# SPATIAL AND TEMPORAL DISTRIBUTION OF TROPOSPHERIC OZONE OVER SOUTHERN AFRICA

**Peter Miriti Bundi**

# ABSTRACT

Tropospheric ozone over southern Africa is characterised using the Southern Africa Regional Science Initiative (SAFARI) 2000 aircraft datasets collected from surface to just above the boundary layer, and satellite remotely sensed ozone column depth. Ozonesonde datasets for Irene, South Africa; Lusaka, Zambia; Nairobi and Malindi, both Kenyan stations were, used to supplement the aircraft and satellite data. The period studied is the dry biomass burning season between August and September, 2000

Source areas of ozone precursors have been identified by trajectory analysis. Five-point, back trajectory clusters in the region reveal well-defined air mass transport corridors. Enhanced ozone concentrations, above 70 ppb, were regularly encountered in the lower troposphere (3.5 km above ground level) in air masses distributed over the sub-region by distinct re-circulation pathways, which prevailed during the study period. Occasional, episodes of significant higher ozone pollution, above 100 ppbv are identified.

Savannah fire products transported from seasonal biomass burning regions of western Zambia, northern Zimbabwe and Mozambique have been found to be the major sources of ozone pollution over the sub-region. Another source, though on a lesser scale, is the Highveld industrial region of South Africa.

*In situ* air observations established that the western and eastern sectors of the southern Africa, north of 23°S latitude, were the major sources of regional ozone precursor gases. The regions southwards of 23°S were observed to have lower ozone pollution.

**DECLARATION**

I declare that this research report is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Peter Miriti Bundi                                    Date

## DEDICATION

To my dear wife

JANE KINANU MIRITI

and our three children.


To my parents

Rev. and Mrs GEOFFREY K. BUNDI.



And he prayed for me:

**Let the knowledge you acquire shape you
to be more useful to the society.**

Prayer from my father, on the day of my departure for further studies.

# PREFACE

Ambient ozone ($O_3$) in urban and regional air pollution represents one of the most persistent environmental problems. Despite decades of costly efforts to bring this problem under control, ozone abatement progress is lacking in several regions of the world. Ozone remains the most prevalent photochemical oxidant and an important component of "smog". The most critical aspects of this problem are the formation of ozone in and downwind of large urban areas where under certain meteorological conditions, emissions of NO and volatile organic compounds can result in ambient ozone concentrations higher than levels considered protective of human public health and of the natural environment. During the past decade, an increase of approximately 10% (1% per year) in ozone throughout the height of the troposphere has been demonstrated. The build up in tropospheric ozone has broad implications for atmospheric chemistry. Ozone and associated atmospheric oxidants play a significant role in controlling the chemical lifetimes and reaction products of many atmospheric species and influence organic aerosol formation. Additionally, tropospheric ozone is a green house gas whose increase might contribute to a warming of the Earth's surface. The study of global tropospheric ozone and its associated precursor gases is therefore very important.

In Africa and particularly over southern Africa, tropospheric ozone studies have been carried out mostly through atmospheric campaign events. Strong ozone and biomass burning links have been established by airborne and ship-based measurements over southern Africa and the adjacent Atlantic Ocean. Other observations however have shown that large-scale dynamics and lightening are prominent factors in tropospheric ozone distributions. Over the equatorial and southern Africa ozonesonde observations have shown episodes of enhanced mid-tropospheric ozone, also at locations distant from potential precursor source regions.

To improve knowledge of tropospheric ozone at regional scale, including the causes and significance of the above-mentioned mid-tropospheric anomalies, further intensive studies need to be conducted to investigate the vertical and lateral distribution of ozone. Some ozonesonde studies have been undertaken previously at sites such as Irene and Lusaka, where routine upper-air sondes are conducted. These studies form a

good basis for starting similar work in less studied areas like the equatorial eastern Africa. However, additional measurements are needed between these widely separated points to understand the formation and dynamics of regional ozone chemistry.

The sub-equatorial and southern Africa regions experience intense seasonal biomass burning in Austral spring. Biomass burning emissions, coupled with industrial and biogenic emissions from the vast savannah, are major precursor influences on ozone concentrations. In contrast, Kenya is relatively free of biomass burning and industrial emissions. Comparison of measurements in these contrasting regimes could provide further insights on factors influencing regional ozone.

The aim of this study is to contribute to understanding of factors affecting the precursors, formation and distribution of regional tropospheric ozone over southern and eastern Africa. The objectives of this study are thus to:

- identify sources of ozone precursors, specifically occurrence of seasonal biomass burning emissions
- characterise vertical and lateral spatial distributions of tropospheric ozone over the study region
- investigate seasonality of tropospheric ozone in the region
- explore relationships between synoptic meteorology and ozone levels
- determine prevailing air transport pathways in relation to ozone levels.

This research report is divided into five chapters. Chapter 1 provides a description of the study area and gives a background to the tropospheric studies globally and at regional levels. Chapter 2 contains a description of methods of measurement and the data sets used. In chapter 3 results of troposphere ozone distributions are presented. Chapter 4 gives detailed analysis of transport pathways and associated meteorology during Austral Spring of 2000. Chapter 5 is a summary of the findings and conclusions. Parts of this work have been presented at the Southern Africa Society for Atmospheric Sciences (SASAS) 26 to 28 August 2002, Pretoria, South Africa; SAFARI 2000 data Synthesis Workshop at the University of Virginia, Charlottesville, Virginia, 5 - 11 October 2002.

The SAFARI 2000 ozone aircraft data sets were availed by Dr. Stuart Piketh while the ozonesonde data was obtained from the SHADOZ website, courtesy of Dr. Anne Thompson, South African Weather Service and the Kenya Meteorological

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# ABBREVIATIONS

| | |
|---|---|
| ECC | Electrochemical cell |
| H | High-pressure cell |
| ITCZ | Inter Tropical Convergence Zone |
| L | Low-pressure cell |
| N – S | North –South Orientation |
| ppbv | Parts per billion by volume |
| SAFARI-92 | Southern African Fire - Atmosphere Research Initiative 1992 |
| SAFARI 2000 | The Southern African Regional Science Initiative 2000 |
| SAGE | Stratospheric Aerosol and Gas Experiment |
| SHADOZ | Southern Hemisphere Additional Ozonesondes |
| TOMS | Total Ozone Mapping Spectrometer |
| US | United States |
| VOC's | Volatile Organic Compounds |
| WMO | World Meteorological Organisation |
| ESO | El-Ninõ Southern Oscillation |
| DRC | Democratic Republic of Congo\ |
| QBO | Quasi Biannual Oscillation |
| NAPAP | National Acid Precipitation Assessment Program |
| SI | Smoke Index |
| EO | Enhanced Ozone |
| BB | Biomass burning |
| ECMWF | European Centre for Medium Weather Forecasts |
| NOAA | National Oceanic and Atmospheric Administration |
| CAB | Congo Air Boundary |

# CHAPTER ONE

# TROPOSPHERIC OZONE

## Introduction

Ozone is one of the most important chemical species involved in atmospheric chemistry, owing to its role in oxidising many atmospheric trace species and its potential impact on the environment (chemical oxidation capacity, health, greenhouse effect and vegetation). Great concern has always been attached to the elevated tropospheric ozone concentrations, particularly in densely populated urban and suburban areas. Photochemical ozone formation involving its chemical precursors and ozone transport from upwind air are the two major anthropogenic sources of ozone in rural and urban areas (Logan, 1989). Ozone in high concentration can impose direct adverse effects on human health and ecosystems (National Research Council, 1991). Unfortunately, ozone distributions within the troposphere are not sufficiently known and increasing trends in average tropospheric ozone concentrations remain a matter of discussion (Bojkov, 1988; Logan, 1994). The budget, and therefore the trend, of tropospheric ozone are highly dependent on precursor emissions into the atmosphere of carbonaceous and nitrogenous precursors (Crutzen, 1988) occurring mainly in the boundary layer. Human activities contribute significantly to increased levels of certain precursors in relation to natural sources.

Emission of precursors like carbon monoxide, methane and hydrocarbons during biomass burning activities contribute to the formation of ozone. Other biomass combustion by-products include primary and secondary aerosols that result in intense regional haze. Over the months July to October, biomass burning in Africa, believed to be largely human initiated, progresses southward from tropical West Africa toward Congo and Angola and ultimately south-westward across Zambia, Zimbabwe and Mozambique, to ~25°S (Cahoon *et al.*, 1992). Smoke and excess tropospheric ozone emitted by this biomass burning have been observed over large regions of the tropics with satellites (Fishman *et al.*, 1997; Ziemke *et al.,* 1998; Thompson *et al.*, 2001),

aircraft, balloons and ground-based instrumentation (Kirchhoff *et al.,* 1991; Taupin *et al.,* 1999; Thompson *et al.*, 1996b).

High smoke aerosol and enhanced tropospheric ozone concentrations have been observed over the adjacent Atlantic Ocean (Fishman *et al.,* 1997; Thompson *et al.*, 1996a; Thompson *et al.*, 1999), where strong ozone-biomass burning links have been confirmed by airborne and ship-based measurements (Andreae *et al.,* 1994; Jacob *et al.,* 1996; Weller *et al.,* 1996) (Figure 1.1). It is evident that the highest values of tropospheric ozone were over the Atlantic Ocean, adjacent to the heavy biomass burning areas of Africa and Brazil. Vertical ozone measurements during SAFARI-92/TRACE-A showed that this ozone enhancement over the mid-Atlantic occurred in an elevated mid-tropospheric layer, between 2 and 10 km altitude (Thomson *et al.*, 1996).
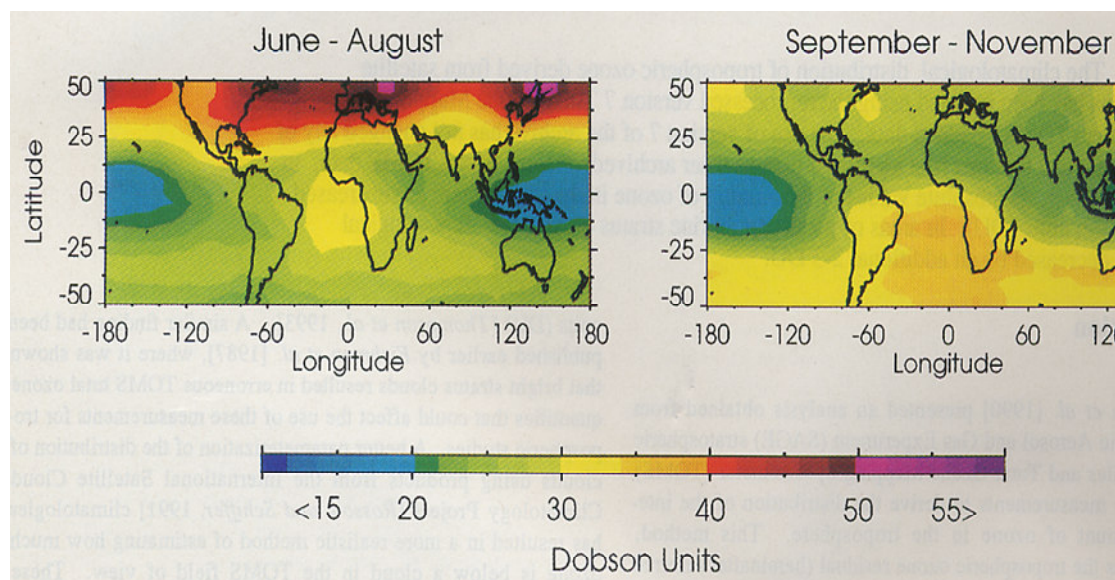


Figure 1.1    Depiction of the seasonal climatological distribution of the tropospheric ozone residual derived using the Total Ozone Mapping Spectrometer (TOMS) data archive and Stratospheric Aerosol and Gas Experiment (SAGE) measurements (after Fishman *et al.*, 1997).

Recent studies of vertical ozone profiles using ozonesonde measurements over Lusaka have shown elevated ozone in the boundary layer and mid-troposphere, thus providing an indication of enhanced ozone levels in the vicinity of biomass burning over the continent (Thomson *et al.,* 2002).

Photochemical modelling using observed ozone, nitrogen oxides, carbon monoxide and hydrocarbon concentrations throughout the troposphere show ozone formation rates and lifetimes consistent with observed ozone column depths (Jacob *et al*., 1996; Thompson *et al*., 1996b; Zenker *et al*., 1996) and confirm that biomass burning is a major contributor to seasonal ozone enhancement throughout southern Africa and the adjacent Atlantic.

These previous studies on ozone concentrations over the region gave an indication of the state of the atmosphere, using sparse data sets collected by few ozonesondes launched at widely separated sites. Satellite data from the TOMS provide only the vertical column measurements, with no capacity to reveal ozone levels within the lowest layers of the troposphere. Understanding of regional generation, transport and impacts of tropospheric ozone requires more detailed lateral and vertical measurements, with concurrent knowledge of fire source activity and meteorological transport fields. It is anticipated that aircraft ozone data collected during the SAFARI 2000 intensive field campaigns will fill these gaps and provide new knowledge on the concentrations of ozone and its precursor gases in the lower troposphere over southern and central Africa.

**Aims and objectives**

The aim of this study is to better understand the sources, transport and meteorological conditions leading to the observed spatial and temporal distribution of tropospheric ozone over southern Africa. The approach taken is the acquisition of new ozone measurements by a series of airborne measurements, involving vertical ascents and lateral traverses in the mid and lower troposphere. These experimental observations are interpreted in the context of synoptic meteorology, supported by Lagrangian trajectory analyses of air masses, to provide explanations for enhanced ozone episodes. The scope of the study covers selected flights from the SAFARI 2000 Regional Science Initiative campaign during the biomass-burning season August – September 2000.

The specific objectives of this study are:

- to measure and assess vertical and horizontal ozone distributions over southern Africa during the biomass-burning season.
- to generate and interpret air mass trajectories linking precursor source regions to receptor regions
- to interpret high ozone episodes in terms of associated synoptic patterns and trajectories.

**Hypotheses**

The hypotheses to be tested are that:

1. Enhanced high ozone levels over southern Africa are due to biomass burning

2. There exists a N - S ozone gradient during burning season over southern Africa

3. Particular synoptic conditions link the most intense biomass fire region, in the tropical belt (0º - 15º), leading to enhanced ozone concentrations to the sub-tropical belt (15º - 25º).

The scope of this research includes the whole of SAFARI 2000 dry season intensive field campaign period, from August 11 to September 27, 2000. The months of December to February, which is the wet season in Southern Africa, will be studied for comparison with the dry months in winter. The period, spanning the end of winter and start of spring, ahead of the summer rains, is the period of most intense regional biomass burning.

The study region lies between 4.5°N and 35°S and between longitudes 10°E and 42°E. The region is bounded to the east by the Indian Ocean, to the west by the Atlantic Ocean and the other neighbouring countries north of the equator (Figure 1.2). The study region covers the whole of southern Africa together with Kenya but excluding Democratic Republic of Congo (DRC), Angola and Tanzania due to lack of data in these countries.
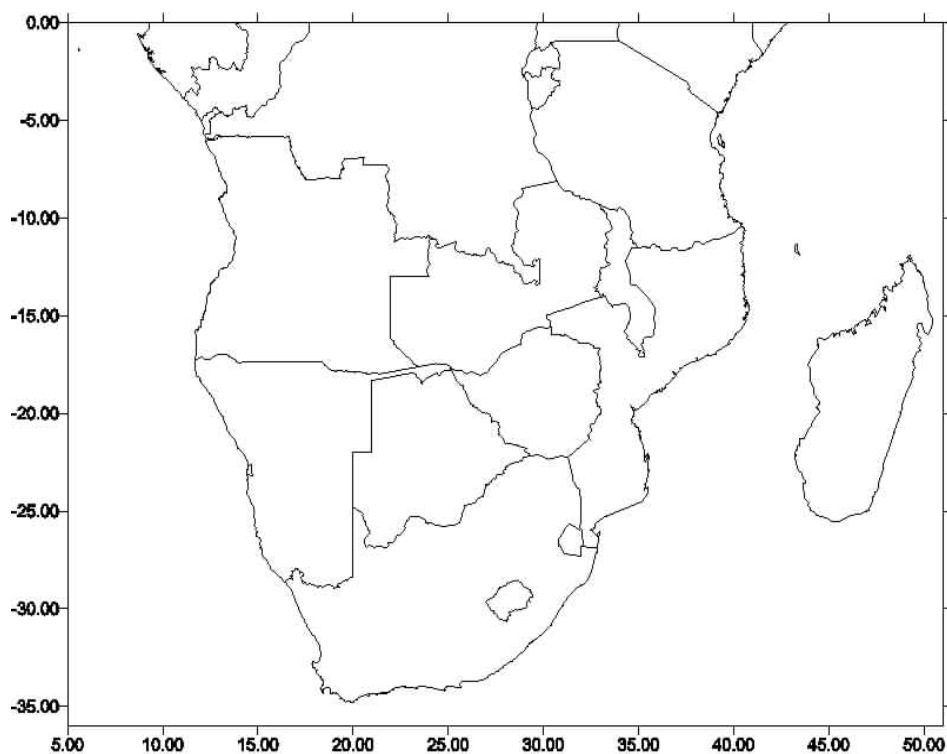
Figure 1.2    Map of study region.

The remainder of this chapter deals with an outline of applicable tropospheric ozone chemistry; atmospheric circulation patterns over central and southern Africa; and a review of recent literature on large-scale atmospheric field campaigns over southern Africa and adjacent oceans.

## Sources of ozone in the troposphere

On a global scale, biomass burning contributes ~9% of all tropospheric ozone. It is estimated that Africa contributes ~40% to the global biomass burning activity (Helas, 1995). The other important regions include Brazil, India and China with biomass burning related ozone contributions of ~17%, ~10% and ~7% respectively. Biomass burning in general contributes ~13% to tropospheric ozone over Africa (Marufu *et al.*, 2000). About 16% of the total tropospheric ozone over African continent is found in the boundary layer. In a case where only boundary layer is considered, the contribution of surface sources (biomass burning, soil and industry) to the ozone abundance is relatively high (Marufu *et al.*, 2000). Of this, pyrogenic emissions contribute 24%,

fossil fuel burning and industrial related activities contribute 28%, biogenic emissions 16%, lightning 19%, and stratospheric input contributes 13% (Marufu *et al*., 2000).

Massive burning activity in Africa and South America causes tropical ozone ˈsmogˈ formation in plumes that can extend over thousands of kilometres (Thompson *et al*., 1996). Biomass burning is a huge source of tropospheric ozone in southern Africa in particular (Tyson *et al*., 1988; Crutzen *et* al., 1990; Piketh *et al*., 1993; Helas and Pienaar, 1996). The biomass burning plumes are initially confined to the boundary layer below the 2 km altitude (Andreae *et al*., 1992) before transport, decoupling from the surface and subsequent dispersion. It is widely accepted that the ozone formation through industrial emissions contributes strongly to ozone concentrations in the lower atmosphere in the northern hemisphere. Despite the smaller role of industrial activities in the tropics and subtropics, particularly in the southern hemisphere, large-scale ozone perturbations in these regions have been detected from satellite observations (Marufu *et al*., 2001).

The presence of ozone in the troposphere is understood to arise from two basic processes: Tropospheric/stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere (Logan, 1985); and production of ozone from photochemical reactions occurring within the troposphere. Similarly, removal of tropospheric ozone is accomplished through two competing processes: transport and dispersion; and *in situ* photochemical destruction (Diab *et al*., 1996).

Worldwide expansions in agriculture, transportation and industry are increasing the burden of waste gases, particularly oxides of nitrogen (NO and $NO_2$, designated as NOx) and volatile organic compounds (VOCs), which enter the atmosphere and cause photochemical production of ozone (National Research Council, 1991).

Long-range horizontal advection influences ozone distributions by transport of both ozone and its precursors from source areas into other regions, including the marine environment. Over the tropical South Atlantic Ocean, high carbon monoxide and tropospheric ozone originate from adjacent continents, namely southern Africa and central South America (Watson *et al*., 1990; Fishman 1991; D'Abreton, 1996). This type of long-range transport has been shown to be an important factor in the generation of regional-scale episodes of elevated ozone (Logan, 1989; and Sillman, 1990).

Large quantities of ozone are generated over tropical Africa. This source is reported as being most prominent during the burning season which lasts from May to October, the dry winter season (Silva *et al*., 2003) Since industrial inputs to the atmosphere from this region are small, it is suggested that the ozone is formed by gaseous precursors derived from biomass burning (Otter *et al*., 2001).

Natural variations in ozone are induced by meteorological phenomena such as *El Ninõ* - Southern Oscillation (ENSO), and the Quasi-Biannual Oscillation (QBO) (Zerefos *et al*., 1992). Thus, the observed global ozone anomalies since 1991 can be attributed to prolonged ENSO event that lasted throughout 1992/1993. Other dynamical influences, which can strongly affect total tropospheric ozone on a regional basis, are persistent blocking anticyclones, which persist for a week or longer (Farman *et al*., 1994).

**Tropospheric ozone trends and impacts**

There is concern that the concentration of ozone in the troposphere may be increasing in recent times (Kley *et al.,* 1994). During the decade, an increase of approximately 10% (1% per year) in ozone throughout the height of the atmosphere has been demonstrated over Europe (WMO, 1986; 1990). Ozone measurements made in relatively remote European sites indicate 1 - 2% annual increase in average concentrations over the past 30 years (Janach, 1989). Equally significant are the reported trends (at the surface and from ozonesondes below 8 km altitude), which consistently show increases of about 1% per year over the past decade or two at northern mid-latitudes (Logan, 1985; Oltmans and Komhyr, 1986; Bojkov, 1988).

With the advent of industrialisation and increased use of coal and petroleum products, emissions of VOCs resulting from fossil fuel combustion has resulted in increased photochemical smog levels in most urban areas of the world. These events have produced a situation in which large numbers of people are exposed to high levels of ozone resulting to increased risk of both acute (short-term) and chronic (long-term) health effects (National Research Council, 1991).

As human exposure to ozone has increased, so has also been an increase in exposure and damage to agricultural crops, forests and ecosystems, as well as to materials such as rubber, paints and dyes. The USA's National Acid Precipitation Assessment Program (NAPAP) found that air pollutants could be ranked in the

following order of importance, in terms of their potential to negatively impact the growth, yield or quality of agricultural crops: ozone > $SO_2$ > acidic deposition > $NO_2$ (Shriner *et al*., 1990). More specifically ozone was found to be a significant stress factor in agricultural production.

The understanding of the ways in which ozone is formed, accumulates and moves through space and time is very important especially in the southern hemisphere, where relatively less research has been carried out due to scarcity of data (Kirkman *et al*., 2000). Ozone pollution may not entirely be confined to the anthropogenic source region but can spread to a large geographical extent due to different scales of transportation of pollution plumes from the source region. Its impact has previously been reported to reach a regional and continental scale in Asia, Europe and North America (Parrish *et al*., 1993). The most critical aspect of the tropospheric ozone problem is its formation downwind of large urban and sub-urban areas, where under certain meteorological conditions, emissions of $NO_x$ and VOCs can result in ozone concentrations greater than 100 ppbv.

