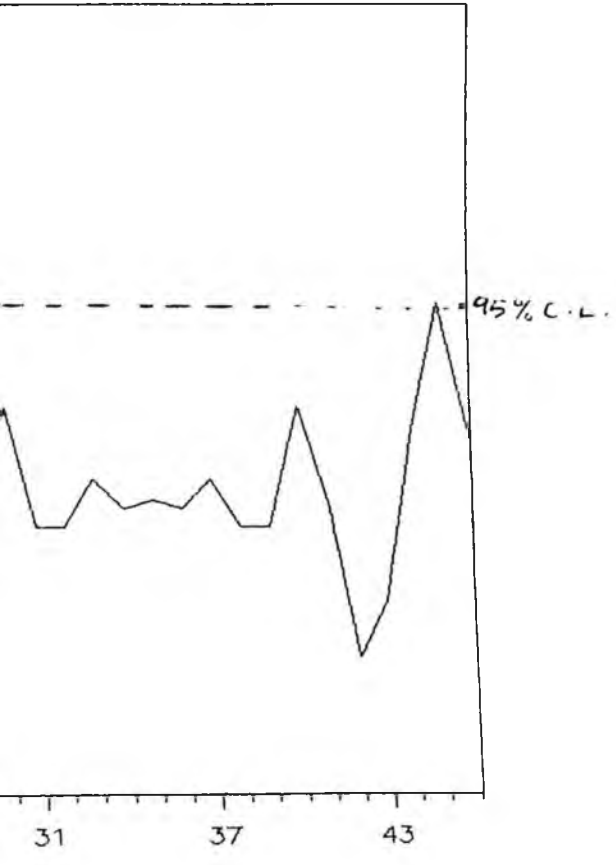
The physical reality of the 45 months cylcle may not be conclusively documented from the 62 months of ozone records used here. However, a four year oscillation of total ozone has been recorded over the high latitudes (Hasebe, 1980).

The physical reality of the 6 months oscillation may be connected with six months oscillations which have been observed in the stratospheric

Fig 11 SPECTRAL ESTIMATES



AGAINST



winds of the tropics (Craig, 1965; Wilcox, et al., 1977).

The 16 and 40 months oscillations are however not common in the tropical weather systems. Their physical reality may be difficult to be determined from this study.

4.5 LINEAR CORRELATION

The correlation coefficients between ozone amounts and total solar radiation, rainfall, Tropopause height and cloud amounts over Nairobi are given in table (3). The vertical profiles of the correlation values are however given in table (4) and figures (12) and (13).

TABLE 3

Correlation coefficients of Meteorological Parameters with total ozone

Parameter	Linear correlation coefficient (r)
Rainfall	-0.269
Cloudiness	-0.102
Total solar radiation	-0.125
Tropopause height	-0.782

Table (3) indicates that the only significant relationship was obtained with the tropopause height. The table indicates that the correlation between

ozone amounts and tropopause height was negative indicating increasing/decreasing ozone values with decreasing/increasing tropopause height. This was clearly evident from the seasonal graphs of the total ozone and tropopause height as shown in figure (9).

The negative correlation can be explained in terms of the general circulation processes as highlighted in the previous section. These processes include advective and convective activities together with the relative thickness of the troposphere over the tropics.

Table (4) indicates a significant correlation between ozone and temperature at low levels (surface and 700mb) and lower stratosphere (50mb).

At lower stratosphere, temperature plays a major role in ozone production by sustaining the photochemical dissociation of oxygen. Basically, the dependence of chemical reaction rates upon temperature is the primary cause of the ozone sensitivity to temperature, and hence the observed positive correlation coefficient.

The temperature at low levels is negatively correlated with above. This may be explained by the fact that high low level temperatures, which generally prevail during hot seasons, coincide with low total ozone amounts as explained in section (4.3) above. the concerse is also true.

A negative correlation between relative humidity of low levels and ozone is evident from table (4). No clear physical significance of the

correlation may be obtained from the present study due to the following consideration. High relative humidity generally coincides with cold seasons. The cold seasons have however been shown to coincide with high ozone amounts (section 4.3 above). From this argument therefore, a positive correlation between ozone and low level relative humidity may be expected.

Table (4) indicates that total ozone was positively/negatively correlated with the zonal winds at the upper/lower levels respectively. The magnitudes of the correlations were noted to be generally small. Table (4) however indicates that the values at 70mb, 200mb, 300mb, and 700mb levels were statistically significant. The positive significant correlation values may be connected to the quasi-biennial oscillation.

TABLE 4

Vertical profile of correlation coefficients of ozone with some meteorological elements.

Pressure Level in mb	Temperature r	Zonal Wind r	Relative Humidity r
Surface	-0.517	+0.127	-0.408*
700	-0.43*	-0.32*	-0.013
500	-0.288	-0.230	-0.323*
300	-0.119	-0.40*	-0.292
200	+0.017	-0.299	
150	-0.178	-0.107	
100	+0.048	+0.163	
70	+0.194	+0.38*	
50	+0.60*	+0.034	
30	+0.24		

*Correlation coefficients which are significant at 95% confidence level.

and other atmospheric mixing processes which were discussed in section (4.4).

The negative correlation between ozone and lower level zonal wind may signify the effects of advection. Stronger zonal winds would increase the advective terms which may in turn lower the degree of the vertical mixing processes.

4.6 CROSS-SPECTRAL ANALYSIS

Results from cross-spectral analysis are summarised in tables (5), (6), (7) and (8). It can be observed from these tables that the values of the coherence were not significant at many levels, signifying low phase relationship between the ozone amounts and the meteorological parameters at various levels. The observed significant coherence were randomly distributed to give any conclusive results.

Significant phase relationships have however been observed by many authors using daily records (Barnett et al., 1975 , Barth et al., 1983., WMO, 1986. The low phase relationship values which were observed here could therefore be attributed to the fact that only monthly ozone records were used in this study.