**Ozone photochemistry**

Precursor gases (e.g. $NO_x$ and VOCs) are very important in ozone photochemistry. The sources of precursor gases include VOC emissions from vegetation, industrial and commercial facilities and motor vehicles and $NO_x$ emissions from motor vehicles, power plants, industrial facilities, and to a lesser degree, biomass burning, soil and lightning. The sinks include dry deposition of VOCs and $NO_y$ to vegetation, land and water surfaces. The resulting products can re-enter the gas phase as cloud droplets evaporate, or can be deposited to the ground as precipitation (National Research Council, 1991).

The reactions of precursor gases (for example $NO_x$ or VOCs) in the troposphere that leads to ozone formation are shown below:

$$NO_2 + hv \rightarrow NO + O \tag{1}$$

$$O + O_2 (+ M) \rightarrow O_3 \tag{2}$$
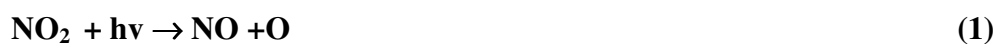
where *hv* is the electromagnetic energy from the sun and M is the catalyst.

The photolysis reactions in the troposphere add to the photochemical pollution, with the ozone concentrations being enhanced. European studies have shown that one

ozone molecule per carbon atom is formed from oxidation of hydrocarbons in the air masses (Flocke, 1992). Thus, increased burden of waste gases (precursor) in the atmosphere, exacerbate the photochemical production of ozone (National Research Council, 1991).

The production of ozone in the troposphere is accomplished through a complex series of reactions referred to as the "photochemical smog mechanism". This mechanism involves the photo-oxidation of volatile organic compounds (VOCs) and carbon monoxide (CO) in the presence of $NO_x$ (NO, $NO_2$). The ozone present in the troposphere is important in the atmospheric chemistry because the OH radical is generated from the photolysis of ozone at wavelengths <319 nm (Demore *et al.*, 1990). The formation of OH radicals leads to the cycles of reactions that result in the photochemical degradation of organic compounds of anthropogenic and biogenic origin, the enhanced formation of ozone, and the atmospheric formation of acidic compounds (WMO, 1986). Typical of these reactions are shown below:

$$RH + OH = R^{\cdot} + H_2O \qquad\qquad\qquad (R\text{ - }1)$$

$$R^{\cdot} + O_2 + M = RO^{\cdot}_2 + M \qquad\qquad\qquad (R\text{ - }2)$$

$$RO^{\cdot}_2 + NO = RO^{\cdot} + NO_2 \qquad\qquad\qquad (R\text{ - }3)$$

$$RO^{\cdot} + O_2 = HO_2 + R'CHO \qquad\qquad\qquad (R\text{ - }4)$$

$$HO_2 + NO = OH + NO_2 \qquad\qquad\qquad (R\text{ - }5)$$

$$NO_2 + h\nu = NO + O \qquad\qquad\qquad (R\text{ - }6)$$

$$O + O_2 + M = O_3 \qquad\qquad\qquad (R\text{ - }7)$$

$$\textbf{Net:} \qquad RH + 4O_2 + 2h\nu = R'CHO + H_2O + 2O_3$$

where an initial reaction between a hydrocarbon (RH) and a hydroxyl radical (OH) results in the production of two ozone molecules and an aldehyde R'CHO or a ketone. Additional ozone molecules can then be produced from the degradation of R'CHO. In addition to the oxidation of hydrocarbons, ozone can be generated from CO oxidation in reactions (R - 8) and (R - 9) followed by (R – 5), (R - 6) and (R - 7).

Thus,

$$CO + OH = CO_2 + H \qquad\qquad\qquad (R\text{ - }8)$$

$$H + O_2 + M = HO_2 + M \qquad\qquad\qquad (R\text{ - }9)$$

$$HO_2 + NO = NO_2 + OH$$

$$NO_2 + hv = NO + O$$

$$O + O_2 + M = O_3 + M$$

$$Net: \quad CO + 2O_2 = CO_2 + O_3$$
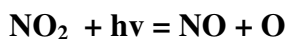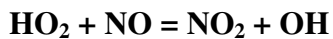
Hydrocarbons and carbon containing compounds provide the fuel for the production of tropospheric ozone and are consumed in the process. In remote areas of the troposphere, carbon and methane typically provide the fuel for ozone production (Seiler and Fishman, 1981). In urban locations, reactive hydrocarbons (often but not exclusively of anthropogenic origin) are usually the dominant fuel, while in rural areas reactive biogenic VOCs such as isoprene often dominate (Trainner *et al*., 1987; Chameiders *et al*., 1988).

**Atmospheric circulation patterns for southern Africa**

The air in the atmosphere over any region is always in motion and circulating on a variety of scales ranging form the local and meso-scale to the synoptic and larger. The constituents of air, including trace gases, particularly those near the surface will be transported in the same respective scales by the air in circulation.

The lifetime of ozone is an important factor when considering its transport. The abundance of water vapour and solar radiation in the tropical boundary layer shortens the lifetime of ozone to only 2 - 5 days (Fishman *et al.,* 1991b). Thus, ozone in the lowest levels will not survive long enough to be transported long distances (Krishnamurti *et al*., 1993). The lifetimes in the middle troposphere are much longer, approximately 90 days. This means that ozone can travel much farther if it rises out of the boundary layer to where its lifetime is longer and winds are stronger. Vertical motion on the convective scale is a mechanism by which burning by-products are lifted to higher levels where they may contribute significantly to enhanced ozone production in the upper troposphere (Chatfield and Delany, 1990; Pickering *et al*., 1992).

Due to the coincidence between high ozone during periods of biomass burning, research to track trace gases back to their source regions has been undertaken in the last decade. Piotrowicz *et al*. (1989) used trajectories to explore variations in shipboard ozone and carbon monoxide concentrations in the equatorial Atlantic Ocean. During periods of maximum gas concentrations, the air could be traced back to Africa where

significant biomass burning was occurring. Pickering *et al.* (1992) using isentropic trajectories indicated that a large fraction of air arriving at the ozone maximum off the west coast of Africa had passed over regions of intense burning within Africa.

Several studies of transport processes in the atmosphere, for example long-range transport coupled with horizontal and vertical mixing of aerosols and trace gases, have been undertaken (Crutzen and Andreae, 1990; Watson *et al.*, 1990; Fishman *et al.*, 1991). Most of these studies were done to understand the higher than anticipated concentrations of aerosols and trace gases in non-urban environments. Atmospheric transport studies over southern Africa and adjacent oceans have been undertaken extensively as part of the Southern African Fire Atmospheric Chemistry Research Initiative 1992/Transport and Atmospheric Chemistry near the Equator – Atlantic (SAFARI-92/ TRACE-A) in the austral spring of 1992 (Garstang *et al.*, 1996; Swap *et al.*, 1996; Tyson *et al.*, 1996a, 1996b).

Recently, the discovery of a tropospheric ozone maximum over the tropical Atlantic Ocean (Fishman *et al.,* 1990; Fishman *et al.*, 1991) has resulted in increased interest in trajectories to explain the ozone maximum and trace gas transport. Special attention has been focused on southern Africa as a possible source region for the trace gases, which are eventually transported westward over the tropical Atlantic Ocean (Krishnamurti *et al.*, 1993; Swap *et al.*, 1996; Garstang *et al.*, 1996; Thompson *et al.,* 1996b).

Typically superimposing many individual trajectories on a single diagram has implied transports. Although these diagrams provide a good impression of transport, the method does not lend itself to quantitative determination of transport. Garstang *et al.* (1996) have defined the dominant circulation types prevalent over southern Africa using a Tyson classification of 1988. Diab *et al.* (1996) have similarly used the classified synoptic types after Garstang *et al.* (1996) to determine the dominant features during high ozone episodes during the SAFARI-92 campaign. Mid tropospheric layers of suppressed ozone level were associated with marine air invasion from the encroaching anticyclone to the subcontinent during westerly wave patterns (Diab *et al.*, 1996).

The vertical transport is controlled by the stability structure of the atmosphere and horizontal transport by the local topographic winds near the surface or by large scale circulation in changing synoptic flow fields (Tyson *et al.*, 1988; Sillman *et al.*, 1990).

Tyson *et al*. (1988) produced air transport climatology for southern Africa in which various transport scenarios have been postulated for the five dominant circulation types that affect the subcontinent. The patterns are semi-permanent subtropical anticyclones, ridging anticyclones, westerly baroclinic disturbances and baroclinic quasi-stationary easterly waves and cut-off lows. The anticyclonic conditions prevailed over the region of interest on approximately 55% of all the days during SAFARI-92, August – September period (Lindesay *et al*., 1996). The major circulation types controlling transport of aerosols and trace gases over southern Africa are shown in (Figure 1.3).
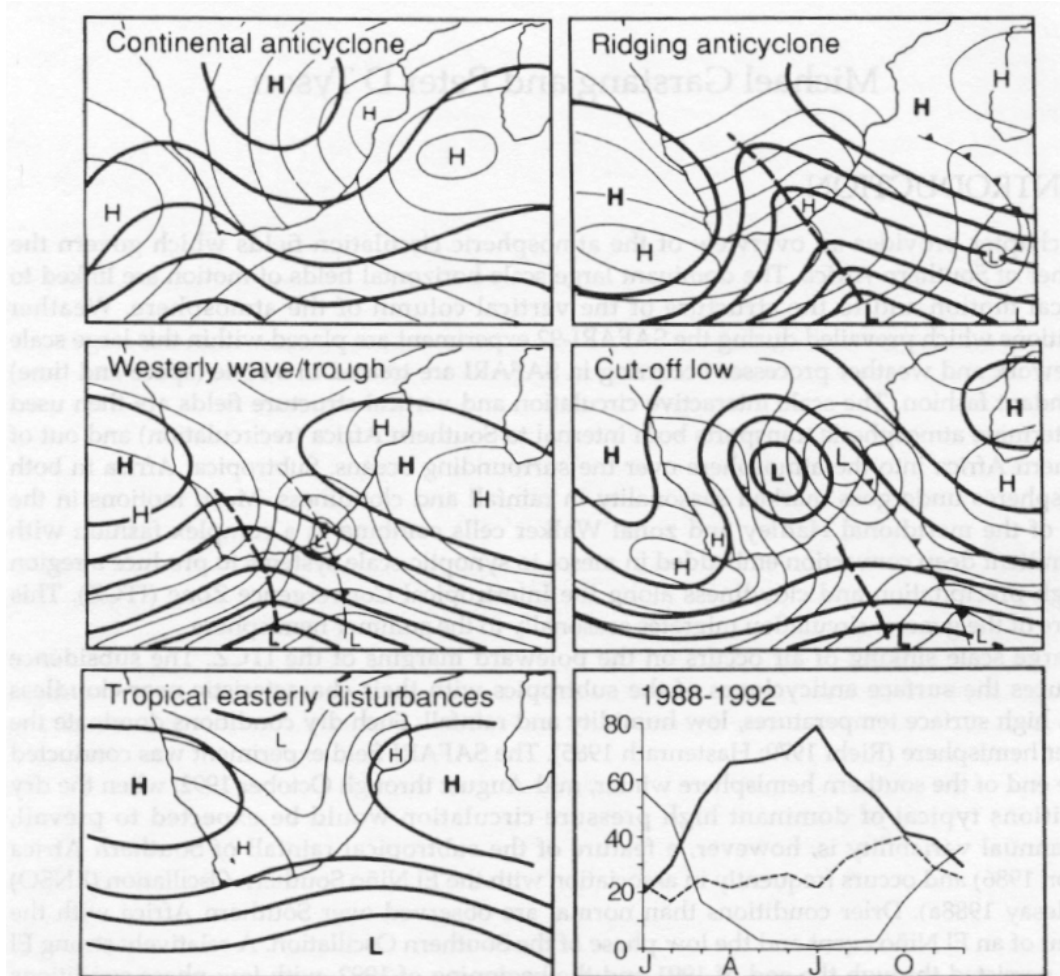


Figure 1.3    Major circulation types controlling the tropospheric transport of aerosols and traces within the atmosphere over southern Africa, together with frequency over the period 1988-1992 of, first, the combined continental and ridging anticyclonic classes (heavy solid line). Second, combined westerly waves and cut-off low (light solid line) and third, easterly wave disturbances (dashed line) (After Tyson, 1988).

The continental anticyclone is a feature that creates subsidence and stable conditions particularly when coupled with surface ridging divergence. This inhibits upward motion of the pollutants causing them to linger in the lower troposphere for long periods.

**Circulation climatology for southern Africa**

Three transport modes are found over southern Africa: direct transports, indirect transports and recirculation (Garstang *et al*., 1996). The direct and indirect transports are to the east and west with exit into the atmosphere over the respective oceans. They emanate from westerly troughs coupled with subtropical frontal systems. Recirculation is in the form of anticyclone gyres over the subcontinent. Moody *et al*. (1995) and Dorling *et al*. (1992) have used a similar approach that uses synoptic climatology to place the transport findings in the context of larger scale processes. Easterly, westerly and circulation modes of transport, developed using trajectory analyses, are shown in Figure 1.4 (Tyson *et al*., 1996).
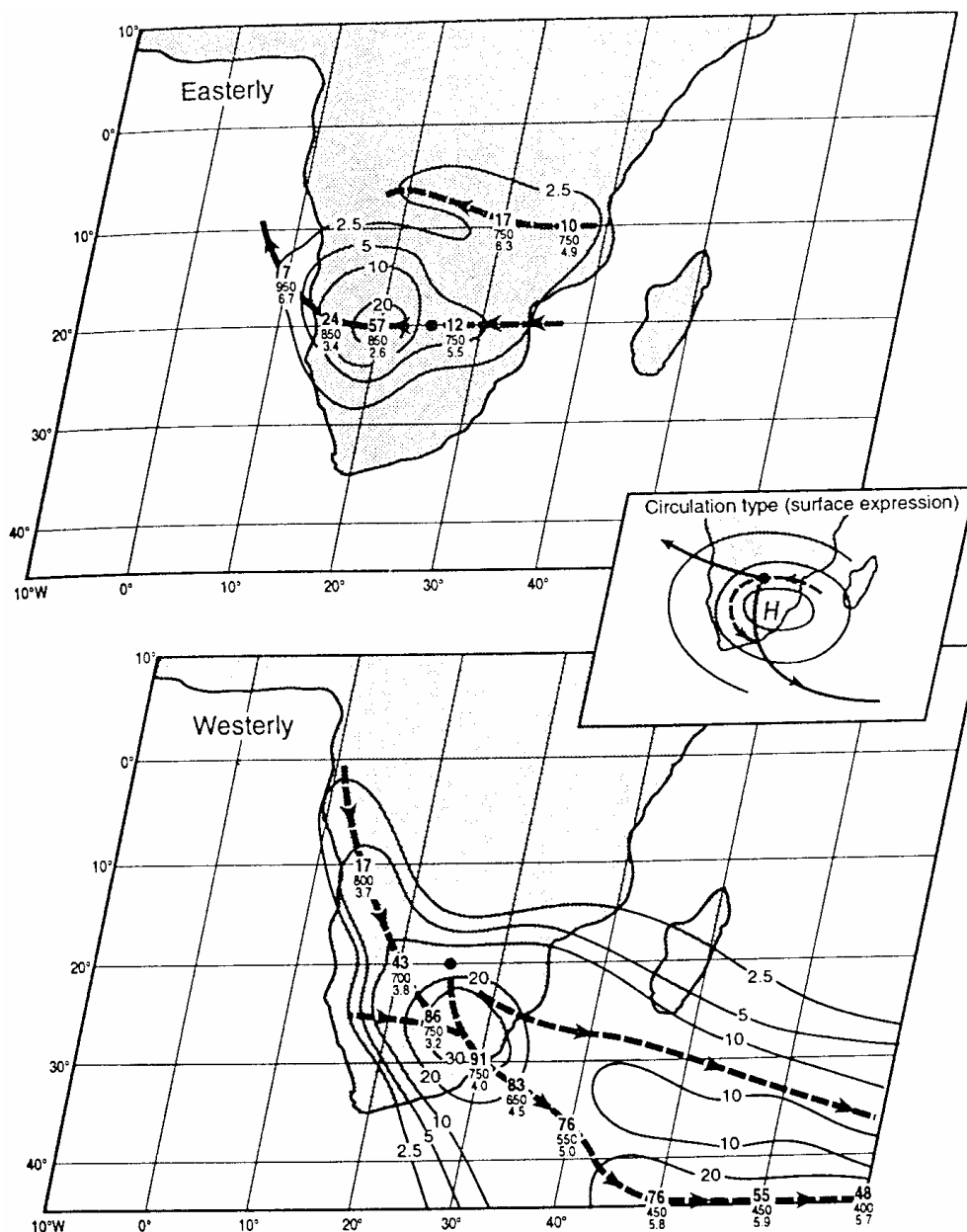
Figure 1.4    Isopleths of percentage vertically integrated surface -850 hPa zonal transport in easterly and westerly directions with the continental anticyclone type. Solid heavy lines indicate the core of direct maximum frequency transport; broken lines indicate the core of the maximum frequency re-circulated air transport. (After Tyson *et al.*, 1996).

**Air circulation climatology for central East Africa.**

An air circulation climatology for central East Africa has been developed similarly from trajectory ensembles (Gatebe, 1999). Air reaching Kenya originates mainly from the Saharan region and the north-western Indian Ocean of the Arabian Sea in the Northern

Hemisphere and from the Madagascar region of the Indian Ocean in the Southern Hemisphere (Figure 1.5).
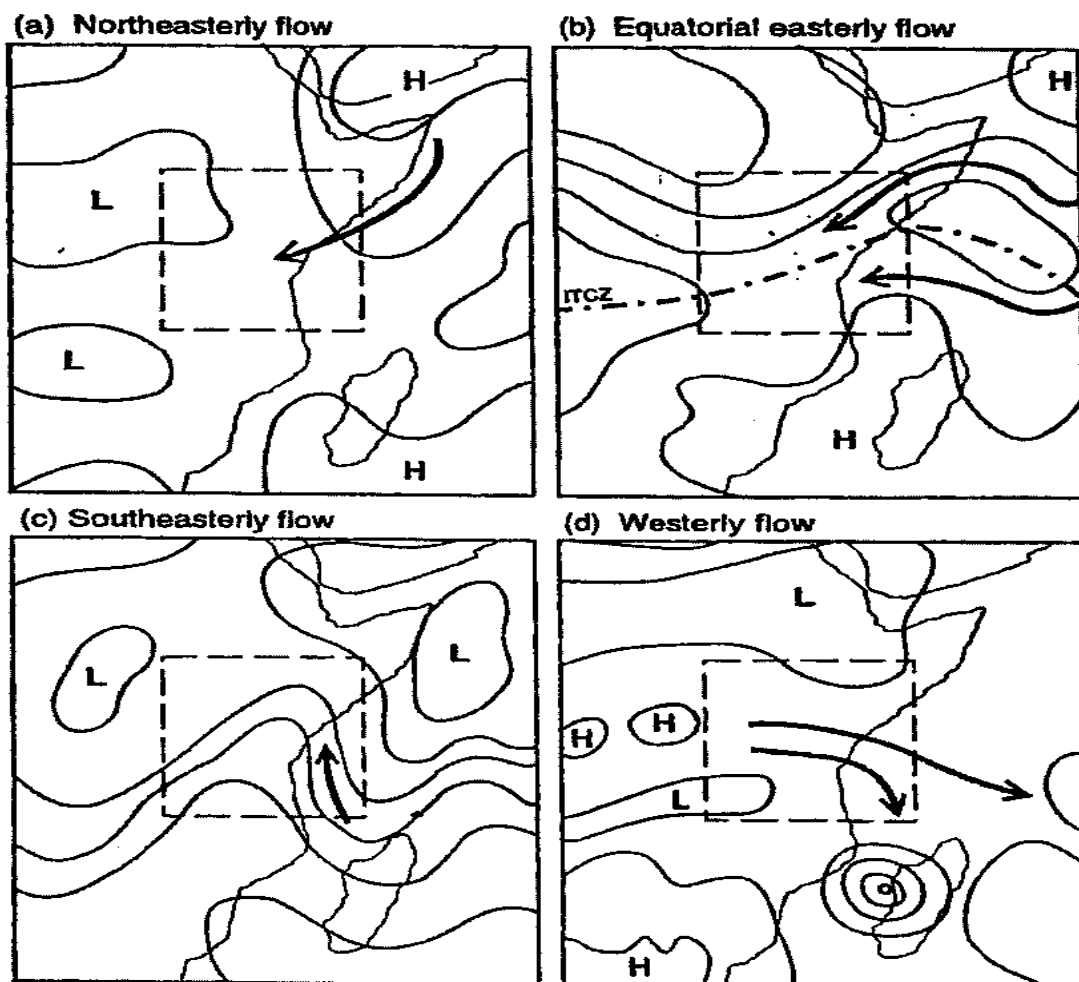


Figure 1.5     Major synoptic circulation types over Kenya and eastern Africa:
a) north-easterly flow associated with the Arabian Ridge of high pressure;
b) equatorial easterly associated with the equatorial ITCZ; c) south-easterly flow associated with a ridge of high pressure over East Africa; and d) westerly flow associated with a ridge of high pressure over Congo and low pressure or tropical cyclones in the south Indian ocean (after Gatebe, 1999).

The transport corridors or plumes arriving over Kenya are clearly bounded and well defined (Figure 1.6). North-easterly and south-easterly transport from the north-western and south-western Indian Ocean corresponds to their seasonal monsoon airflow counterparts. Anticyclonic Sahara transport is a prominent feature and westerly transport mode is evident (Gatebe *et al.,* 1999).
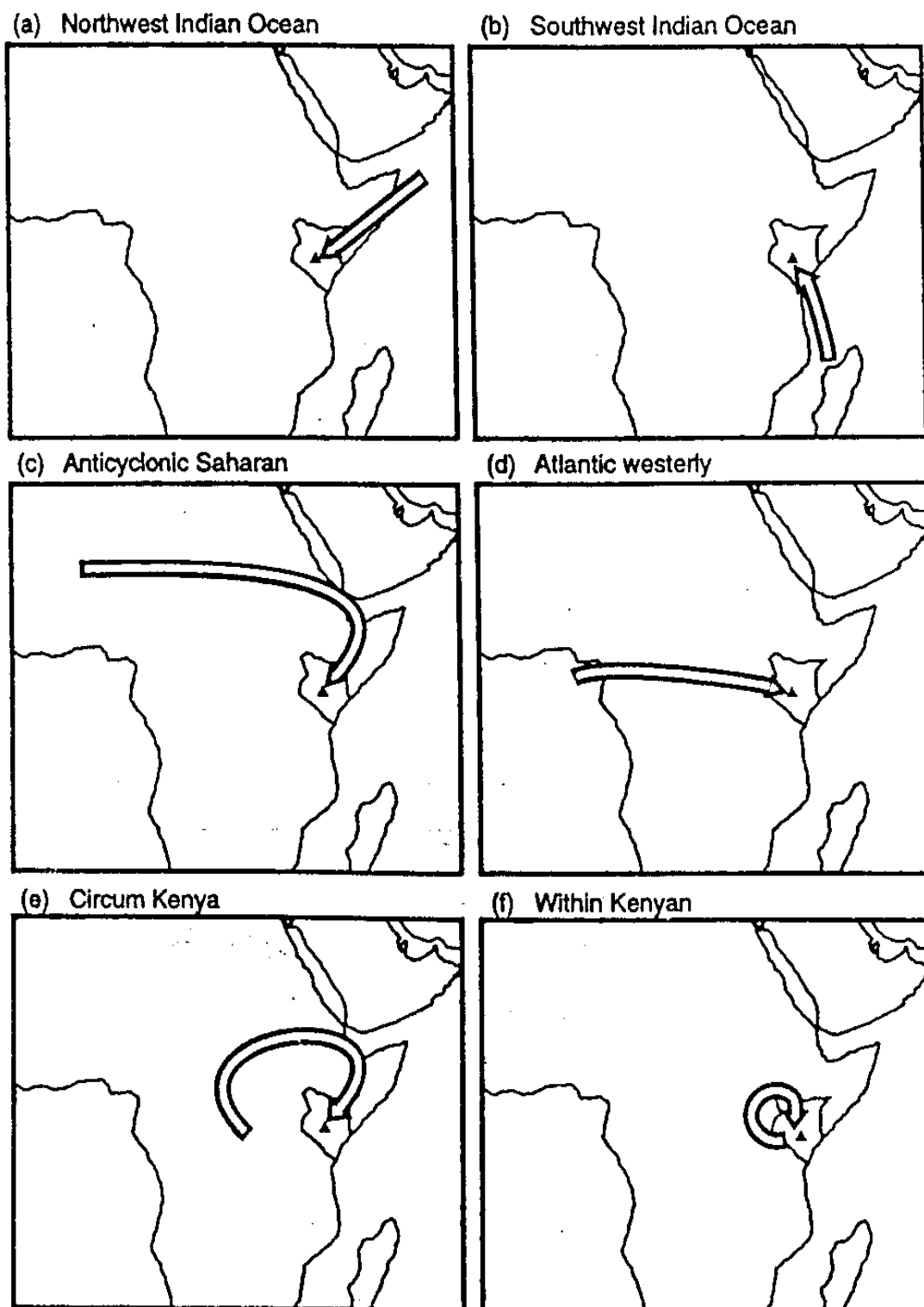
Figure 1.6     Predominant atmospheric transport modes conveying air to Kenya as determined by back trajectories modelling ending at Mount Kenya (triangle): (a) from the north west Indian Ocean, (b) from the southwest Indian Ocean, (c) anticyclonic Sahara transport, (d) in the Atlantic westerlies, (e) circum Kenyan transport, and (f) localized within Kenyan transport (after Gatebe *et al.*, 1999).

## Previous tropospheric ozone studies in southern Africa

Amongst the earliest studies to note ozone maxima in the south tropical Atlantic region were conducted by Fishman *et al*. (1990) and later findings associated the ozone maximum to biomass burning in the African savannah and/or Amazon forest (Fishman *et al*., 1991; 1992; Kim *et al*., 1996; Ziemke *et al.,* 1996; Kim and Newchurch, 1998; Thompson *et al*., 1996a; 1996b). The atmospheric feature is highly seasonal and most pronounced during the austral winter - spring transition (August to October) (Fishman *et al*., 1991). Biomass burning of the African savannas is known to produce large amounts of photochemically active aerosols and trace gases that are necessary precursors of tropospheric ozone (Crutzen and Andrea, 1990).

The near coincidence of the maximum in southern Hemisphere biomass burning and the ozone maximum over the south Atlantic gave rise to the hypothesis that the transport of biomass burning emissions from southern Africa to the tropical central south Atlantic are responsible for the formation and maintenance of this feature (Fishman *et al*., 1991). The excess ozone in mid-tropospheric maximum is between 1 and 5 km above the ocean surface (Fishman *et al*., 1991; Thompson *et al*., 1996). Krishnamurti *et al.* (1993) and Pickering (1994) examined the metrological environment of this region and concluded that the ozone maximum is supported by products derived from biomass burning over both southern Africa and Brazil.

It is against this background of insight about existence of seasonal biomass burning activities over southern and the dramatically elevated tropospheric ozone over southern tropical Atlantic Ocean between South America and equatorial Africa that led to the initial large field campaigns in Southern Africa. Two such large campaigns were conducted during the austral winter - spring transition of 1992. The Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A) experiment was conducted over the South American-Atlantic Ocean-African region of the Southern Hemisphere and was directed at determining the existence, characteristics, and the formation of tropospheric ozone previously reported to be one of enhanced austral spring concentrations over the tropical South Atlantic Ocean (Fishman 1991). Concurrently, the Southern African Fire Atmosphere Research Initiative (SAFARI-92) was conducted under the umbrella of TRACE-A, and directed towards the determination of production of biomass burning products over the southern Africa

subcontinent and their transport vertically and horizontally in the atmosphere within and beyond the region (Andreae *et al*., 1994).

**Balloon-borne measurements during SAFARI-92/TRACE-A**

Balloon-borne ozonesondes play an essential role in monitoring stratospheric and tropospheric ozone (Logan, 1994), preparing climatologies (Logan, 1999), developing satellite retrieval algorithms (Bhatia *et al*., 1996) and for evaluating the accuracy of space-borne instruments, satellite data products and model calculations of ozone. For example, during the SAFARI-92/TRACE-A campaign, more than fifty soundings were taken at five sites over a six-week period in 1992 (Diab *et al*., 1996; Kirchhoff *et al*., 1996). The sites were Ascension Island (19°S, 14°W), Brazzaville, Congo (4°S, 15°E), Okaukuejo, Namibia (19°S, 15°E), Irene, South Africa (25°S, 28°E) and Reunion Island (east of Madagascar). Routine soundings in the western Indian Ocean commenced in 1992 - 1993. The only long term ozone remote monitoring site in the tropics is the sounding station at Natal, Brazil, which has operated continuously since the late 1970's (Kirchhoff *et al*., 1991). Long term surface data for ozone and precursor gases like carbon monoxide are available from the Cape Point, South Africa monitoring site.

The seasonal ozone maxima over Okaukuejo and Irene were much lower compared to Ascension and Brazzaville during SAFARI-92 (Diab *et al*., 1996). This implied that tropospheric ozone at Okaukuejo was not enhanced by biomass burning as consistently as Ascension and Brazzaville because savannah fires were north (Angola) and northeast (Zambia) of Okaukuejo (Justice *et al*., 1996).

The monthly mean ozone from ozonesonde observations, 1991 - 1993, for Irene shows a seasonal maximum, which peaks between August and November. The lower tropospheric ozone for Irene in SAFARI-92 compared to all the other sites, results from its southerly location relative to the major regions of biomass burning. (Cahoon *et al.,* 1992) and like Okaukuejo, from highly variable transport patterns (Garstang *et al*., 1996). However, the ozone enhancement in Irene extends to the summer, indicating an urban-industrial photochemical origin of ozone, as suggested by Zunckel *et al*., 1992. Back trajectories for Irene run a cluster of 5 around a point from a single level within each 5 km layer showed intermittent effects of biomass burning (Thompson *et al*., 1996). Thompson *et al*. (1996) further demonstrated that for 6 of 15 individual episodes of enhanced ozone in Irene, the origins of low and middle–tropospheric air masses were

from biomass burning regions. A clear latitudinal dependence in ozone concentration was evident in the SAFARI-92 studies (Diab *et al*., 1996). A north - south ozone concentration gradient is established over the sub-continent during the biomass-burning season (Justice *et al*., 1996; Thompson *et al*., 1996). This gradient has been found for other atmospheric constituents such as CO and aerosols during the burn season (Kirkman *et al.,* 2000). This pattern is linked to biomass burning, which has been shown to be greater north of 20°S (Justice *et al*., 1996). Thompson *et al*. (1996) confirmed the latitudinal gradient.

Gaps in ozonesonde operations limit the profile database for satellite algorithm and trends research in the tropics. This has been compounded by the fact that ozonesonde launches in the tropics have been highly sporadic, with a dozen or so stations operating intermittently since the mid-1980's. With the 1998 initiation of the SHADOZ (Southern Hemisphere *Additional* Ozonesondes) project, a systematic effort was made to collect regular ozone profile data at stations throughout the southern hemisphere tropics and subtropics (Thomson *et al*., 2003a).

Recent studies conducted using SHADOZ data for Nairobi, at the Equator; at Irene, South Africa in the subtropics; and at Lusaka, Zambia, central Africa (SAFARI 2000), indicate that during the fire period of September Lusaka has the highest concentrations of ozone throughout the troposphere (Thompson *et al*., 2002). Thompson *et al*. (2002) showed that on 6 September 2000, Lusaka recorded ozone values exceeding 100 ppbv at a 2 - 5 km (800 - 500 hPa) stable layer. Surface concentrations of 95 ppbv at Lusaka, the highest readings measured to date in southern Africa, were greater than surface ozone at Nairobi and Irene (Thompson *et al*., 2002). The high ozone values at Lusaka were shown to originate from biomass burning in the neighbouring countries through back trajectories (Thompson *et al*., 2002).

**Satellite and aircraft measurement studies**

The application of ozone remote sensing to the troposphere, in a series of studies by Fishman and co-workers (Fishman *et al*., 1986; 1990; Fishman and Brackett, 1997), gave insight into the extent of biomass burning effects on tropospheric ozone. A new method of using satellite measurements of the total ozone column obtained from the Total Ozone Mapping Spectrometer (TOMS) instrument aboard the Nimbus 7 satellite to infer information about the distribution of ozone in the troposphere was first

proposed by Fishman *et al*. (1986). Fishman *et al*. (1986) examined the formation of elevated total ozone amounts in conjunction with the presence of biomass burning in the tropics

The TOMS instrument scans across the path of the satellite and can obtain a horizontal resolution of 80 - 120 km. Theoretically, TOMS can obtain signals due to the presence of ozone in both the stratosphere and the troposphere, though TOMS instruments can underestimate the amount of ozone below 500 hPa (Thompson, 2003), but the vertical characteristics of enhanced ozone seen from space can easily be confirmed by ozonesondes (Fishman *et al*., 1992). Despite this limitation, Fishman *et al*. (1990), by use of TOMS data, showed that in the tropics, the highest tropospheric ozone residual amounts coincide with the dry season of intense biomass burning. Fishman *et al*. (1990), further demonstrated a high correlation between the distribution of tropospheric residual and the distribution of total ozone at low latitudes. Because of this strong relationship, maps of total ozone, which are available on a daily basis from TOMS, can be used as a surrogate for tropospheric studies. Satellite images showing the extent of biomass burning regions in Africa, confirm that they lie predominantly to the north of 20°S (Cahoon *et al*., 1992).

The launch of Earth Probe - Total Ozone Mapping Spectral meter (EP/TOMS) has facilitated real time processing of absorbing aerosol (smoke) and tropospheric ozone. It has provided a way of daily tracking of these pollutants at 1.0° latitude by 1.25° longitude resolution. The TOMS smoke aerosol index is used as proxy for biomass burning because it has daily global coverage and more consistent calibration and sampling than satellite fire counts (http://toms.gsfc.nasa.gov).

Aircraft measurements of the troposphere have shown enhancements of ozone and its precursors associated with the tropical burnings in South America and in Africa (Andreae *et al*., 1994). These observations confirmed that a large amount of ozone precursors and aerosols are emitted from fires and that tropospheric ozone was produced photochemically near the burning plumes. Observed ozone increases due to the burning emissions were mostly in the range of 40 - 100 ppbv and sometimes up to 160 ppbv.

Thomas *et al*. (1996), by using aircraft measurements showed that CO and ozone distributions had mixing ratios that were significantly elevated during the period of these flights. This suggested a higher input of combustion emissions to the atmosphere,

coinciding with more fire activity in September and relatively few fires in October (Justice *et al*., 1996). The same flight (Thomas *et al*., 1996) showed evidence of NE - SW gradient of trace gas mixing ratio (CO and $O_3$) distributions, with higher values in the northern parts closer to more concentrated fire areas in Mozambique, north Zambia and east Angola (Justice *et al*., 1996). It is worth noting that through the analysis of SAFARI-92 aircraft and ozonesonde data revealed that the highest ozone concentrations were found north of 15°S (Thompson *et al*., 1996).

Kirkman *et al*. (2000) combined the SAFARI-92 and SA'ARI-94 aircraft measurements to develop a southern African continental air mass chemistry. It showed that during the burn season, trace gas concentrations increased towards the equator in accordance with the fire-prone character of the tropics.

Despite obtaining much valuable information during SAFARI-92, pyrogenic emission studies were limited to only a few controlled burns during a narrow period at widely separated sites. Other important sources of aerosols and trace gas emissions were identified but only partly quantified, and the processes generating them were not studied (Swap *et al.,* 2002). Therefore, SAFARI 2000 was designed as a more comprehensive study of processes driving emissions in southern Africa, necessary for understanding and predicting regional sensitivity to and effect upon global change. The aim of the SAFARI 2000 initiative was to identify and understand the relationships between the physical, chemical, biological and anthropogenic processes that underlie the biophysical and biogeochemical systems of southern Africa. It placed particular emphasis upon biogenic, pyrogenic and anthropogenic aerosol and trace gas emissions, their characterisation and quantification, their transport and transformations in the atmosphere, their influence on regional climate and meteorology, their eventual deposition, and the effects of this deposition on ecosystems.

# CHAPTER TWO

The Southern Africa Regional Science Initiative (SAFARI 2000) was a multi disciplinary project incorporating ground, airborne and space borne measurements carried out in southern Africa in 2000. The SAFARI 2000 addressed a broad range of phenomena related to land-atmosphere interactions and the biogeochemical functions of the southern African system.

This study has extensively utilised datasets collected during the SAFARI 2000 campaign period. Some of the datasets used include ozonesonde and aircraft acquired ozone data. The methodologies used for data collection and analytical methods will be described in this chapter.

# DATA ACQUISITION AND METHODS

## Measurement of atmospheric ozone.

Various ozone-measuring instruments have been available for observational purposes over the southern Africa subcontinent. The five methods currently in use are: surface measurements, passive samplers, Dobson total column spectrophotometer, satellites, balloon-borne ozonesonde instrument and aircraft platforms.

The unique feature of SAFARI 2000 intensive field campaign was the large spatial extent of the investigations that utilised different instruments to gather data. Some of the instruments used to take ozone measure during this period are discussed. The study partly utilises ozonesonde data and therefore, some detailed discussion of the ozonesonde instrument is desirable.

### Aircraft-borne measurements

Data sets acquired during SAFARI-92 (Southern African Fire/Atmosphere Research Initiative) and SA'ARI-94 (Southern African Atmosphere Research Initiative), and ARREX using instrumented aircraft, before SAFARI 2000 (Southern African Regional Science Initiative), have proved invaluable in the study of aerosols and trace gases over southern Africa. The aircraft observations have the advantage of fine spatial resolution

and measurements of several parameters are recorded simultaneously. Vertical distributions and lateral extent can be computed from aircraft measurements.

One major feature of the SAFARI 2000 was the large spatial extent of the data collection (Annegarn *et al.,* 2002), which involved coordinated measurements across nine countries of southern Africa. The number of aircraft was increased during SAFARI 2000 campaign to cover most of the southern African region, including the Mozambique Channel and parts of southern Malawi.

The SAFARI 2000 builds upon the success of the SAFARI-92. The measurements were taken using 5 aircraft. The aircraft flight missions were designed according to synoptic conditions satellites overpasses and ground based validation targets, with some flights designed to provide the maximum synchronous underflight time of the ER-2 remote sensing aircraft in relation to Terra satellite. After underflying Terra, research aircraft flew on to other targets of interest (Swap *et al*., 2002). The research flights began on 15 August 2000, with the operations focused on the observation of biomass burning (including prescribed fires and fires of opportunity, during both flaming and smouldering phases), industry (power generation, including metallurgical and petrochemical industries) and biogenic emissions. The following aircraft constituted airborne platforms and their instrumentation for the SAFARI 2000 campaigns (Swap *et al*., 2002).

**South African Weather Service Aerocommander research aircraft (690A)**

Two Aerocommander 690A research aircraft, called JRA and JRB were operated *in situ* platforms during the dry season, to fly from the lower boundary up to 5 km above ground level. The two Aerocommanders flew about 50 daytime missions during August and September. The aircraft were used together in order to measure different parts of the same circulation pattern. The flight strategies of the two aircraft involved profiling the atmosphere in the vertical along horizontal transects and spiralling above key ground based sites. After 14 September 2000, only one aircraft was flown with a new suite of instruments. The objective in this later half of the campaign was to obtain emission data from various sources, particularly biomass burning.

Two Aerocommanders, namely JRA and JRB, collected data alongside other aircraft during the dry season campaign of 2000. The flight paths followed by the

aircraft are shown in Figure 2.1. The two aircraft collected data from the lower boundary layer up to about 4 km above the ground level.
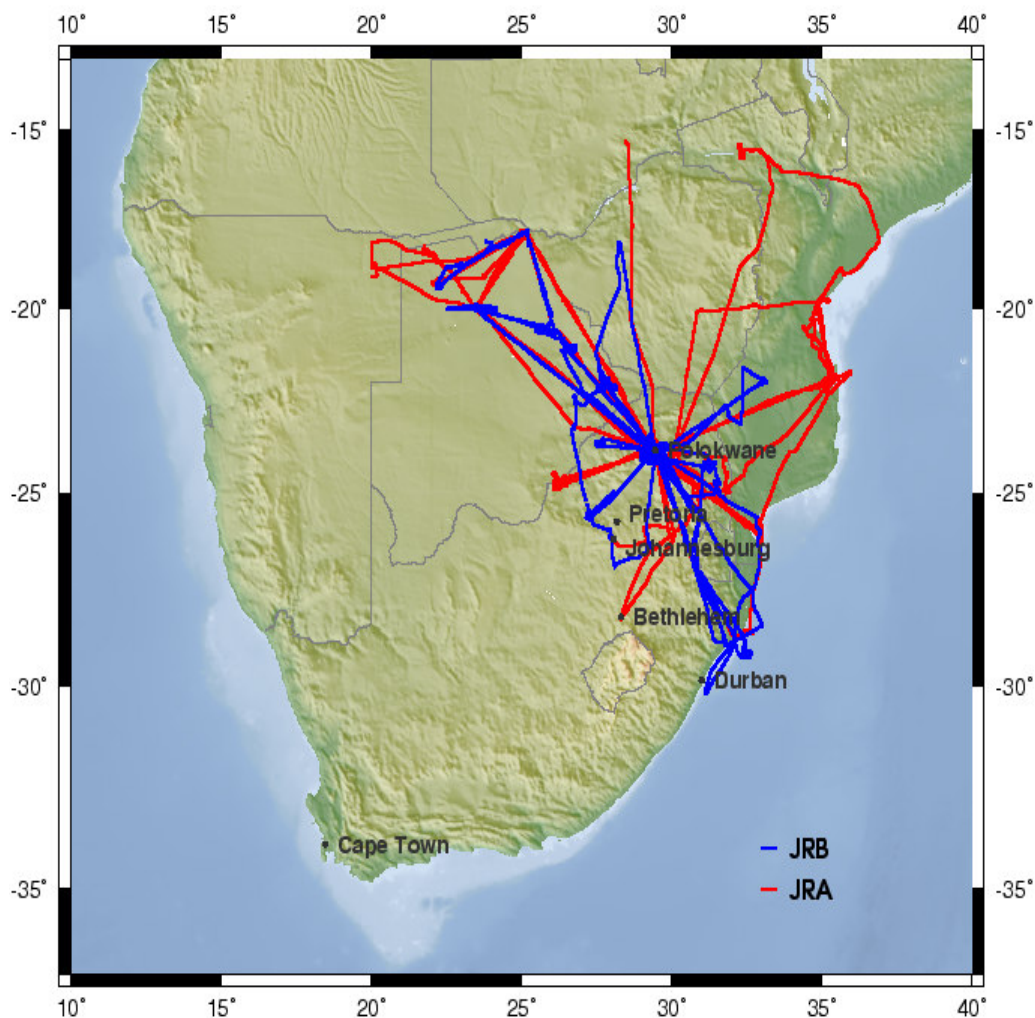


Figure 2.1     SAFARI 2000 flight paths for JRA and JRB Aerocommanders in August –September campaigns.

Therefore, for the purpose of this study, the data from these two aircraft will analysed up to the top of the boundary layer, defined as ~3600 m.

*Criteria for selection of flights*: The days with highest ozone concentrations are identified from the analysed aircraft data sets. The conditions encountered during the flights are also taken into consideration as part of criteria in selecting the desired flights for analysis. The results from the aircraft data analysis will be useful in showing the

spatial distribution of tropospheric ozone, both horizontally and vertically in the sub-region.

The study region was sub-divided into three latitudinal bands according to respective sub-tropical, tropical and equatorial climatic zones in which the observation sites are located as well as the transects of the flight paths. Thus, 0 - 10°S, 10 - 20°S and 20 - 30°S constitute the equatorial, tropical and sub-tropical latitudinal bands respectively. The respective sites represented in these bands are: Nairobi, Kenya (1.3°S, 36.8°E); Lusaka, Zambia (15.3°S, 29.4°E); Irene (25.9°S, 28.2°E) and Polokwane (23.8°S, 29.4°E), both in South Africa. Polokwane refers to Pietersburg International Airport, Polokwane, the operational base of the research aircraft. Useful data were collected during landing and take-off at Polokwane.

**Ozonesonde/SHADOZ - SAFARI 2000**

As a complement to airborne monitoring, ozonesonde flights were released for six days from Lusaka, Zambia, Irene, South Africa and Nairobi, Kenya sites (SHADOZ program) to obtain more information concerning the vertical distribution and ozone origin above these sites. The two permanent SHADOZ stations in Africa, Irene (near Pretoria, 25.9° S, 28.2° E) and Nairobi (near the equator, 1.3° S, 36.8° E) are several hundred kilometres removed from major areas of biomass burning. Springbok, South Africa is another site where ozonesonde measurements have been conducted in the past.

SAFARI 2000 offered an opportunity to increase SHADOZ network by launching ozonesondes in Lusaka, (15.5°S, 28°E) Zambia, a country that experiences a high level of savanna burning in August and September. The Lusaka sonde observations lasted for a week during the dry season SAFARI 2000 campaign.