Fig. 12 TEMPERATURE CORRELATIONS WITH

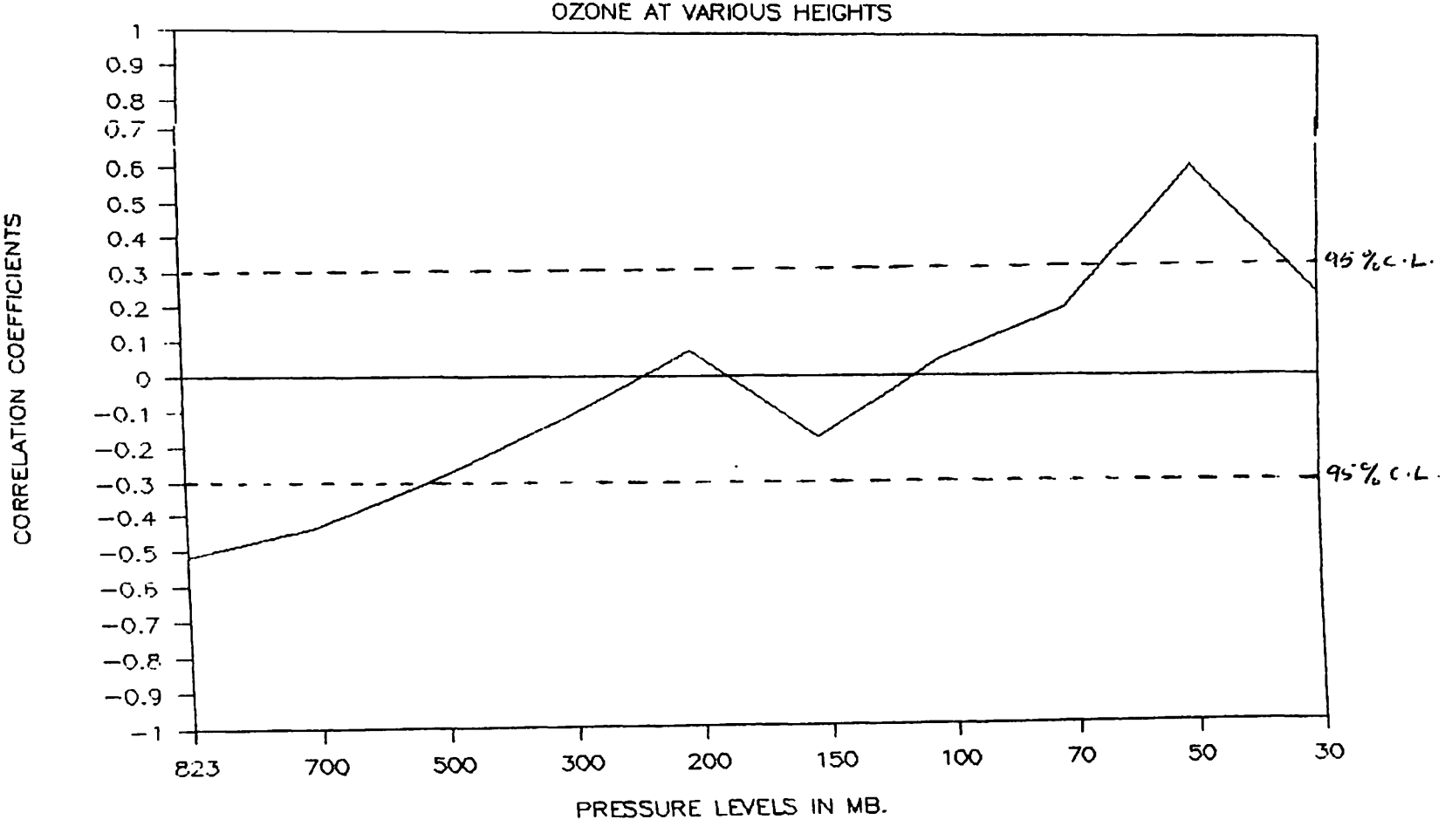
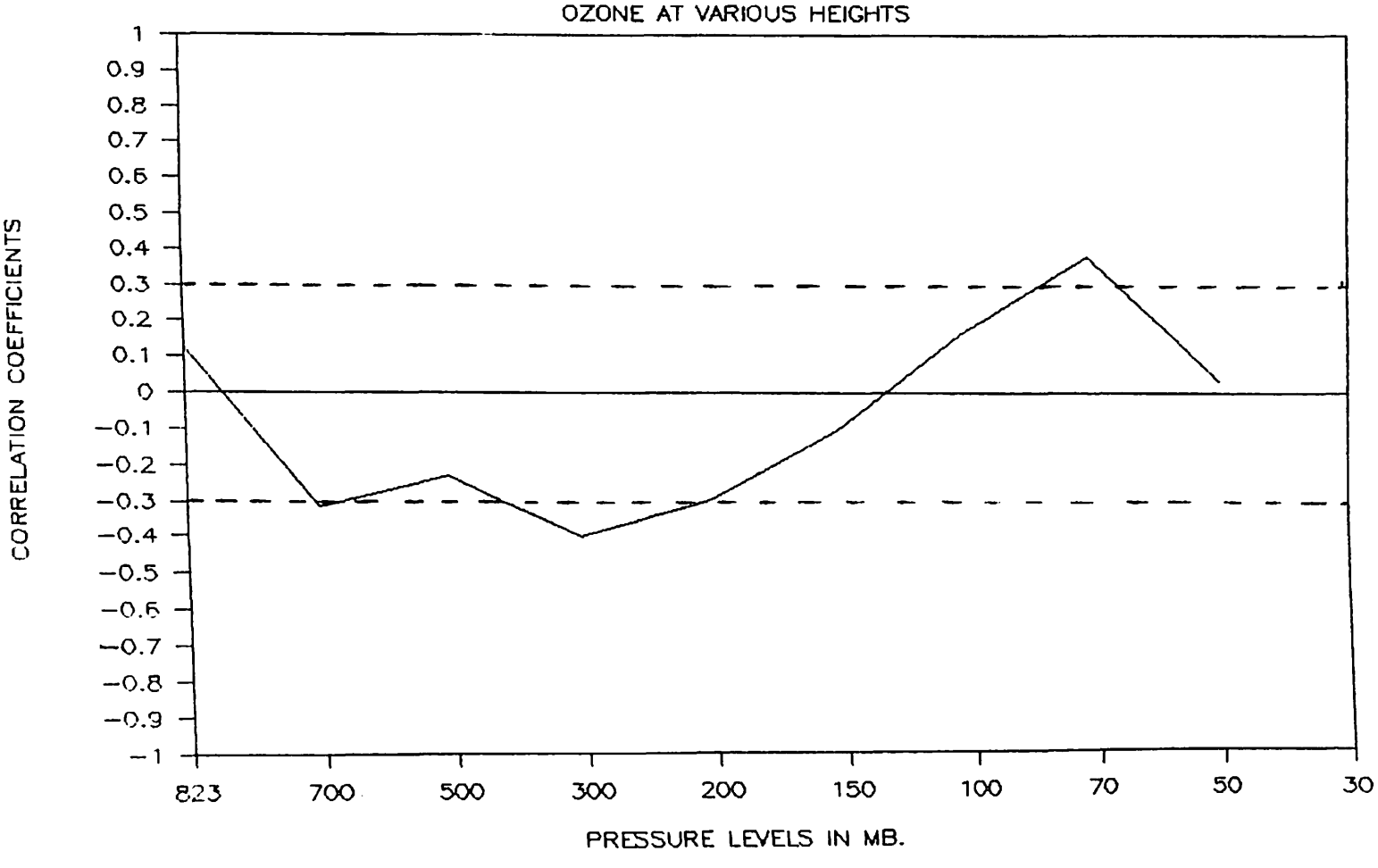