The global sites involved with the SHADOZ programme are shown in Figure 2.2. Data from SHADOZ sites near the Atlantic and Indian Oceans coastlines, where an accumulation of tropospheric ozone and associated pollutants have been observed in September, 2000 will be invaluable in determining the origin and eventual deposition of the pollutants.
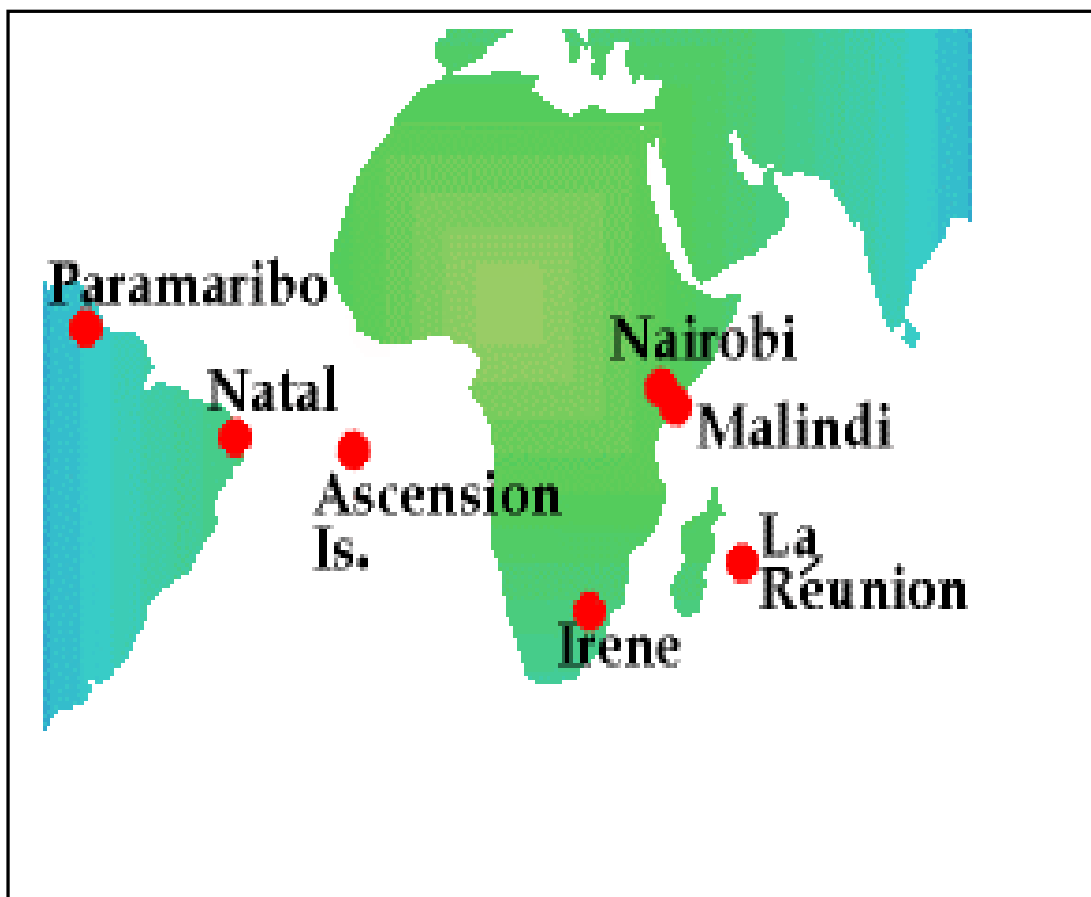
Figure 2.2    Equatorial SHADOZ Ozonesonde sites with regular ozone measurements.


The increased network of ozonesonde measurements during SAFARI 2000 would be very useful in studying the vertical ozone profile as well as the N-S ozone gradient over the region.

**Ozonesonde instrument**

The ozonesonde has the advantage of providing detailed vertical ozone distribution, including temperature and humidity in the troposphere through to the lower part of the stratosphere. The sondes are usually launched once per week for several years.

Ozonesondes are electrochemical cells sensitive to the presence of ozone that are carried on small balloons to altitudes above 30 km. Several versions of sondes have been used and the important ones for ozone trend determination are the Brewer-Mast (BM) and the Electrochemical Concentration Cell (ECC) (Kombhyr *et al.,* 1995). An example of ECC sonde is shown in Figure 2.3. All ozone-measuring sites in southern Africa, including Kenya (equatorial), use ECC technology.
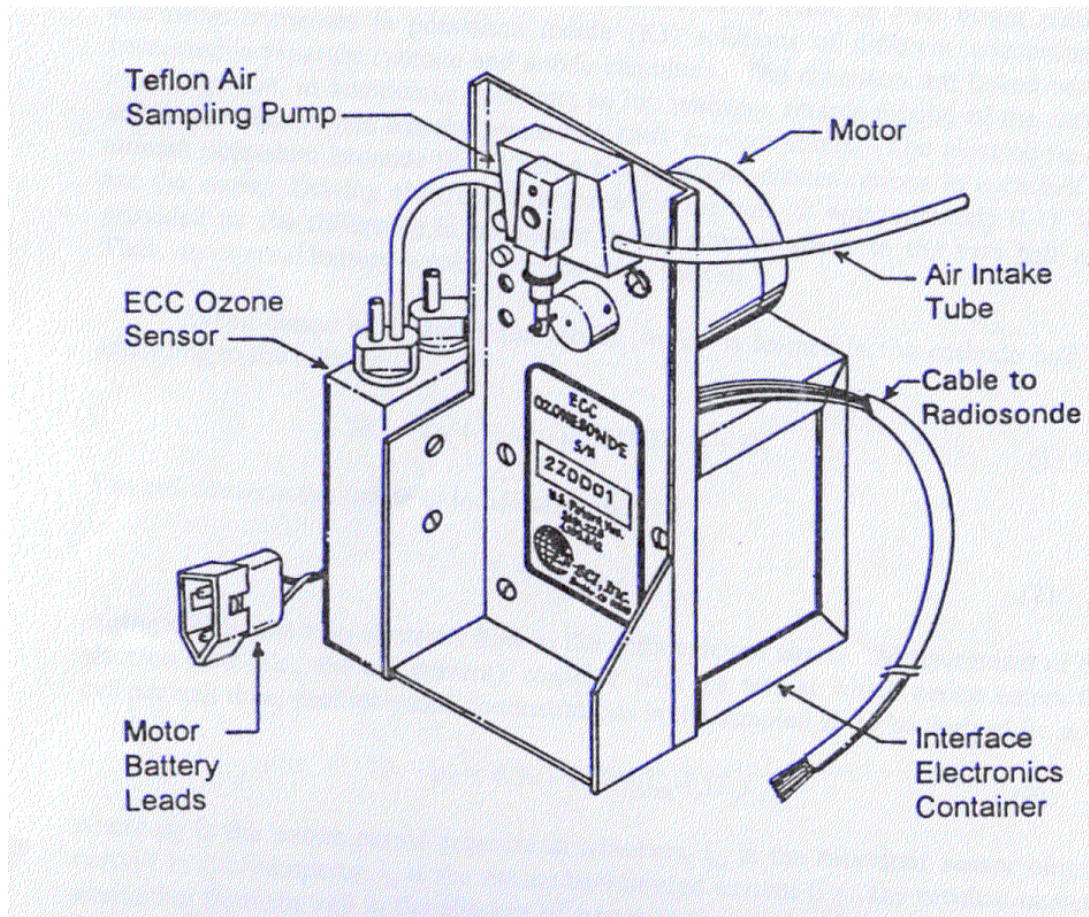
Figure 2.3     Balloon-borne Model 2Z ECC (electrochemical Concentration
Cell) Ozonesonde.


The stations prepare their sondes and process them differently, because the sonde
technology is continuously evolving. The principal of an ECC sensor is easy. A
potential difference is set up between two cells of different strength of KI (potassium
iodide) solution. The ozone sensor of the ECC ozonesonde is made of two bright
platinum electrons immersed in potassium iodide (KI) solutions of different
concentrations contained in separate cathode and anode chambers. The chambers are
then connected with an ion bridge, that in addition to providing an ion pathway, retards
mixing of the cathode and anode electrodes thereby preserving their concentrations. The
electrodes also contain potassium bromide (KBr) and a buffer whose concentrations in
each half-cell are the same. Thus, when atmospheric ozone enters the sensor iodine is
formed in the cathode half-cell according to the relation

$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$
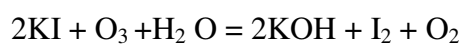
Conversion of iodine to iodide, $I_2 + 2e = 2I^-$, during which two electrons flow in the cell external circuit. Measurement of the electron flow (cell current), together with the rate at which the ozone enters the cell per unit time, enables ozone concentrations in the sampled air to be derived from:

$$P_3 = 4.307 * 10^{-3} (i_m - i_b) T_p t$$

where $P_3$ is partial pressure in nanobar, $i_m$ is the measured sensor output in micro-Ampere, $I_b$ is the sensor background current (i.e. the residual current emanating from the cell in the absence of ozone in the air) in microamperes, $T_p$ is the pump temperature in Kelvin and t is the time in seconds taken by the sonde gas sampling pump to force 100 ml of air through the sensor.

As a volume-mixing ratio in air, the ozone is derived from:

$$O_3 (ppbv) = 1000 P_3 / P$$
$$= 4.307 (i_m - i_b) T_p t / P$$

where $O_3$ (ppbv) is the measured ozone in parts per billion by volume and P is the ambient air pressure in millibar.

Uncertainties in the ozonesonde data are due to: pump flow rate at surface (1 - 2%), extrapolation to the top of the atmosphere based on climatology (balloon reaches 4 to 7 hPa level), the pump efficiency correction and the response time of the solution. Additional uncertainty comes from the strength of the KI solution used (Boyd *et al.*, 1998; Johnson *et al.*, 2002).

An example of ozonesonde data (Figure 2.4) shows a vertical profile of ozone over Malindi, a Kenyan SHADOZ ozonesonde site on 23 September 2000. The ozone concentration increases suddenly with a corresponding temperature inversion at 1 km.
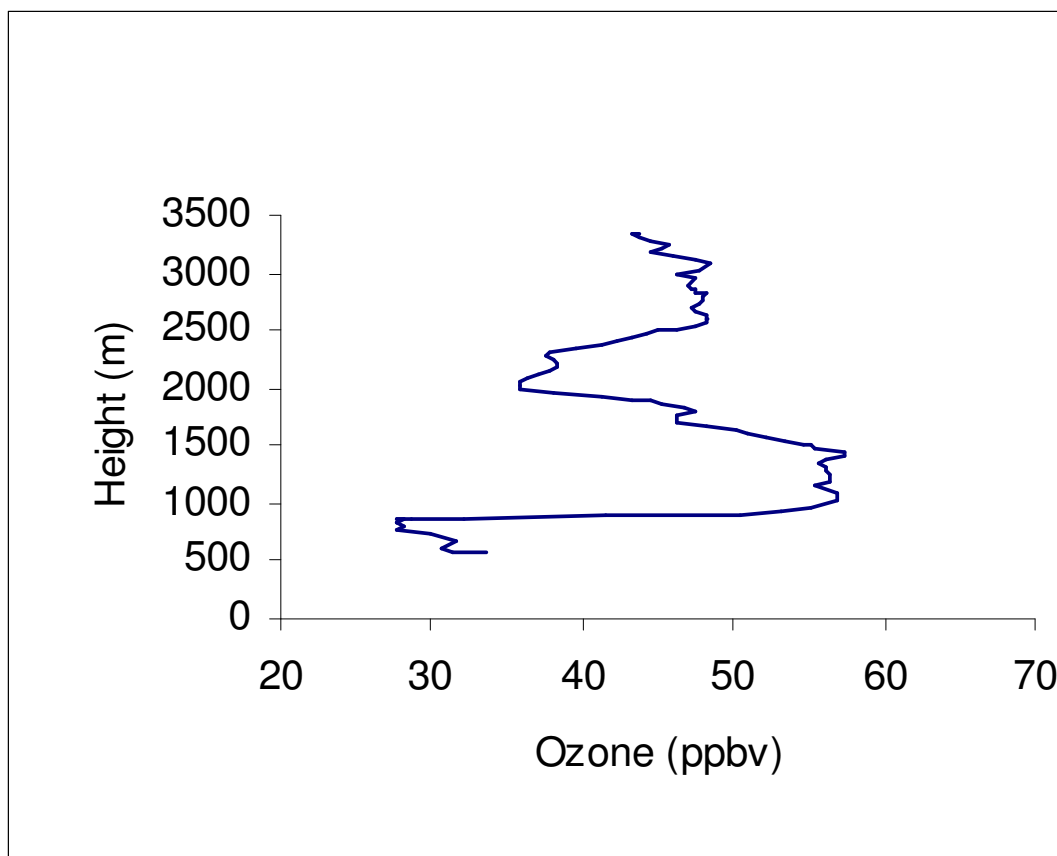
Figure 2.4    Vertical ozone distribution on 23 September 2000 over the
SHADOZ site at Malindi, Kenya.

## Satellite imagery

The Total Ozone Mapping Spectrometer (TOMS) satellite instrument has contributed
tremendously to ozone studies due to its global coverage capability. It gives daily
observations of total column, at 1.0° latitude by 1.25° longitude, resolution showing
lateral extent but no vertical distribution. The TOMS aerosol index is used as a proxy
for biomass burning because it has daily global coverage and more consistent
calibration and sampling than satellite fire counts. Some of the ground data collected
during SAFARI 2000 campaigns have been very useful as ground truth for the satellites
that passed over the region in the study period.

During periods of specified fires (SAFARI 2000), simultaneous measurements
were required as the Terra satellite passed overhead; the ER-2 flew on a parallel track to
be overhead at the same time, the sampling aircraft was on hand to investigate the
chemistry of the plume, and ground-based stations were present to place reflective

targets for calibration. Terra is equipped with the Moderate Resolution Imaging Spectrometer (MODIS), with a 250 m resolution. This is complemented by ASTER, an instrument with 15 m resolution. Imagery from this new generation of spaceborne sensors is available at no cost, courtesy of the U.S. government. MODIS data have been used in this study for processing fire images during biomass burning days.

The limiting factor in this study is that the aircraft did not fly on certain days or instruments failed during some flights, thus creating in gaps in the campaign period data sets. Similarly, the aircraft never used the same route for more than 2 days, thus limiting study of the same area consistently and establishing any specific temporal patterns in ozone concentrations. However, an attempt will be made to establish the duration of the existence of these ozone maxims.

## Fire counts in biomass burning areas

The region covered by fires will be divided into blocks of 10º by 10º, between latitudes 0º - 30ºS and 10ºE – 40ºE. The fire counts distributions are then condensed into 5-day clusters.

Categorical classification will then be carried out for each block in the six respective fire 5-day clusters. For example when a block had full fire coverage in the respective six blocks, a score of six was apportioned. An example of a 5-day fire cluster is shown in Figure 2.5.
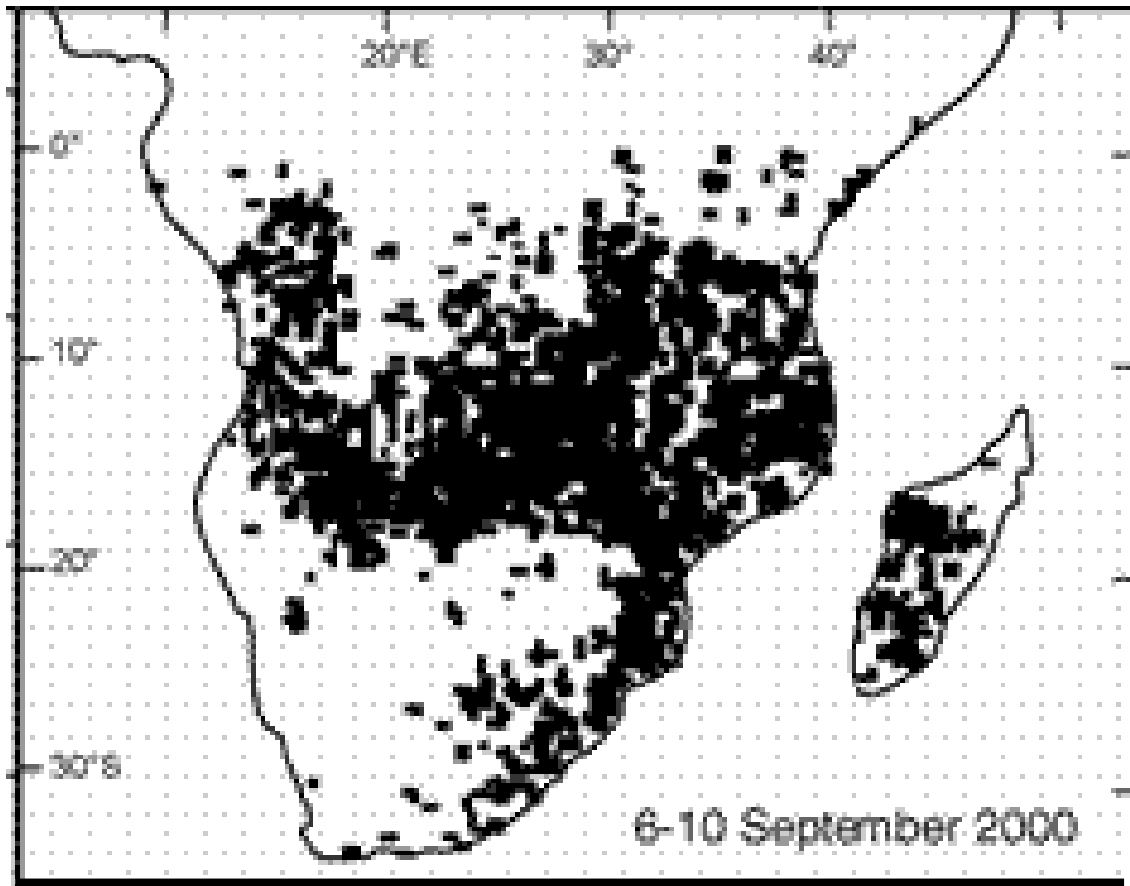
Figure 2.5      Fire distributions in 5-day fire clusters.

## Classification of dominant meteorological synoptic systems

The circulation classification example is drawn from southern Africa (Tyson *et al.*, 1988; Garstang *et al.*, 1996). Tyson *et al.* (1988) had averaged circulation types in the latitudinal band 30°S to 20°S, from surface to 500 hPa level (entire troposphere), as shown in chapter 2, Figure 1.2. Garstang *et al.* (1996) modified this classification further by addressing conditions at surface and 500 hPa levels separately.

This study undertook a similar circulation classification for two latitudinal bands (30°S - 20°S, 20°S - 10°S) for the period of August to September 2000. The terms Band 1, Band 2 and Band 3 will be used to denote the latitudinal bands (30°S - 20°S), (20°S - 10°S) and (10°S - 0°S) respectively. The classification procedure of Garstang *et al.* (1996) is followed, thus developing two separate classifications based for near surface (850 hPa) and mid-tropospheric (700 - 500 hPa) levels for both Band 1 and Band 2. However, for Band 3, the classification developed by Gatebe *et al.* (1999) is utilized.

Kanyanga (2003) developed a classification for Band 1 region for August - September 2000 based on Tyson *et al.* (1988).

Synoptic classifications for the three key sites of Irene, Polokwane (Band 1) and Lusaka (Band 2) are developed in this study. The approach used, while based on the Garstang *et al.* (1996) method, incorporated additional information. Any event likely to influence the ozone concentrations was included in the classification. Examples are days of high smoke index (SI), observed biomass burning (BB) or enhanced ozone (EO), which are documented alongside the various synoptic systems.

## Trajectory computation

A trajectory is a calculated transport pathway of an infinitesimally small air parcel. Trajectories provide a useful tool for understanding the three dimensional transport of airborne material in the atmosphere (D'Abreton, 1996). Backward trajectories are particularly useful in tracing aerosols and trace gases back in time and space to ascertain their origins. On the other hand, forward trajectories provide a guide on the locations where pollutants are likely to be deposited. Thus, trajectories corresponding to individual transport events provide an indication of the mean motion of an advected air parcel.

A kinematic trajectory model uses simulated wind velocity vectors. This model works well with data from ECMWF (European Centre for Medium Weather Forecasts). The model uses the explicit method of integration defined by:

$$x(t+dt) \quad = \quad x(t) + v(t) \, dt$$

where x(t+dt) is the three-dimensional parcel position at t+dt; x(t) is the old position; and v(t) is the parcel velocity vector and d(t) is the time step.

However, for the purposes of this research, backward trajectories were computed using HYSPLIT 6.0 (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model from the National Oceanic and Atmospheric Administration (NOAA).

The HYSPLIT model is the newest version of a complete system for computing single air parcel trajectories to complex dispersion and deposition simulations. The model was upgraded through joint efforts between NOAA and Australia's Bureau of Meteorology. The added features include improved advection algorithms, updated

stability and dispersion equations, and an option to include modules for chemical transformations. The HYSPLIT model computes the advection of a single pollutant particle, or simply its trajectory.

The model was run interactively on the Web through the READY system on NOAA's site. The model is based on the principle of Lagrangian advection with u, v and w wind components at a time, atmospheric layer and grid used to compute a new upstream (or downstream) location of an air parcel at chosen time steps. This location is then iteratively re-determined using the components at the new position to calculate the next location. The procedure is then repeated for a starting time (specified) on a desired date for six days to produce a backward trajectory over five days. Vertical velocities are determined from non-linear mode initialisation, which permits diabatic and adiabatic processes to be taken into account. The boundary condition at the surface, where vertical motion is taken to be zero, together with the consideration of atmospheric stability, permits trajectories to follow the terrain or go around obstacles when the trajectories approach the surface.

**Trajectory uncertainties**

In this work, much attention will be given to backward trajectories as a means of studying the history of air masses. A simple definition of backward trajectory would be that it is a meteorological estimate of the history of air mass arriving at a pre-specified location and time. Sources of uncertainty in a trajectory calculation include the meteorological data that drives the model and the physical assumptions by which the trajectory model operates on that data (Point *et al.,* 1996). A major potential source of trajectory error is the presumption that a single trajectory represents the path of all the pollution molecules experienced at a receptor. HYSPLIT tracks the backward path of a single "particle" and does not explicitly incorporate mixing into the trajectory calculations. Under certain atmospheric conditions the "representativeness" of a single trajectory pathway is questionable (Point *et al.,* 1996). The accuracy of the HYSPLIT model based on the southern African data will not be evaluated in this work as it is beyond the scope of this study.

In this chapter, the airborne and ozonesonde data sets measurement methods during SAFARI 2000 field campaigns have been described. The area covered by the all the aircraft missions has also been shown. The areas where there were no flight missions will be complimented by ozonesonde measurements and TOMS satellite data for spatial coverage. The associated data from satellite imagery and synoptic charts have also been described. The methods of trajectory computation and the limitations have been explained in the chapter. The next chapter will present results and interpretation of the findings.

# CHAPTER THREE

# CHARACTERISATION OF TROPOSPHERIC OZONE OVER SOUTHERN AFRICA

Ozone has a short life span in the tropical lower troposphere (~1 week) and exhibits high variability (Krishnarmurti *et al.,* 1993; Crutzen, 1995). At any locality, tropospheric ozone is a function of local production, vertical mixing and horizontal transport (Tyson *et al.*, 1997). Airborne ozone measurements established that concentrations over southern Africa show strong stratification with height (Zenker *et al.*, 1996). The presence of stable layers facilitates the vertical layering, which occasionally persists for weeks, preventing vertical mixing of the troposphere (Cosijn *et al.,* 1996). Ozone concentrations in these layers range from approximately 55 ppbv between 700 and 500 hPa to approximately 80 ppbv between 300 and 200 hPa  (Helas *et al.*, 1995; Thompson *et al.*, 1996; Swap *et al.*, 1999). The southern African tropospheric ozone seasonality reflects the circulation climatology (Tyson *et al.*, 1996) and the input of biomass burning (Justice *et al.*, 1996). The chemical tracer observations in September and October 1992, from SAFARI (Andreae *et al.*, 1997), confirm the presence of products derived from biomass burning in troposphere.

The work in this chapter seeks to quantify ozone concentrations in the lower troposphere between the surface and 5 km altitude over southern Africa during the SAFARI 2000 period. The airborne and ozonesonde data collected during the SAFARI 2000 field campaign will be utilized for this endeavour.

## Ozone distributions over southern Africa

### Temporal distribution of ozone during SAFARI 2000

The southern Africa region shows a general increase in ozone in the fourth week of August and first week of September during the study period. However, the equatorial region demonstrates a decreasing trend in the same periods. The above scenario is better explained by the ozone episodes observed at four representative sites (Irene, Polokwane,

Lusaka and Nairobi) during the dry season campaign of SAFARI 2000 as shown in Figure 3.1. The figures are placed in the order of regional climatic zones: sub-tropical, tropical and equatorial zones respectively.

**Sub-tropical distribution**

The two representative sites in the sub-tropical region are Irene and Polokwane. The ozone values for Polokwane were derived from data collected during landing and take-off flights in August and September.

The data for Irene sites was collected by ozonesondes daily in the first week of September. Under normal circumstances measurements are carried out once per week. The highest ozone episode (85 ppbv) was observed on 4 September. This is relatively high ozone concentration compared to the background values of ~30 ppbv. The high pollution levels were mainly confined to the first week of September (Figure 3.1).
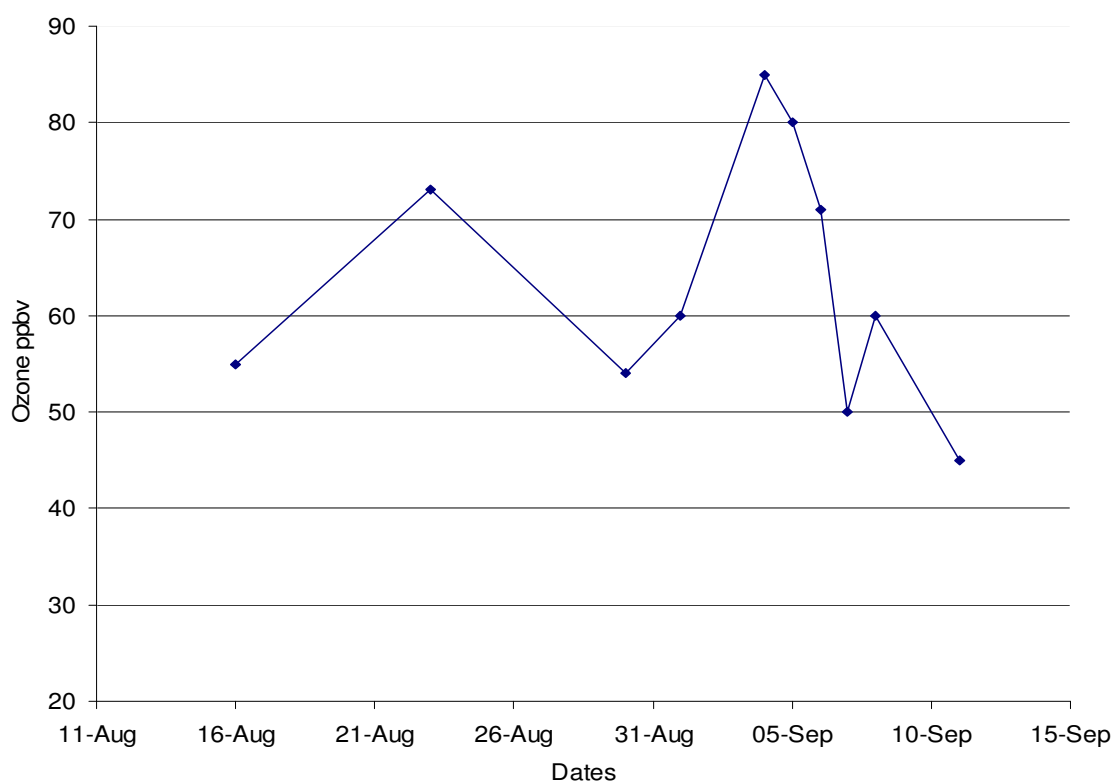


Figure 3.1    Sub-tropical ozone episodes at Irene site during SAFARI 2000.

The ozone concentrations observed at Polokwane site were relatively high, with the highest ozone episode of 93 ppbv being observed on 6 September. High ozone

values were observed in the last week of August and first week of September (Figure 3.2). The ozone pollution measured in Polokwane was much higher that at Irene site, though both fall in the same sub-tropical region. This suggests that Irene was under different transport regime.
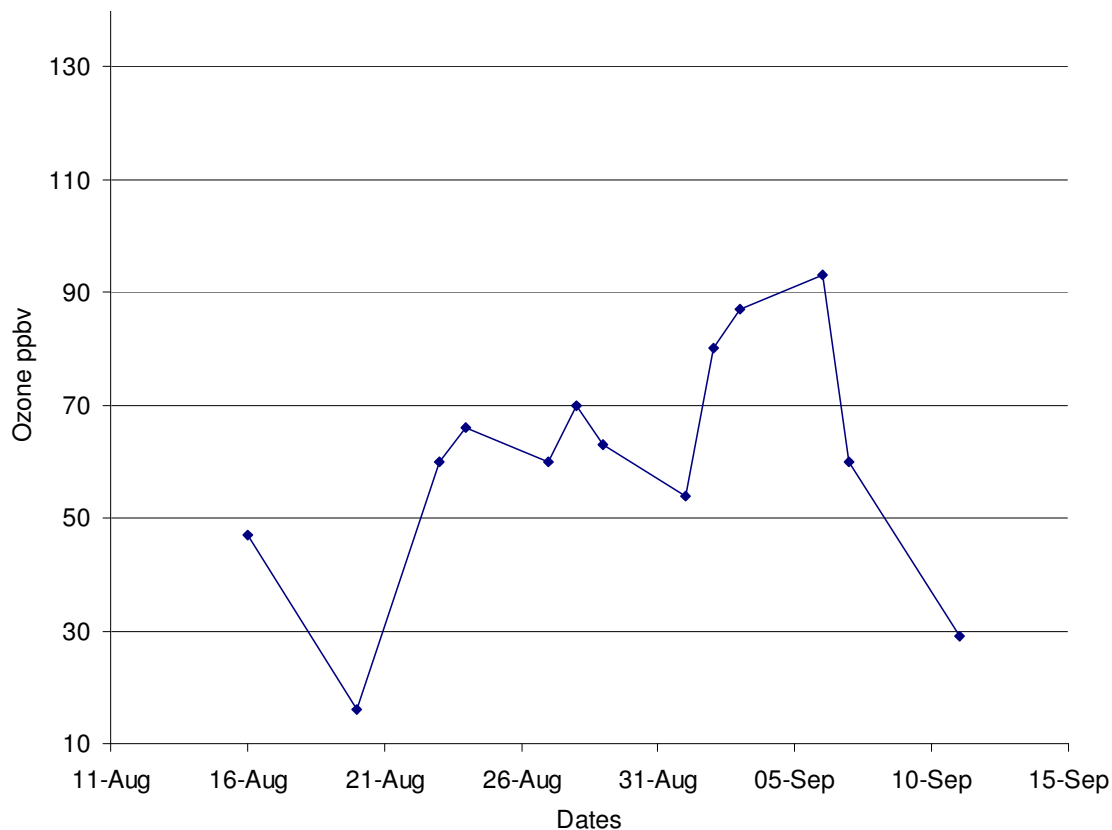


Figure 3.2       Sub-tropical ozone episodes at Polokwane during SAFARI 2000.


**Tropical region distribution**

The representative site in this region is Lusaka, Zambia. The data used in this case is mainly ozonesonde collected vertical profiles. The ozone concentrations remained relatively high throughout the first week of September (Figure 3.3). The episodes are derived from the highest ozone value recorded between the surface and 5 km level daily.
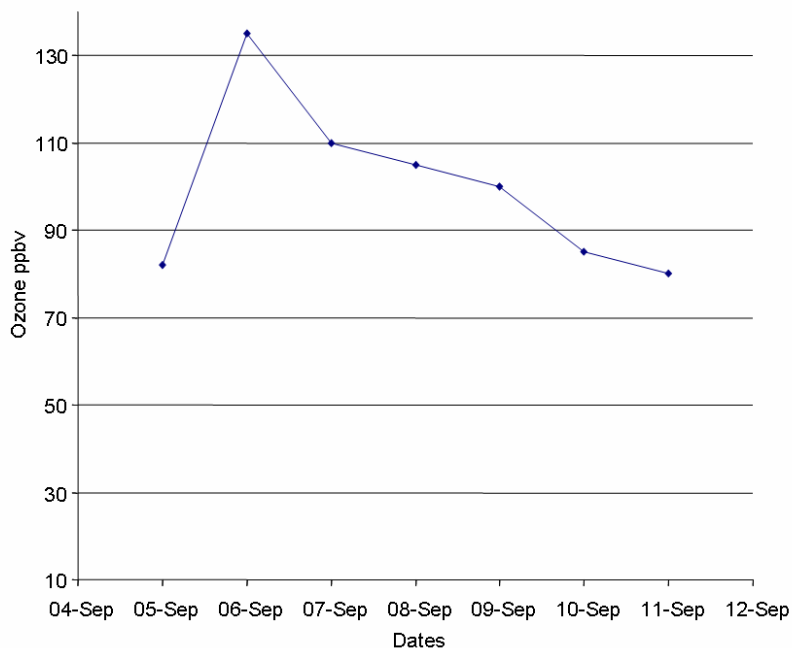
Figure 3.3    Tropical ozone episodes at Lusaka during SAFARI 2000.

The relatively lower ozone pollution over Irene (25.9°S), suggests marked difference in transport pathways or that Irene could be outside the influence of heavy biomass burning. The double stable layers were never observed over Irene, because at 20°S descending motion is dominant throughout the troposphere over the subcontinent, marking the southerly limit of the descending limb of the Hadley cell.

It is worth noting that the levels of ozone remained above 50 ppbv for the three sites in the sub-tropics and the tropical regions respectively in the first week of September. The general spatial trend demonstrates a general increase in ozone concentrations from sub –tropics to the tropics.

**Equatorial ozone**

The ozone episodes at the equator are shown in Figure 3.4. Using ozonesonde results for Nairobi, Kenya (1.3°S, 36.8ºE) located several hundred kilometres away from major areas of biomass burning activities. The highest ozone value noted was about 40 ppbv at 2.5 km above sea level on 6 September 2000. The ozone value over Nairobi was

comparably lower than the ozone concentrations observed on the same day for the all the other sites of southern Africa.
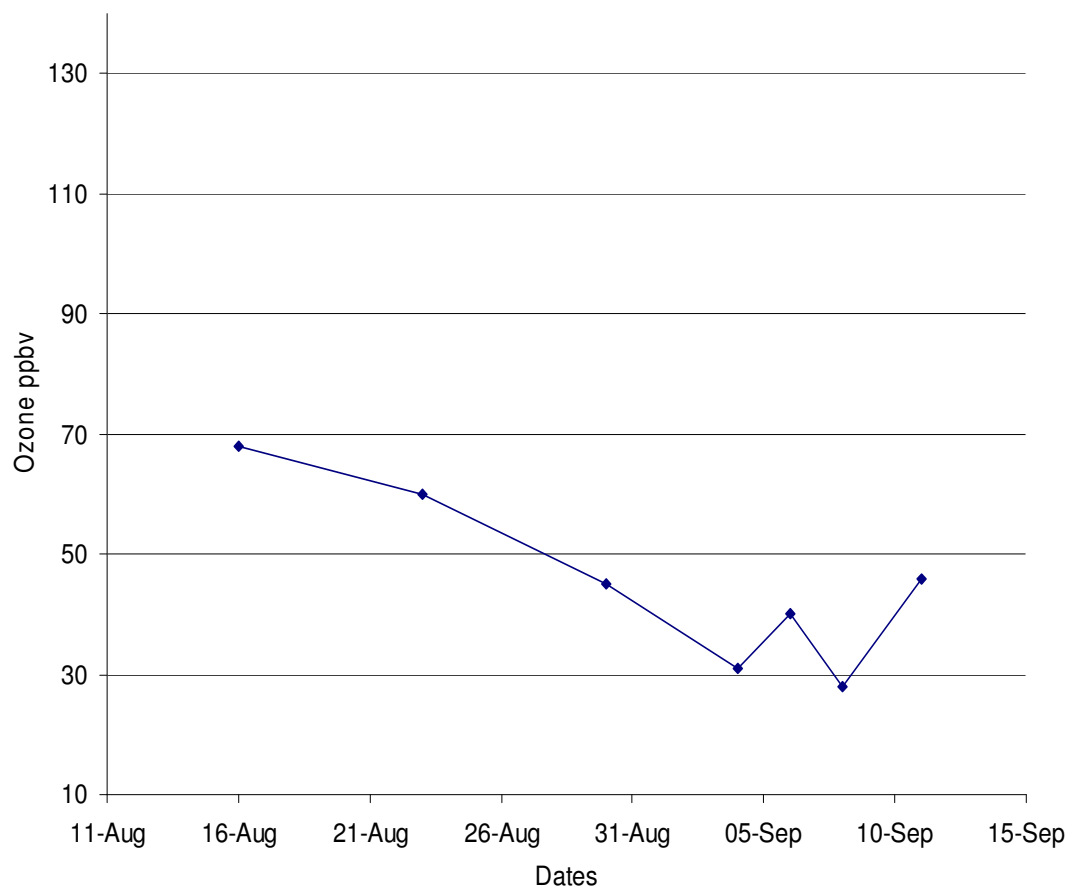


Figure 3.4     Equatorial ozone episodes at Nairobi during SAFARI 2000.

On average, the ozone levels over Nairobi, ranging between 29 - 69 ppbv, during the SAFARI 2000 period were much lower than Irene concentrations for the same period, which ranged between 45 - 85 ppbv and Lusaka with a range of 80 - 135 ppbv. This implies that Nairobi was under distinctly different meteorological transport regimes relative to southern Africa sub-region and was clearly free from any biomass burning influence during the study period. The prevailing wind regime for Nairobi during the month of September is mainly north-easterly from the Arabian Desert in the Middle East, a region devoid of any biomass fire.

**Spatial distribution of ozone during SAFARI 2000**

The analysis of the various aircraft flights for both South African Aerocommanders, during the SAFARI 2000 will provide a better understanding of the spatial distributions

of tropospheric ozone over the region. The spatial distribution from all the JRA and JRB flights is shown in Figure 3.5.

Higher ozone concentrations were observed north of 25ºS towards the tropics. The eastern sector of the southern Africa sub-continent shows equally high levels of ozone concentrations, particularly over most of Mozambique, eastern Zimbabwe and also parts of northern Namibia. The spatial coverage does not include any part of Zambia and therefore individual flights need to be analysed to pick up details from the two flight measurements conducted over Zambia, among other flights of interest.
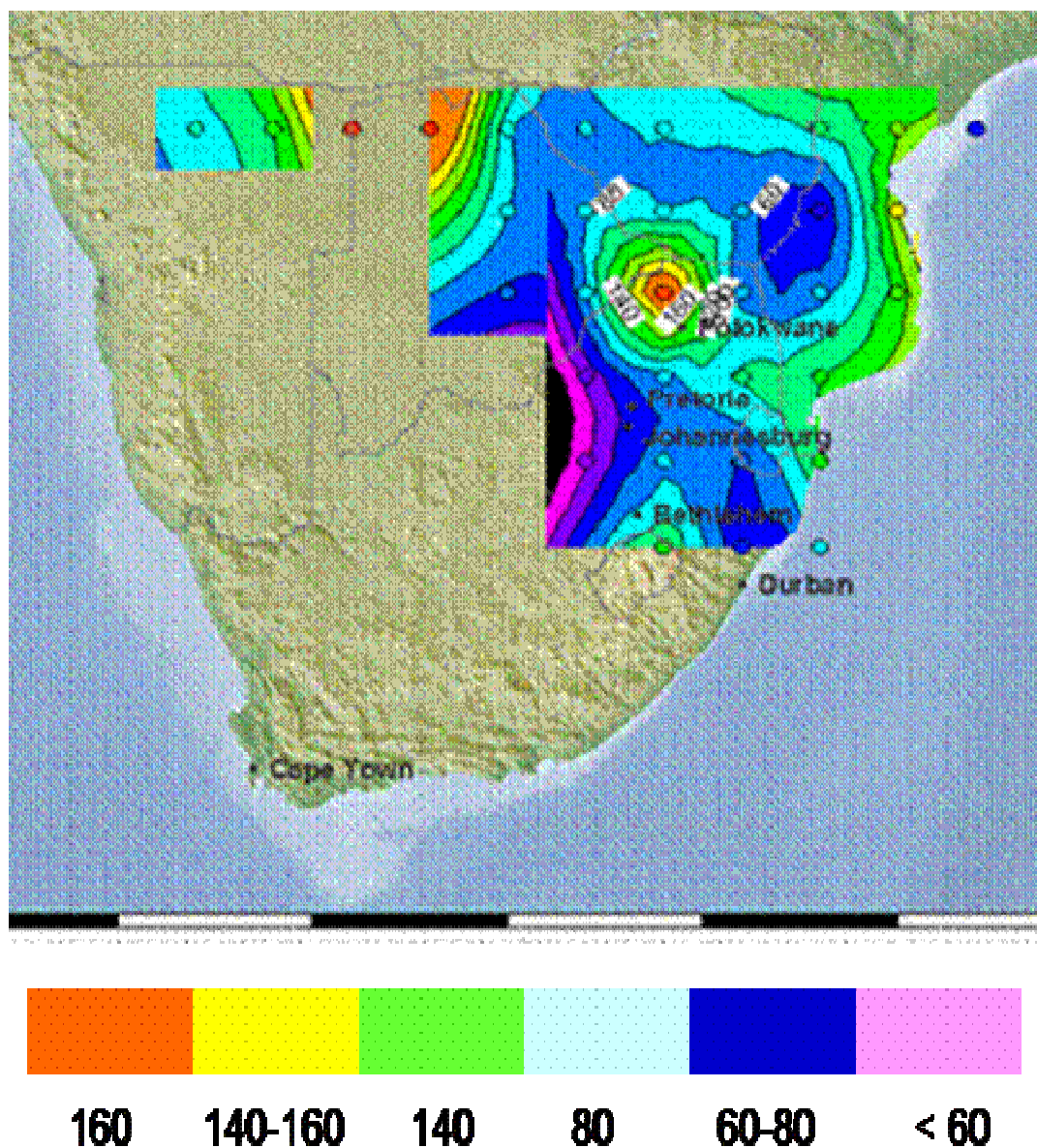


Figure 3.5    Spatial distribution of tropospheric ozone concentrations (ppb) measured by JRA & JRB during SAFARI 2000. Contours were based on average ozone concentrations measured on board the two research aircraft.

In order to study the spatial distribution of ozone in greater detail, flights were retrospectively selected for intensive study. Flights were selected that had recorded regions of enhanced ozone concentrations.

**Polokwane to Inhaca Island, Flt a20000824**

The aircraft flew from Polokwane on 24 August 2000, through hazy conditions till Maputo. It circled at 1000 ft (983 hPa) just north east of *Inhaca Island*. The horizontal transect (Figure 3.6) shows enhanced ozone concentrations of ~70 ppbv and 80 ppbv measured both at Polokwane and Inhaca Island respectively.

The vertical ozone profile (Figure 3.4c) reveals high ozone values (80 ppb) below the boundary layer (1 - 1.7 km) with a gradual decrease aloft. Thus revealing that the high ozone values for this flight were boundary layer phenomena only.

The enhanced ozone values observed over Polokwane can further be attributed to the fires as seen on the satellite fire counts denoted by coloured dots (Figure 3.4d). The purple and orange dots show the fire counts on 24 August 2000. Thus, the Polokwane–Inhaca return flight was mainly through fires *enroute*. However, the higher ozone values over Inhaca Island are not attributable to fires directly as fires were not observed on the island itself. The transport patterns addressed in Chapter 4 will shed more light on this.
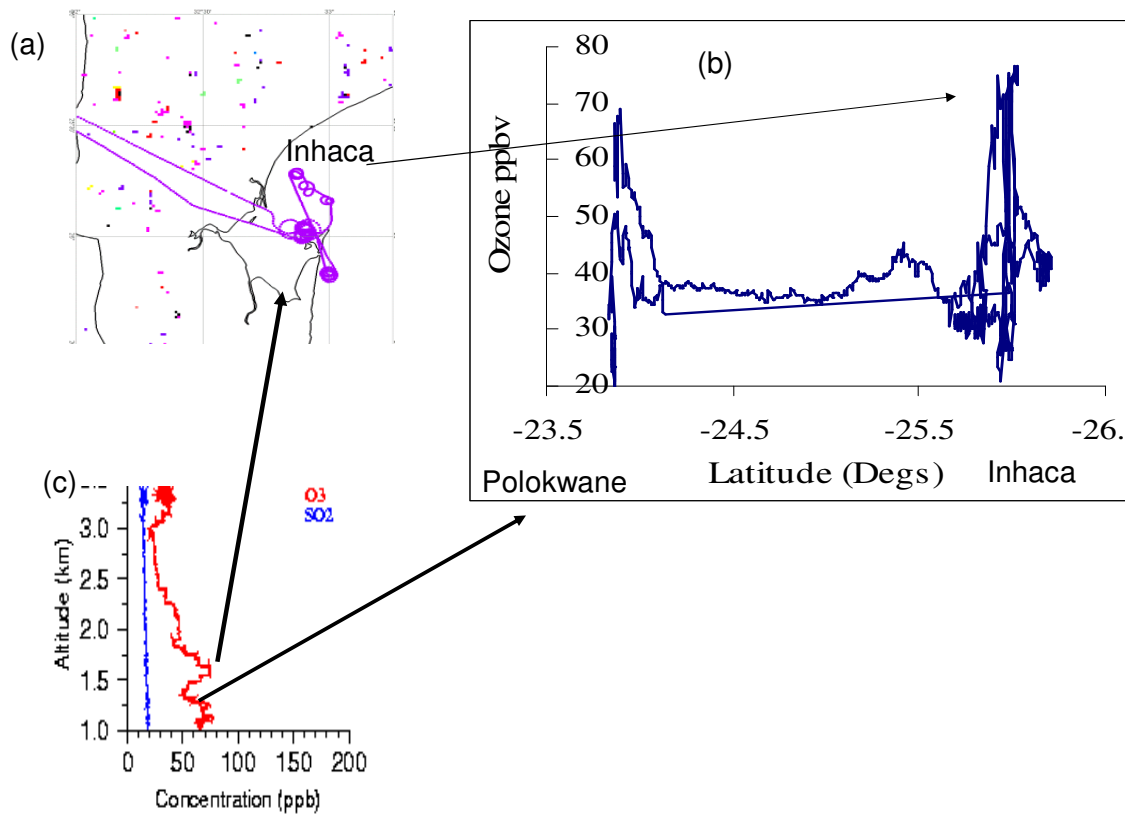
Figure 3.6       (a) Purple spiral path of as the aircraft circles over Inhaca Island
taking measurements on 24 August 2000; (b) Horizontal transect from Polokwane
to Inhaca Island; and  (c) Ozone vertical profile for the flight.