Fig. 13 ZONAL WIND CORRELATIONS WITH



Atmospheric Level (mb)		Period (months) 12	6	3	2	1
Surface	H	-0.136	-0.003	-0.053	0.039	-0.007
	θ	-0.173	+0.607	-1.512	1.268	1.078
700	H	-0.253	0.005	0.014	-0.042	0.004
	θ	-0.366	0.574	-1.480	1.348	1.117
500	H	0.012	0.073	0.264	-0.807	0.456
	θ	-0.139	0.586	1.040	1.250	1.388
300	H	0.073	0.023	0.109	-0.328	0.329
	θ	-0.214	0.629	1.066	1.275	1.386
200	H	-0.000	0.000	-0.000	-0.000	-0.000
	θ	0.861	0.217	-0.511	1.212	0.247
150	H	-0.239	0.017	0.113	0.144	0.169
	θ	-0.076	0.653	0.997	1.298	1.437
100	H	0.002	0.001	0.000	0.064	0.014
	θ	-1.503	0.637	-0.001	-0.956	-0.053
70	H	0.084	0.002	0.004	-0.004	0.012
	θ	-0.305	-0.025	-0.631	+0.437	-0.026
50	H	-0.282	0.001	-0.009	0.041	-0.133
	θ	-0.053	-1.503	0.637	-0.001	1.571
30	H	0.439	0.002	0.018	-0.070	0.177
	θ	-0.095	0.728	0.994	1.286	1.483

Table 5;
Coherence (H) and phase (θ) functions of total ozone with respect to temperature at) various levels.

Atmospheric Level (mb)		Period (months) 12	6	3	2	1
Surface	H	0.309	0.003	0.037	-0.087	0.121
	θ	-0.257	1.199	1.302	0.126	-0.153
700	H	0.193	0.002	0.012	-0.040	0.029
	θ	-0.189	0.636	1.099	1.267	1.398
500	H	0.224	0.002	0.014	-0.046	0.034
	θ	-0.019	0.627	1.095	1.268	1.395
300	H	+0.002	0.000	-0.000	-0.001	0.001
	θ	-0.220	0.420	0.751	1.209	+1.131
200	H	-0.014	0.000	-0.000	0.000	-0.000
	θ	-0.574	0.791	1.237	1.328	-1.370
150	H	-0.004	-0.000	-0.000	0.001	-0.000
	θ	-0.251	0.621	1.144	1.262	1.471
100	H	-0.000	0.000	-0.000	0.000	+0.000
	θ	-1.441	-1.513	0.599	1.266	-1.222
70	H	-0.007	-0.000	-0.001	0.001	0.000
	θ	-0.159	0.642	1.093	1.422	1.432
50	H	0.001	-0.000	0.002	-0.000	-0.000
	θ	-1.222	-1.095	-1.059	0.693	0.746

Table 6;
Coherence (H) and phase (θ) functions of total ozone versus zonal wind at various atmospheric heights.