**Polokwane – Masvingo – Beira, Flt a20000829**

This flight sampled conditions over Zimbabwe and central Mozambique, and did a
vertical profile over Beira on 29 August 2000. The results from the horizontal transect
(Figure 3.7b) show 100 ppbv of ozone measured near Beira, a coastal town of
Mozambique. Otherwise, on average, less than 30 ppbv of ozone was recorded during
most of the flight. Thus, most of the flight sampled background ozone.  The vertical
ozone profile shown in figure 3.7c shows that elevated ozone (100 ppb) was observed at
1500 m above surface at Beira. The transport analysis in chapter 4 will shed light on the
origin of this elevated ozone concentration over Beira.
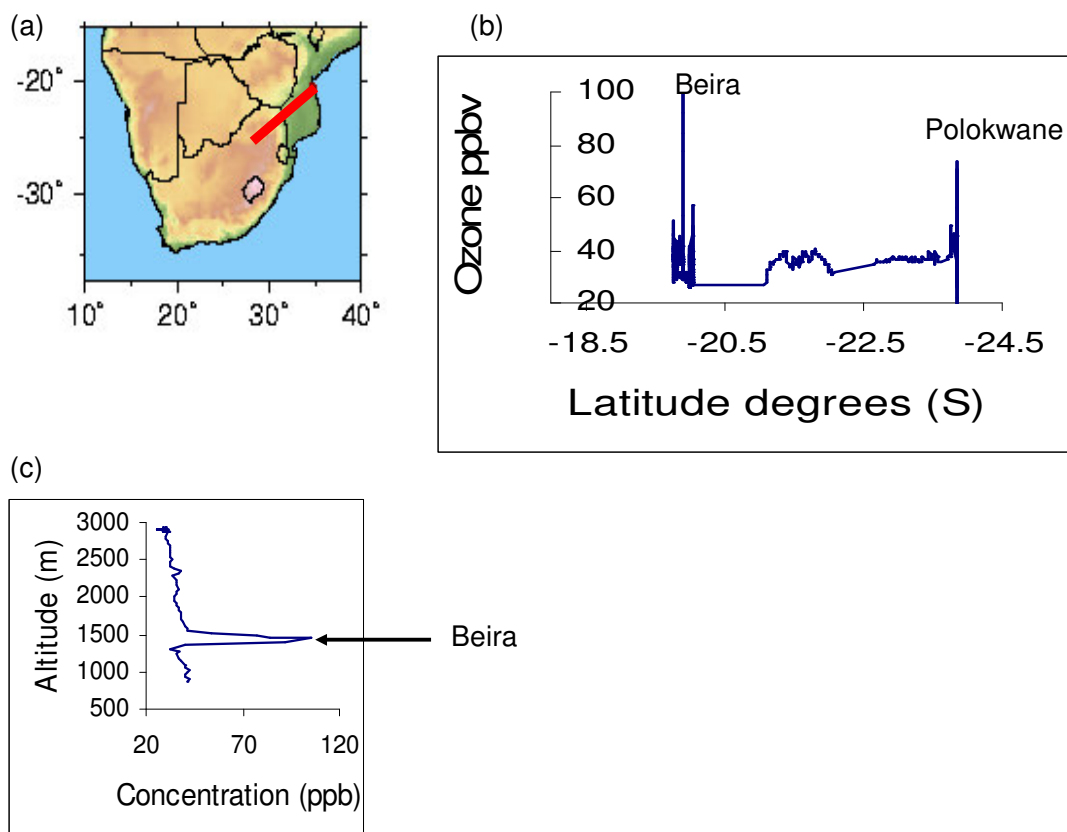
Figure 3.7    (a) Polokwane - Beira flight path; (b) Horizontal transect between Polokwane and Beira; and (c) Ozone vertical distribution over Beira on 29 August 2000.

**Flight through industrial region of South Africa Flt a20000901**

The flight on 1 September 2000 was undertaken to sample boundary layer over the Highveld industrial region of South Africa. The ozone measurements were taken from Polokwane (23.86°S, 29.4°E) to Bethlehem (28.28°S, 28.34°E) on a north - south flight track. The flight steps are shown in Figure 3.8a while the horizontal transect (Figure 3.8b) reveals significant variations of ozone concentrations along the flight.

A - B and C - D denote the areas with the highest ozone concentrations along the flight track. Flight step A - B is close to Polokwane (60 ppb), in the vicinity of biomass burning areas, while C - D was the flight through the Highveld region (>45 ppb). A general north - south decline trend in ozone concentration values is discernable (Figure 3.8c). The ozone concentrations decreased drastically to values below 30 ppbv at Bethlehem. The only part of the flight with ozone pollution slightly above 45 ppbv was over the South Africa's Highveld region, where the country's industries are concentrated and urban influence prevalent. The biomass burning influence on ozone

close to Polokwane shows that this influence extends further than 20ºS to about 25ºS latitude. The spatial variation of ozone concentrations, from Polokwane in the north to Bethlehem in the south, portrays a decreasing N-S gradient (figure 3.8b).
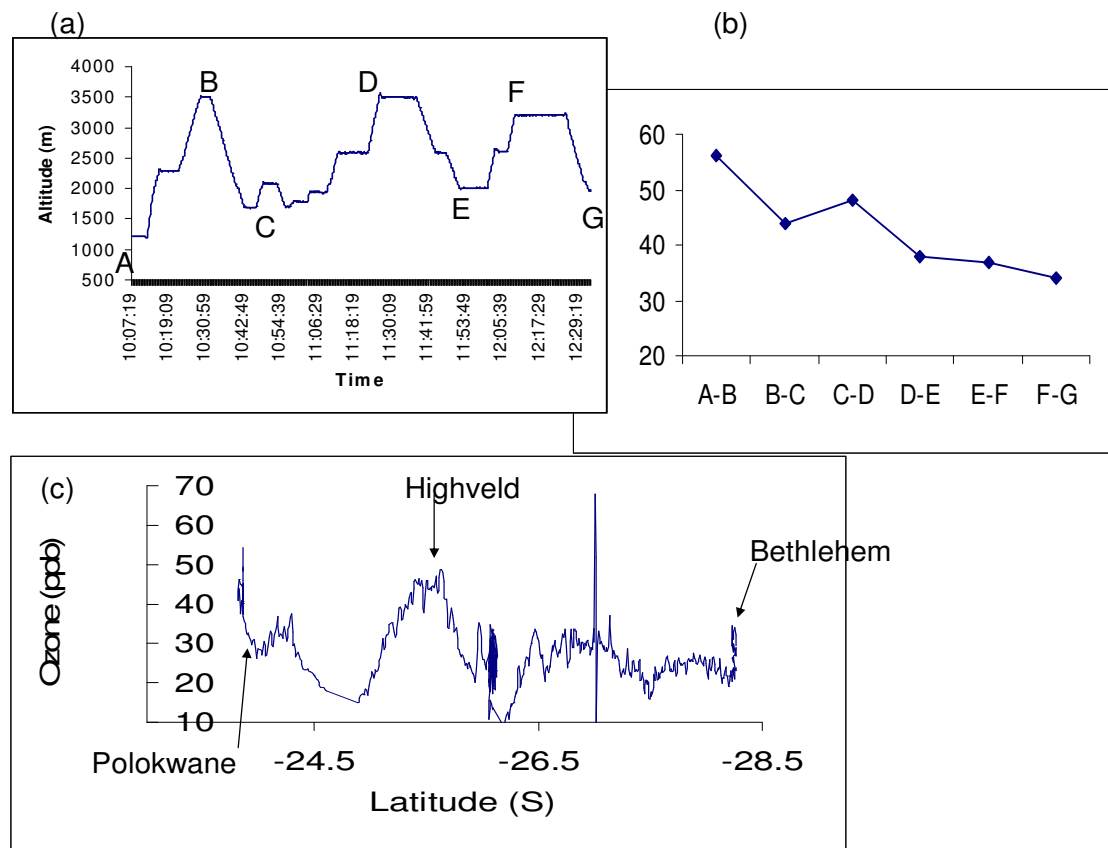


Figure 3.8    (a) Flight steps from Polokwane to Bethlehem; (b) Average ozone concentrations (ppb) measured along the transect between Polokwane and Bethlehem through Highveld industrial region (ppb); (c) Ozone peaks measured between Polokwane and Bethlehem on 1 September 2000.

**Tropical to sub-tropical tropospheric ozone distribution**

The flight path from Polokwane, through Bulawayo, Lake Kariba and finally to Lusaka was intended to measure the characteristics of boundary layer along a N - S transect on 5 September 2000 (Figure 3.9).
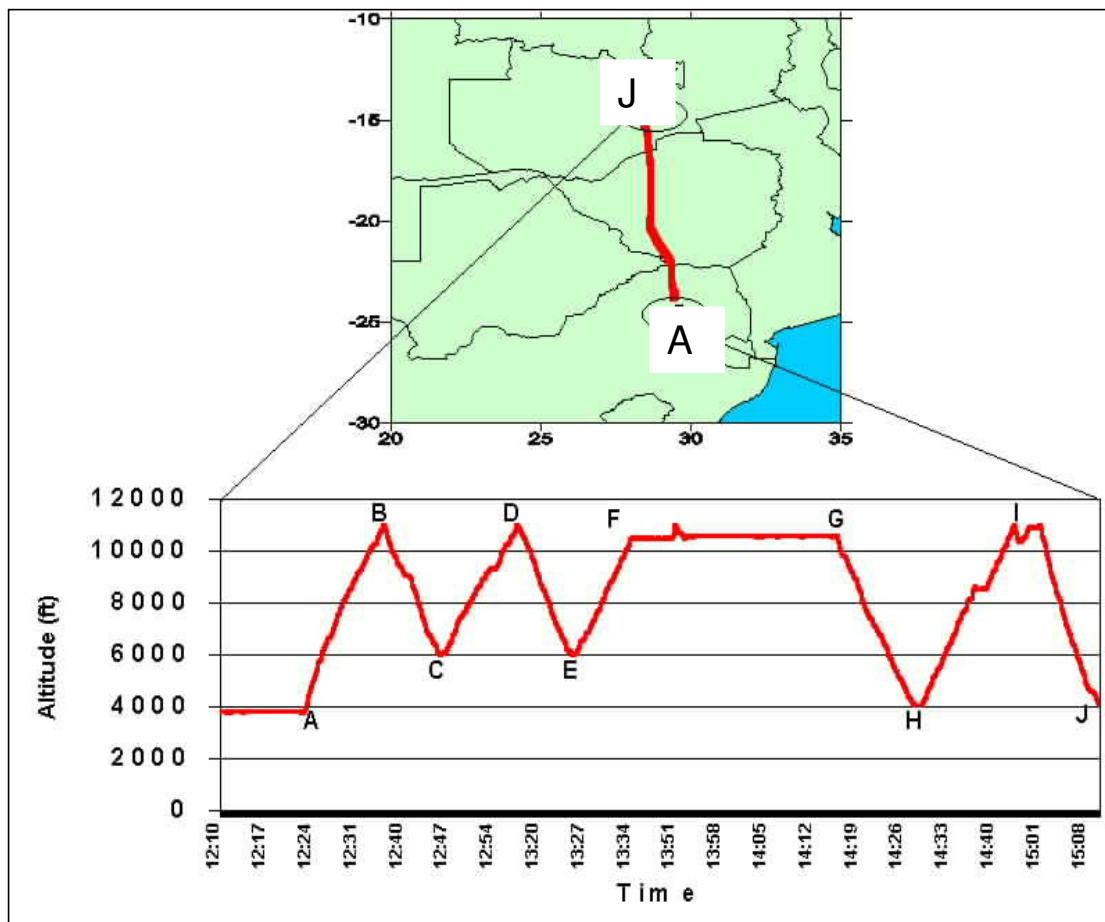
Figure 3.9     JRA flight path from Polokwane to Lusaka on 5 September 2000.


Two distinct ozone maxima of about 60 ppbv were observed on flight tracks B - C and H - I, near Polokwane and Lusaka respectively (Figure 3.10a). These ozone pollution levels were relatively high compared to background levels for southern Africa at 25 - 30 ppbv. The vertical ozone distributions over areas near Polokwane and Lake Kariba reveal relatively high ozone concentrations 73 – 79 ppbv between 1500 m and 3500 m above the ground (Figures 3.10b and 3.10c).

High ozone concentrations observed over Lusaka lasted for one week (5 - 11 September) though on a decreasing trend as discussed earlier on (Figure 3.3).
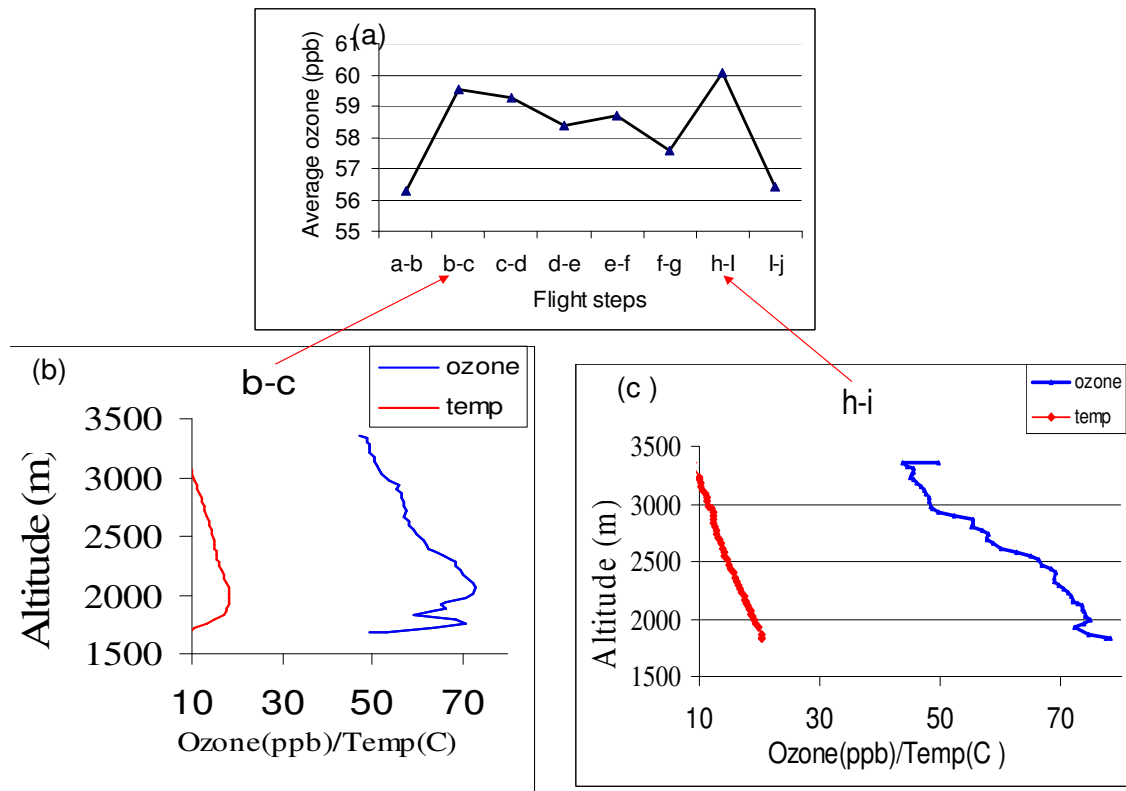
Figure 3.10 (a) Ozone variation between Lusaka and Polokwane on 5 September; (b) vertical distribution along flight step b – c; and (c) vertical distribution along flight step h - i.

Ozone measured on 5 September during the Polokwane–Lusaka flight is illustrated by the horizontal transect in Figure 3.9. The ozone pollution levels remained generally high throughout the flight path ranging between 70 - 80 ppbv. This shows that ozone formation was probably from the same precursor sources, in this case biomass

Intense biomass burning was evident throughout the whole flight from Polokwane to Lusaka (Figure 3.11). This observation suggests that precursor gases from the fires triggered the high ozone levels encountered along this path.
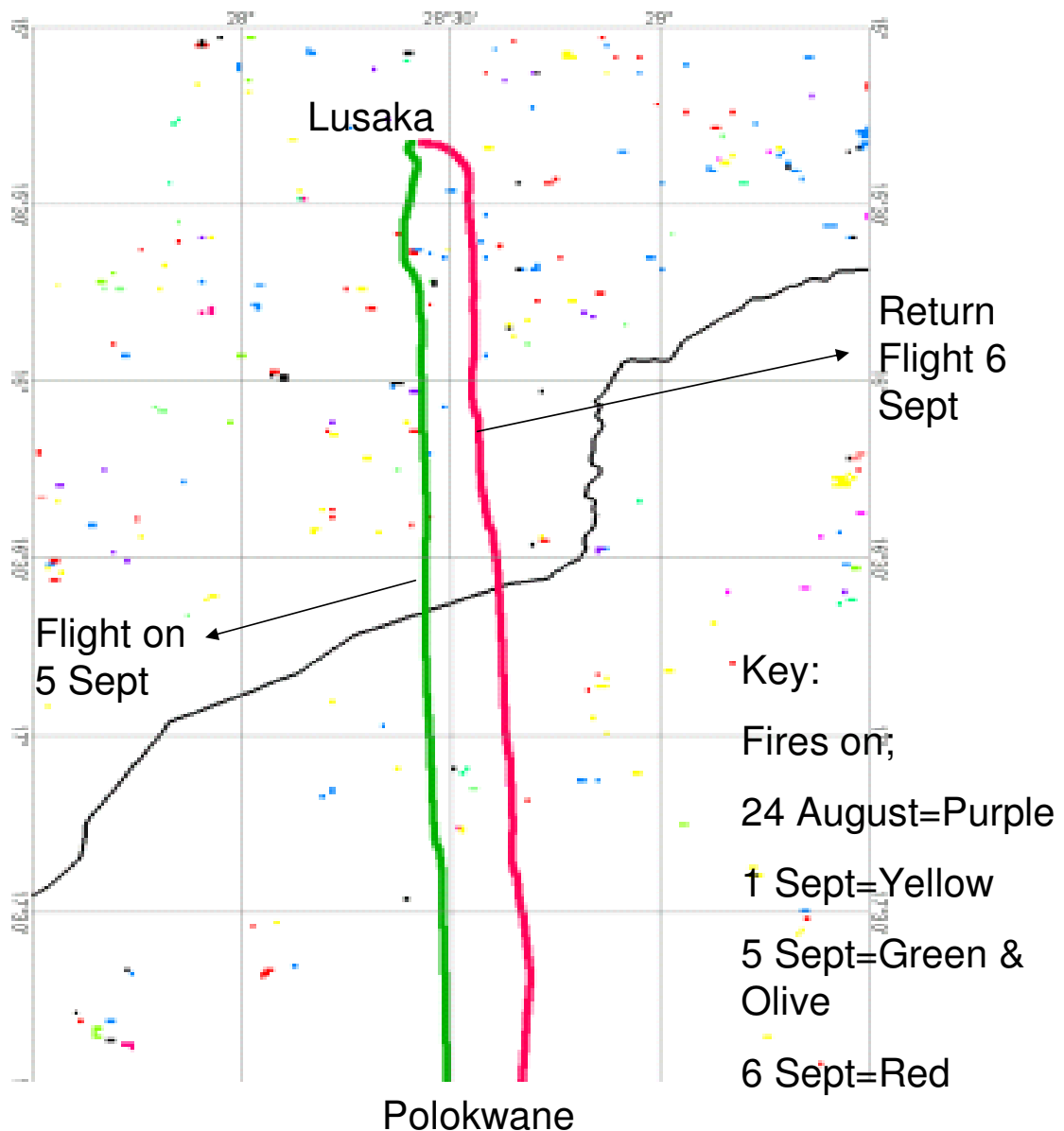
Figure 3.11     Distribution of fires over southern Africa on days corresponding to JRA flights for SAFARI 2000: 24 - 28 August: 1-11 September: 16, 22 and 25 September 2000.


**Satellite view of ozone distributions over southern Africa**

The TOMS tropospheric ozone distribution is illustrated in decadal periods (Figures 3.12a, b, c and d). The four images progressively show a build up of ozone in the tropics. Two distinct ozone accumulation maxima, over the Atlantic Ocean stretching to western parts of Zambia; and over Mozambique and the Indian Ocean are evident in the first and second decadal periods of September (Figures 3.12c and d).

Two ozone maxima are observed on 5 September over Lusaka and Polokwane respectively (Figure 3.10a) corresponding to distinct TOMS total ozone accumulations across the sub-continent.
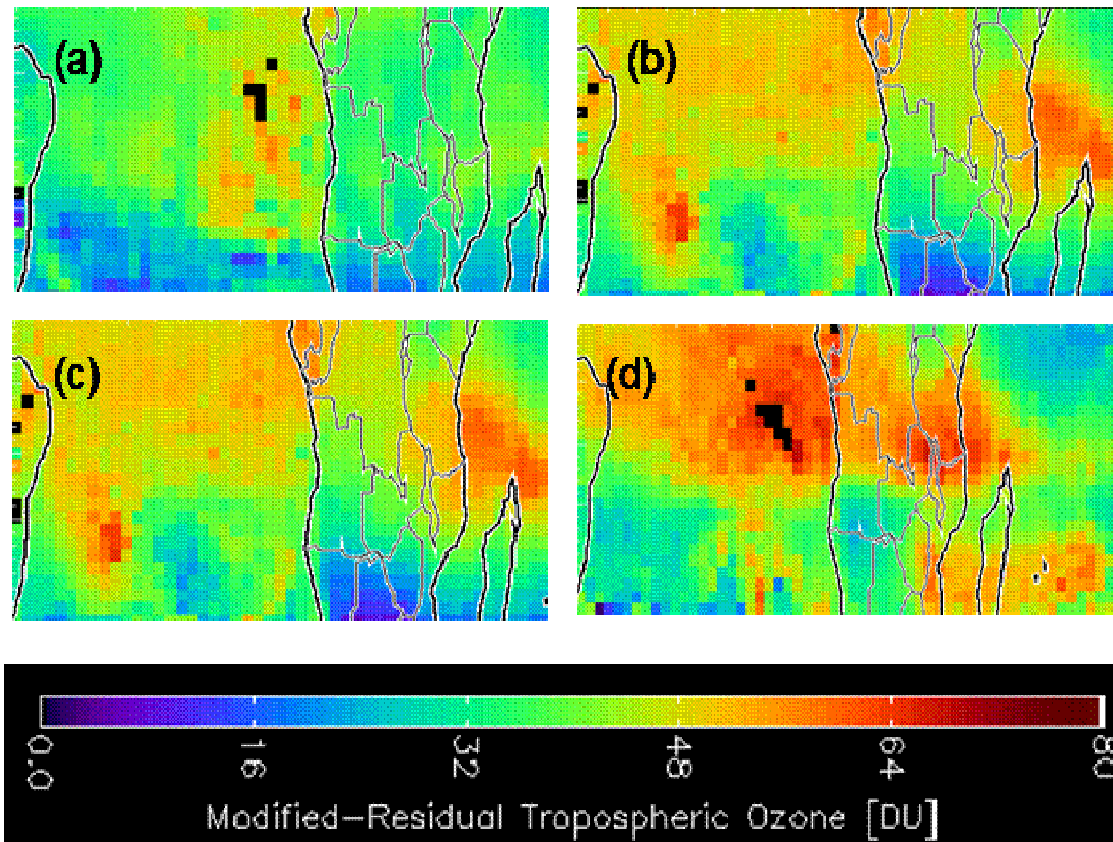


Figure 3.12    TOMS ozone distribution during the decadal of (a) 27 August - 4 September (b) 30 August - 7 September (c) 7 - 15 September (d) 15 - 23 September (Courtesy of NASA/Code 916/SK2/TOMS/AM Thompson).

The TOMS total ozone images indicate a gradual build up of ozone in the eastern sector of southern Africa during September. This temporal trend of ozone concentrations trend is further supported by observations derived from aircraft ascents and descents at Polokwane airport during the August and September (Figure 3.13). Daily ozone values were calculated by averaging concentrations between 1 and 2 km above surface.
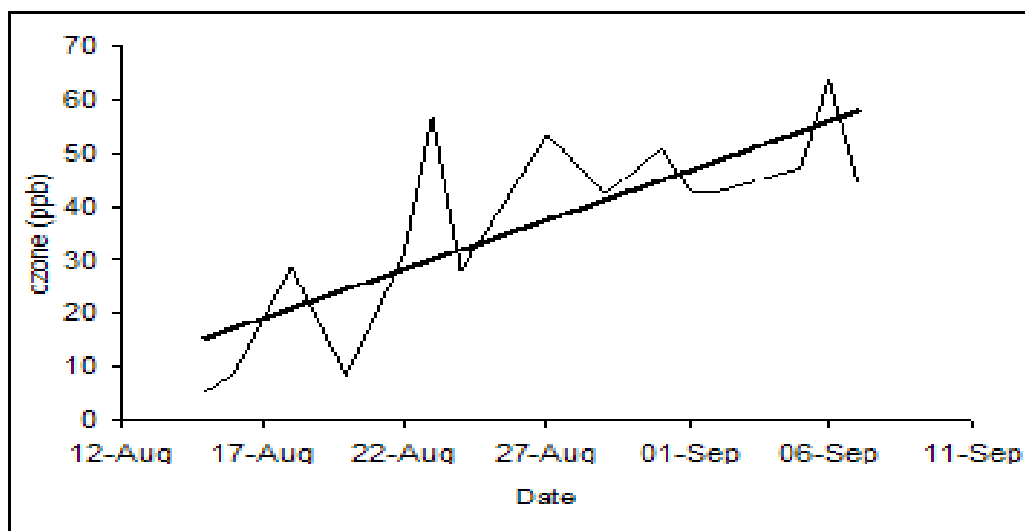
Figure 3.13    Temporal increase in average daily ozone over Polokwane between 1–2 km during August and September 2000.

An increasing trend in daily average ozone ranging from 15 to 60 ppbv at Polokwane is evident in Figure 3.13 This trend is very similar to the TOMS satellite observed tropical increase of tropospheric ozone. Was there a link between this trend and the spread of fires in the region?

## Biomass burning over southern Africa in September 2000

### Distribution of fires over southern Africa

The daily fire counts clustered in 5-day composites in September for southern Africa sub-region are shown in Figure 3.14. The fire counts are shown by black dots on the map. The highest concentrations of fires were observed in first half of September, with the largest spatial extent of intense fires occurring in the period 1 - 5 September (Figure 3.13a). In the second half of the month there was a general reduction of fires on the western sector of the sub-continent while the eastern sector showed an increase.

On the contrary, the TOMS observations showed massive building up in the total tropospheric ozone over the western sector in the second half of the month.
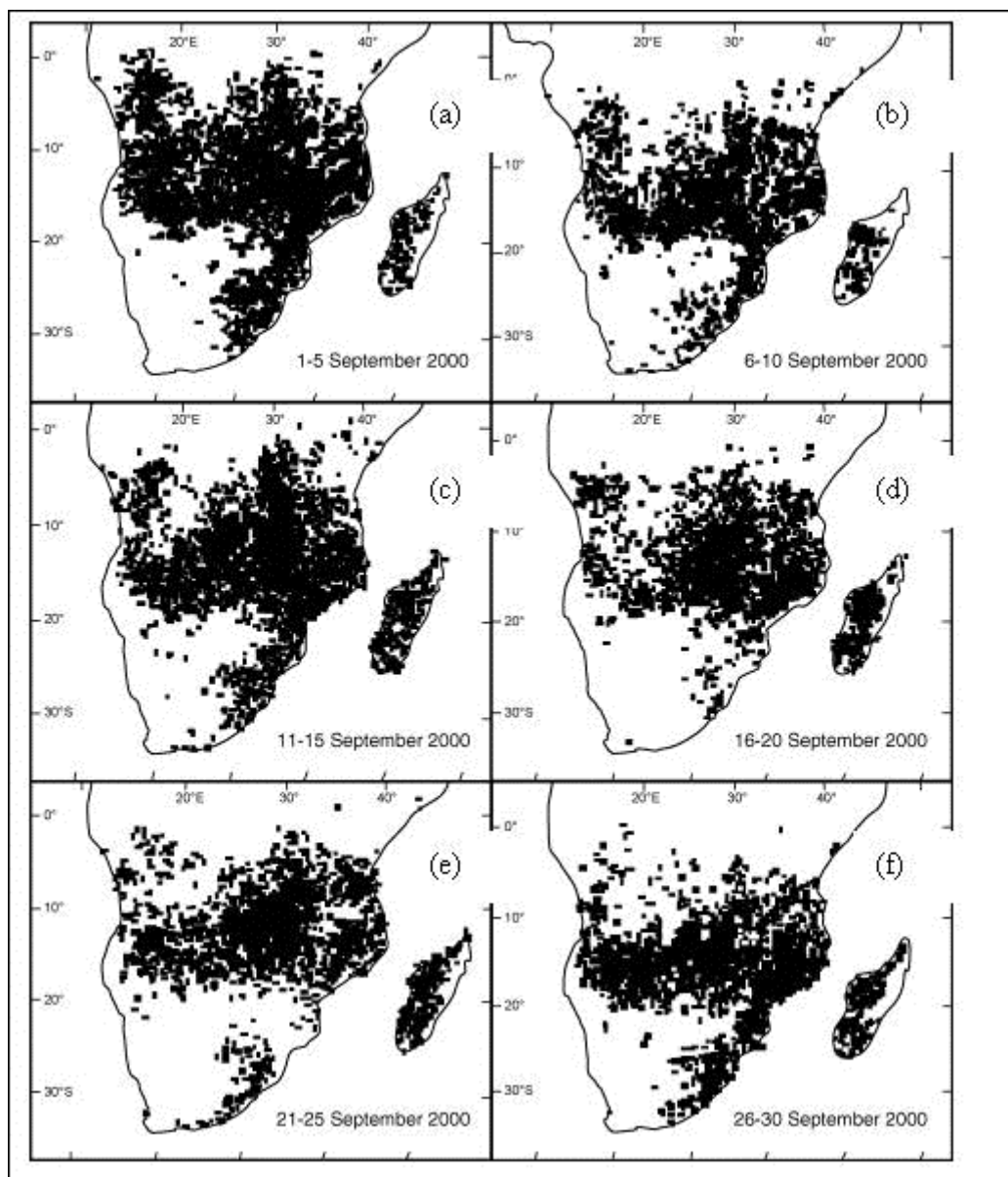
Figure 3.14     Distribution of fires over southern Africa during August - September 2000. The fires are clustered in 5-day composites and respective dates appended on the each fire map.

**Category classification of the fires**

To understand the linkage between the fires and the ozone concentrations, the region covered by the fires with coordinates; (0º, 10ºE), (0º, 50ºE), (30ºS, 10ºE), (30ºS, 50ºE) was sub-divided into 10º by 10º grid blocks. The blocks are denoted A to J as shown in Figure 3.15a.

(a)

| | 10ºE | 20ºE | 30ºE | 40ºE |
|---|---|---|---|---|

10ºS

20ºS

30ºS

| A | B | C |
|---|---|---|
| D | E | F |
| G | H | I |

J

(b)

0º

10ºS

20ºS

30ºS

| 2 | 3 | 4 |
|---|---|---|
| 4 | 6 | 5 |
| 0 | 1 | 1 |

3
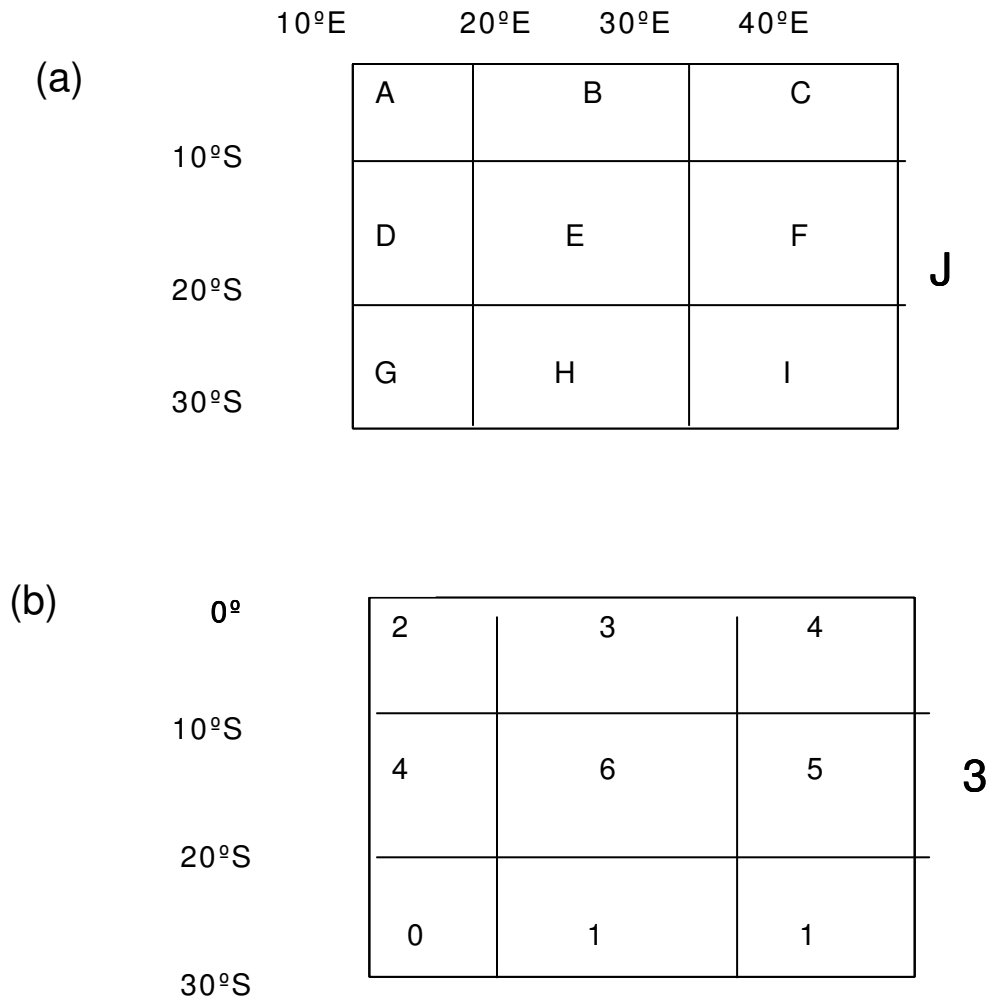
Figure 3.15    (a) 10º by 10º blocks denoted by letters A to J; (b) Scores out of six for fire coverage in the six 5-day clusters composites for the respective blocks.

The highest scores of 6 was observed over Block E, which covers a block on Zambia and eastern Zimbabwe, followed by a score of 5 in block F. Block F covers most of Mozambique as shown in Figures 3.15c. This shows that most of the fires were based in the three respective countries for most of September.

Though high ozone concentrations were measured over the eastern block, the link between fire produced precursor gases and ozone production is not necessarily direct. The TOMS satellite images showed massive build up of total tropospheric ozone over the Atlantic Ocean and western areas of Angola despite the fact that the fires were decreasing towards the end of the month of September.
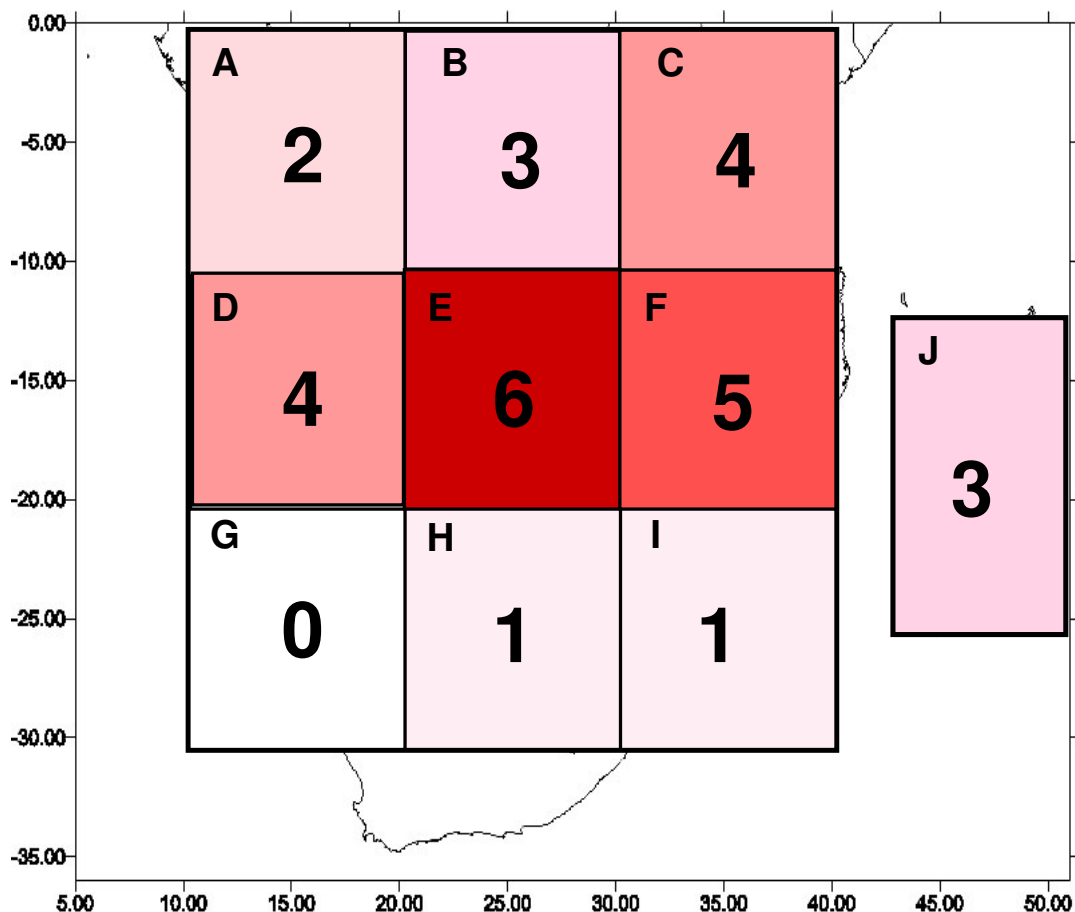
Figure 3.15 (c) Colours that suggest the intensity of the fires in the respective regions denoted by the scores of 1-6 during the campaign period September to October 2000.

The next discussion is an example of a flight through fresh plumes, which does not necessarily indicate high ozone concentrations within fresh plumes.

**Flight a20000818: Polokwane – Madikwe fire**

The flight sampled fire plume (fresh biomass burning plume) from a prescribed burn near Madikwe. Figure 3.16a shows enhanced ozone concentration of 66 ppbv measured near Polokwane. The vertical ozone profile (Figure 3.16b) shows that the enhanced ozone concentration was measured at an altitude of ~ 1.7 km above the ground level at Polokwane. This was the highest ozone concentration measured along the horizontal transect for this flight. On the contrary, about 20 ppbv of ozone concentration was measured at Madikwe, where fresh biomass burning was observed.

It is of interest to note that low ozone values were measured in the fresh plume at Madikwe, indicating that high ozone values were observed far from the fresh plumes

(sources). There is a time lag for the precursor gases to undergo chemical reactions to produce ozone and this takes place during the transport to the receptor areas. Polokwane is likely to be a beneficiary of this transport mechanism.
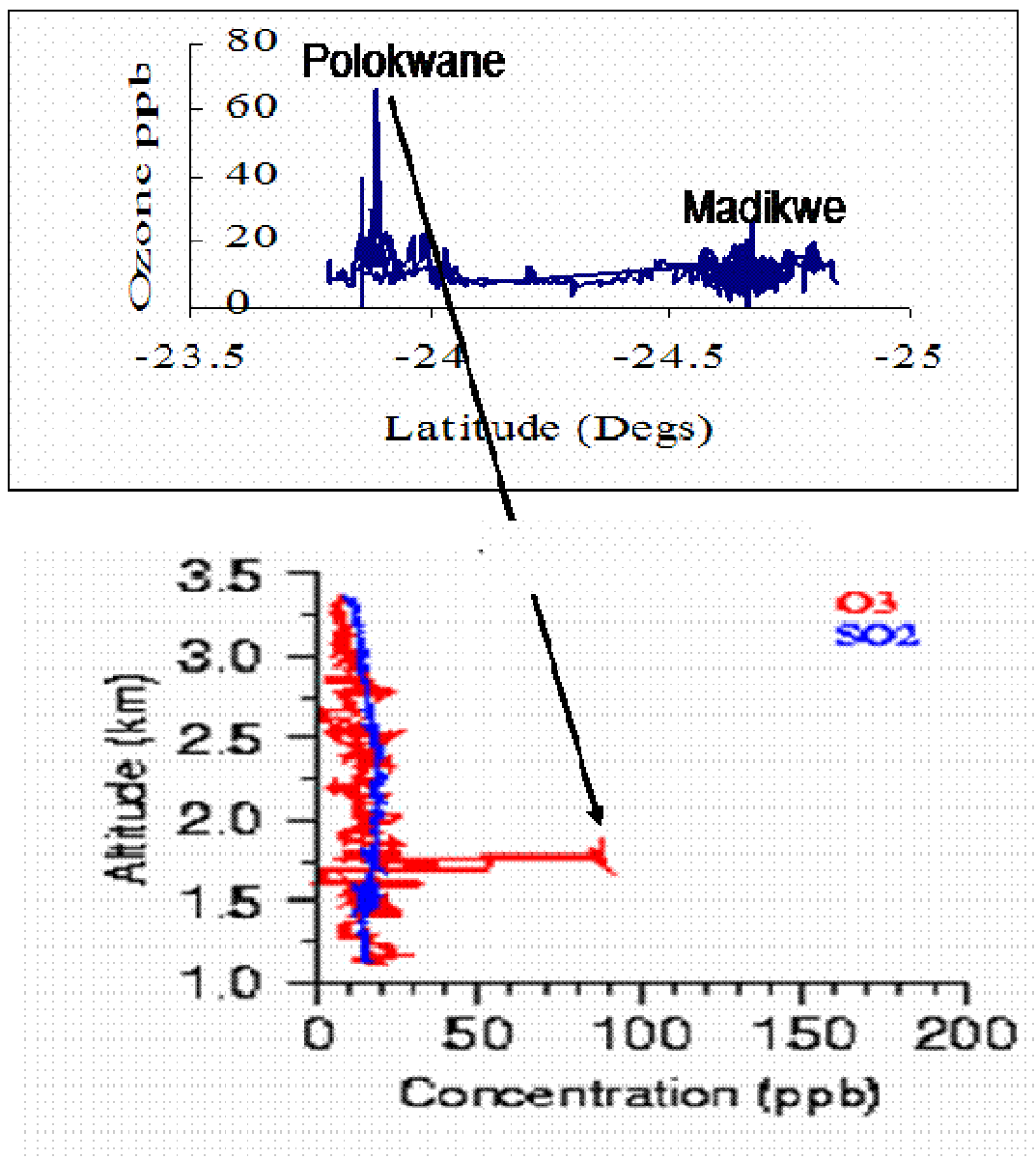


Figure 3.16    (a) Horizontal transect, from Polokwane to Madikwe (b) Ozone vertical profile for the entire flight on 18 August 2000.

**Fire categories and respective trajectory pathways**

Trajectory computations were carried out in an attempt to explain the accumulation of ozone over the western and the eastern sectors of the southern Africa. Each trajectory was computed using the coordinates of the centre of each of the blocks in Figure 3.15. The trajectories are shown in Figure 3.17.