Atmospheric Level (mb)		Period (months) 12	6	3	2	1
Surface	H	-0.035	-0.009	-0.001	0.002	-0.002
	θ	-0.081	0.603	1.187	1.244	1.343
700	H	-0.003	0.000	-0.000	0.000	-0.001
	θ	-0.088	0.893	1.054	1.240	1.370
500	H	0.013	0.000	0.006	-0.001	0.005
	θ	-0.052	0.674	1.021	1.310	-0.509
300	H	0.004	0.000	0.000	-0.000	0.003
	θ	-0.011	0.514	0.876	1.271	-1.502

Table 7:
Coherence (H) and phase (0) functions of total ozone, versus relative humidity at various atmospheric levels.

Weather Parameter		Period (months) 12	6	3	2	1
Rainfall	H	-0.008	-0.001	-0.000	-0.000	0.021
	Θ	-0.088	0.052	-0.006	0.123	-0.385
Cloudiness	H	0.006	-0.007	0.005	-0.013	0.003
	Θ	-0.001	0.622	0.574	-1.235	1.244
Total solar radiation	H	-0.007	0.001	0.000	+0.003	0.122
	Θ	-0.236	0.025	0.436	-1.230	1.233
Tropopause height	H	-0.024	0.037	-0.121	0.000	0.024
	Θ	-0.134	0.013	0.348	1.469	+0.456

Table 8:
Coherence (H) and phase (θ) functions of ozone versus various meteorological elements.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This chapter highlights some of the conclusions which may be derived from the study. Future methods which may be used to improve the work are also suggested.

5.1 CONCLUSION

It was evident from the study that the method which is used to estimate the few missing ozone records was quite appropriate since all the data were declared homogeneous.

Graphical methods of trend analysis showed a generally oscillatory characteristic of the ozone time series without significant trend. Same results were evident from parametric and non-parametric statistical tests.

Investigations of characteristics of ozone data indicated minimum values around January and February with the corresponding maxima during September and October.

The patterns of the computed correlations between ozone and the weather parameters indicated

i) significant negative correlation with Tropopause height.

ii) positive/negative correlations with the upper/lower level zonal winds and temperature.

iii) negative correlation with atmospheric humidity

iv) Low phase relationships between total ozone and the meteorological parameters.

Although the observed correlations could be explained in terms of the atmospheric motions, some of the observed correlation values were too low.

Results from spectral analysis identified quasi-periodic fluctuations from the temporal fluctuations of ozone over Nairobi. These fluctuations were centred around 6, 16, 21 - 25, 40, and 45 months. The 6 and 21 - 25 months cycles could be explained in terms of the QBO and other general circulation systems which include the atmospheric mixing processes. The physical reality of the fluctuations which are centred around 16, 40 and 45 months could however not be identified from the study.

5.2 RECOMMENDATIONS

There were various shortcomings experienced in the study. The major ones include:

i) short period of ozone data records, i.e five years of data;

ii) only monthly ozone data was available for four out of five years of records. One year had hourly ozone records;

iii) lack of vertical ozone profile data, and

iv) only one ozone observatory was available for the entire East African region.

To overcome these shortcomings and thus improve this work, the following suggestions may be advanced.

i) There is need of obtaining ozone's vertical distribution over Chiromo station. With the help of such data inter-diurnal, seasonal, cyclical, random and trend components together with mixing processes of the ozone can be understood more deeply.

ii) No realistic phase relationships were obtained from the study although many others have obtained significant values with daily records. Future examination of phase relationship should therefore use hourly or daily records.

iii) Examination of the physical reality of the observed quasi-periodic fluctuations need further investigation. This would require monitoring of the QBO phases and other general circulation processes which may affect ozone concentrations.

iv) Ozone precursors (such as No_x, S_2O and Hydrocabons) over Nairobi need to be investigated in order to obtain a correlation factor for the total zone amount

v) Surface ozone distribution studies over East Africa need to be studied so as to help in knowing the surface ozone's characteristics especially those which may be anthropogenic.

vi) Setting up of other total ozone observatories is a necessity in the East African region so that the spatial distribution of the gas over the region can be documented.

vii) Modelling of the ozone time series using estimated components can assist in:

a) describing the behaviour of the observed time series,

b) attempting to predict the future of the time series, putting into consideration the increasing trend of ozone depleting chemicals, and

c) determining the impacts of ozone on climate, flora and fauna.

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