The easterlies as well as re-circulation of air helped in building ozone accumulation in the western sector. Transport pathways for Madagascar (block J) in Figure 3.17a show air masses circulating through Indian Ocean and back to the western areas of Angola into the Atlantic Ocean. The air transport to the Atlantic Ocean from the northern parts of Mozambique is shown in Figure 3.17b. This shows that transport of biomass burning products by easterlies and circulation patterns contribute to the build-up of ozone over Atlantic Ocean.
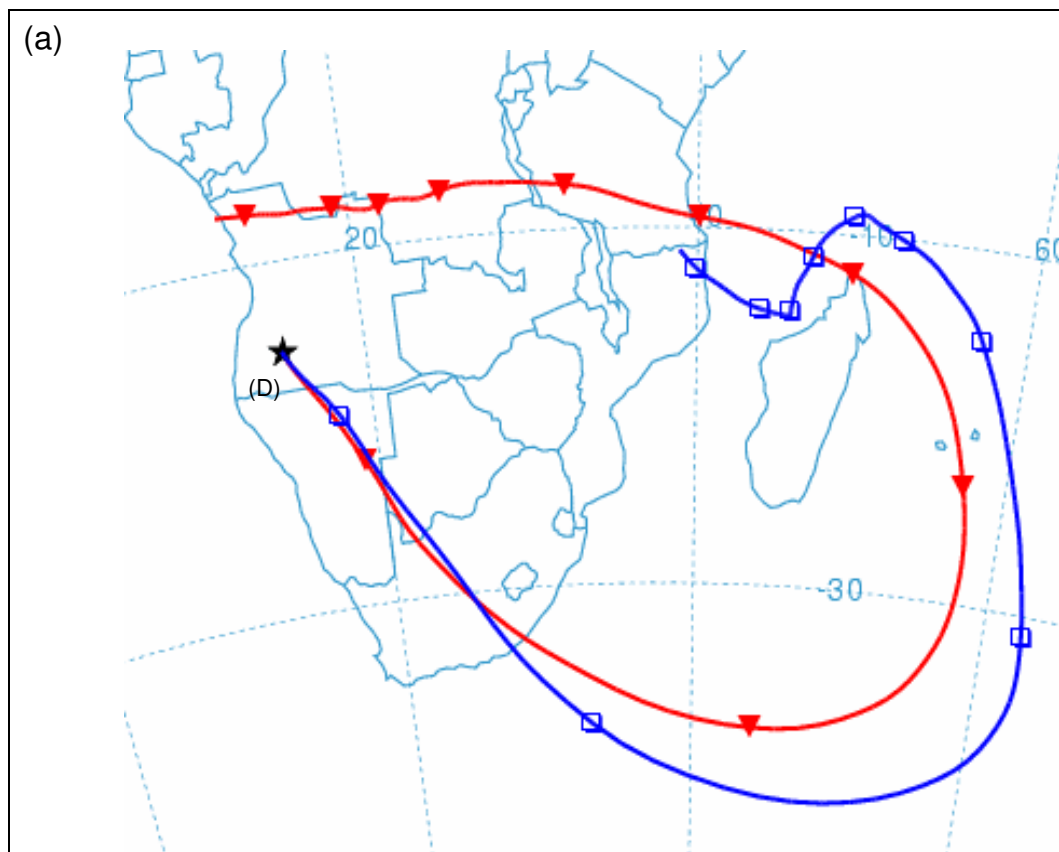


Figure 3.17a   Backward trajectories for block D as shown in Figure 3.15, computed from 15 September for ten days.  Each point along the trajectory pathway represents one day (24h00). colour codes: Red = 5 000m and Blue = 3 000 m.
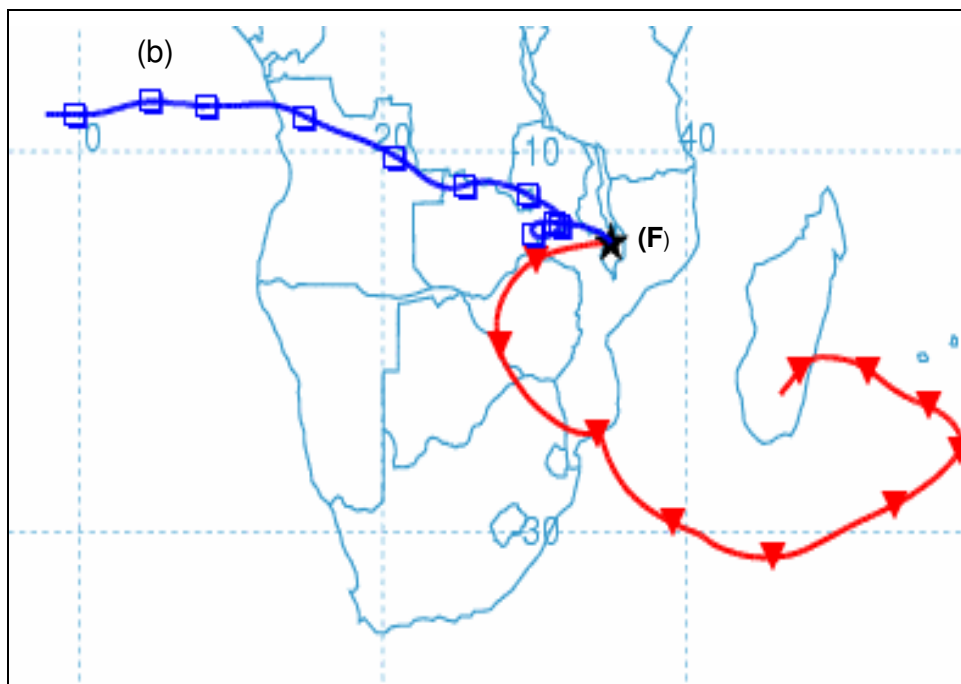
Figure 3.17b   Backward trajectories for block F as shown in Figure 3.15, computed from 15 September for ten days.  Each point along the trajectory pathway represents one day (24h00). colour codes: Red = 5 000m, Blue = 3 000 m

In the last week of September, two distinct accumulation of ozone were observed over Madagascar Island, parts of northern Mozambique and southern Tanzania (Figure 3.12d). Back trajectories were computed for two locations over Madagascar and two locations off the Mozambique coast (Figure 3.18a and b) to establish the origin of the two ozone accumulations.

The back trajectories in Figure 3.18a indicate that precursor gases originated from the fire areas of the eastern sector of the sub-continent all the way across to Madagascar Island.  This contributed to the ozone accumulation over Madagascar Island and its immediate surroundings. Figure 3.18b shows air flow from southern Atlantic Ocean, through the biomass burning areas of the sub-continent, re-circulation over Madagascar fire region and finally to northern Mozambique and southern Tanzania. This accounts for the accumulated total ozone in northern Mozambique and parts of southern Tanzania.
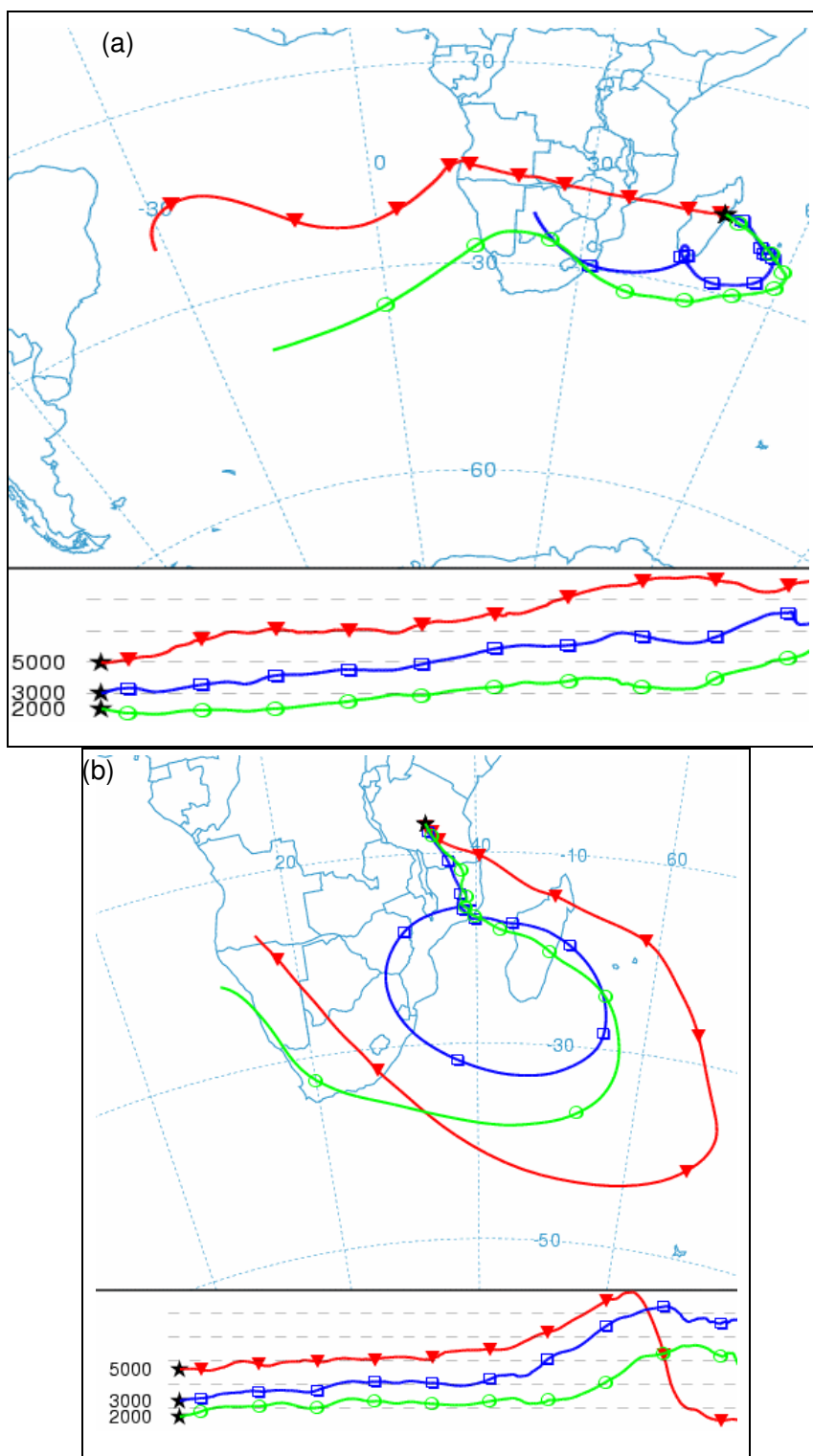
Figure 3.18    Back trajectories for areas (a) at Madagascar Island (b) southern
Tanzania starting from 29 August 2000.  The markers along the trajectories
indicate the start of each day (24h00).

The elevated ozone observed on 29 August at 1500 m above Beira discussed
earlier on (Figure 3.8c), can similarly be explained through back trajectories. The air

transport to areas near Beira on 29 August was from the fire areas of southern Zimbabwe and Zambia 5000 m and near the surface the flow was from the ozone accumulations observed near Madagascar Island (Figure 3.19).
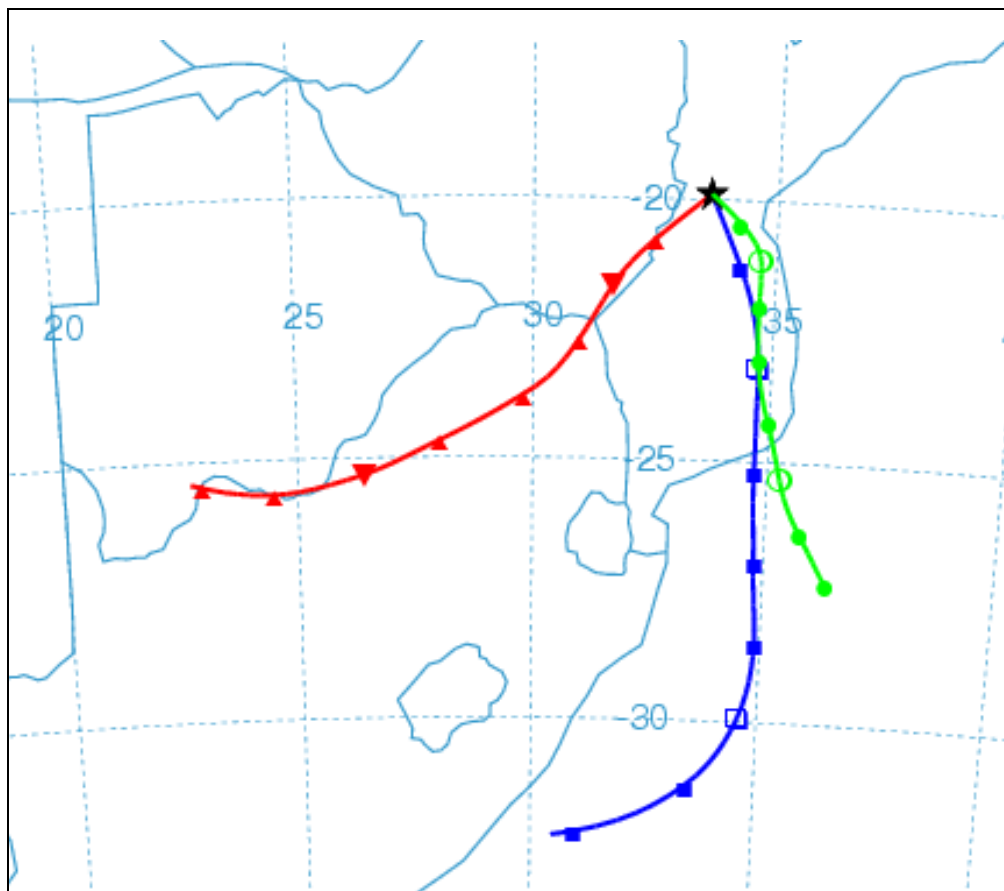


Figure 3.19    Back trajectories ending near Beira on 29 August 2000. colour codes: Red = 5 000 m, Blue = 3 000 m and Green = 2 000 m.


In this chapter, three key findings have been revealed:

- The observed elevated ozone concentrations during SAFARI 2000 campaigns were due to the influence of the regional biomass burning activities.
- The spatial ozone distribution patterns have shown the existence of a N - S ozone gradient in the sub-continent.
- The transport of air masses through the regional biomass burning areas was the major factor in the build-up of the observed TOMS total ozone in the eastern and Atlantic Ocean areas.

The next chapter will address the influence of changing meteorological conditions to the observed ozone concentrations.

# CHAPTER FOUR

# TRANSPORT PATHWAYS AND ASSOCIATED METEOROLOGICAL CONDITIONS

This chapter will examine meteorological conditions alongside the trajectory transport pathways to further characterize the ozone over the southern African region. In order to capture the different meteorological conditions, classification of the synoptic features will be undertaken and highlight the corresponding ozone and other atmospheric constituents.

The monthly variation of ozone at Irene and Nairobi sites will be discussed to establish whether high ozone pollution was only a feature observed during SAFARI 2000 specifically.

## Classification of synoptic features during SAFARI 2000

The synoptic feature classification for the sub-tropical region, band 1, has been based on Polokwane site (Figure 4.1) for the SAFARI 2000 study period

Low surface pressures dominated Polokwane in band 1 during the first week of September (Figure 4.1). A westerly wave was also observed in the lower levels during the same period. High levels of ozone were observed during the period 4-6 September, with 6 September having the highest ozone for Polokwane (Figure 3.1b).

In the same period, Band 2 region was mainly under the influence of extended Congo Air Boundary (CAB) trough at the surface, but in the upper levels, the continental high (CH) was predominant. The classified synoptic patterns with corresponding days of enhanced and low ozone provided a suitable methodology in which to select appropriate flight tracks for analysis.

The period with the most persistent feature was chosen for trajectory analyses. An exception to this criterion was a period in August, which was chosen to establish if the aerosol transport reaches Kenya, as shown by Gatebe *et al.,* 1999. The data on the 850 hPa charts provide a very probable wind flow pattern with best estimate to the existing

regional recirculation system. The works of Garstang *et al*. (1996) and Tyson *et al.* (1996) are good examples.
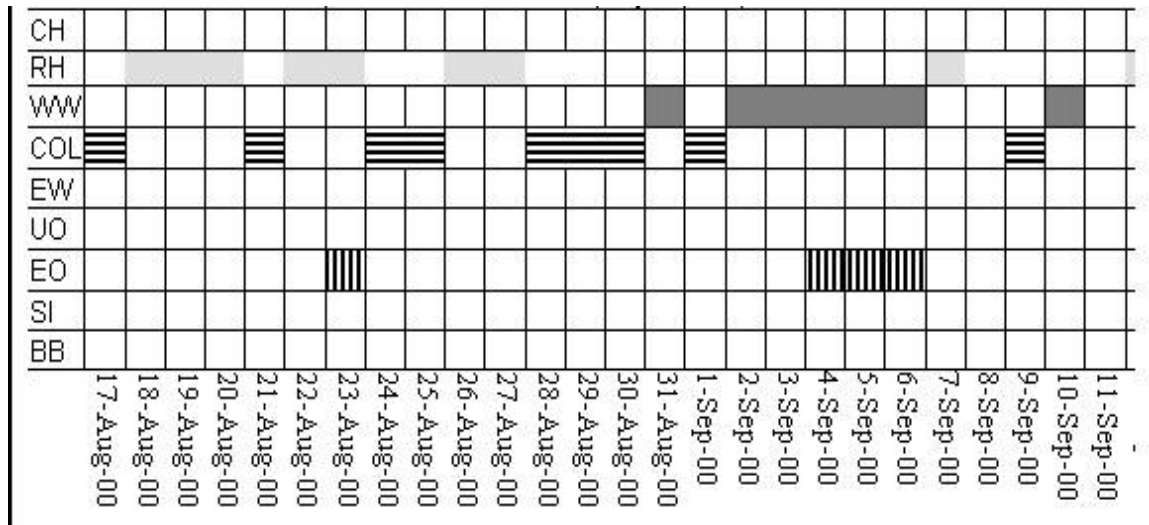


Figure 4.1      Synoptic scale circulation classification at the surface over Polokwane, between 17 August and 11 September 2000. CH = Continental high, RH = Ridging High, WW = Westerly Wave, COL = Cut Off Low, EW = Easterly Wave, UO = Unusual other, EO = Enhanced Ozone, SI = Smoke index, BB = Biomass burning

During the first week of September, the mid-level synoptic features (700 hPa and 500 hPa) were dominated by a trough system in the sub-tropics (Figure 4.2). This was a period with very high levels of ozone, particularly between 4 to 6 September and high smoke index, which preceded the enhanced ozone. Biomass mass burning was not observed during this period, suggesting that the observed high levels of ozone originated from distant fires.
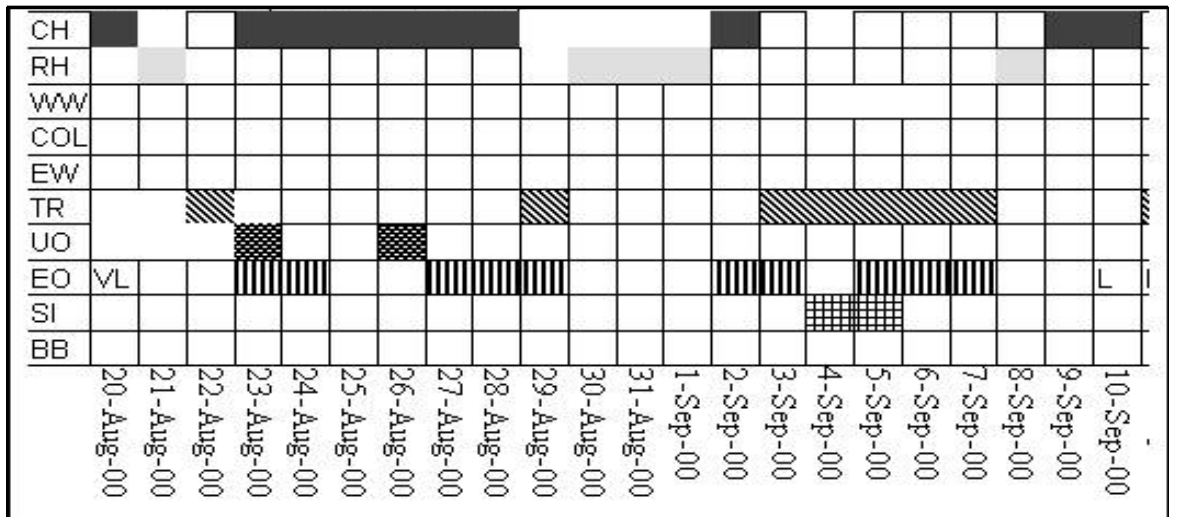
Figure 4.2 Synoptic scale circulation classification over Polokwane at 700 - 500 hPa between 20 August and 10 September 2000. CH = Continental high, RH = Ridging High, WW = Westerly Wave, COL = Cut Off Low, EW = Easterly Wave, TR = Trough system, UO = Unusual other, EO = Enhanced Ozone, SI = Smoke index, BB = Biomass burning

In contrast, on 20th August, very low concentrations of ozone were observed (12 ppbv on average) over Polokwane in Band 1 region (Figure 4.3). It is quite significant that that ozone levels on this day at Polokwane were below the background concentrations for the region. This coincided with a very strong surface Indian Ocean ridging high (RH).
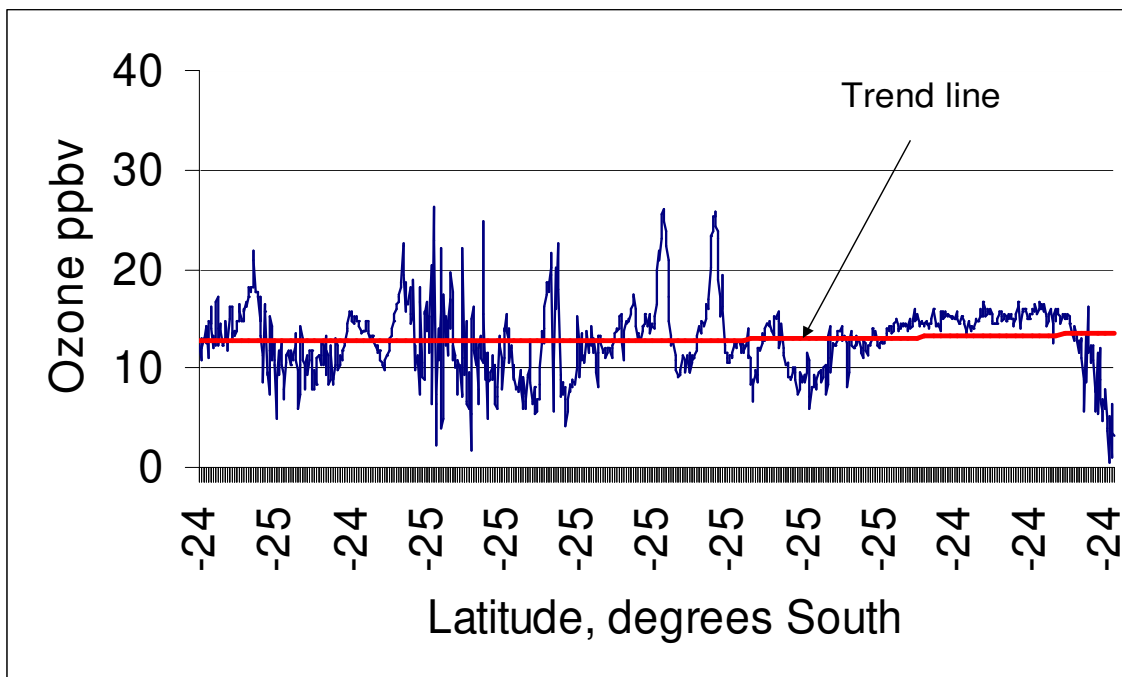
Figure 4.3　　Lowest ozone values during SAFARI 2000, on 20th August, flight measurements around Polokwane.

Surface high ridging pressure system and Congo Air boundary flow were evident for most of the month of August. However, surface trough and easterly winds prevailed in the first week of September (Figure 4.4).
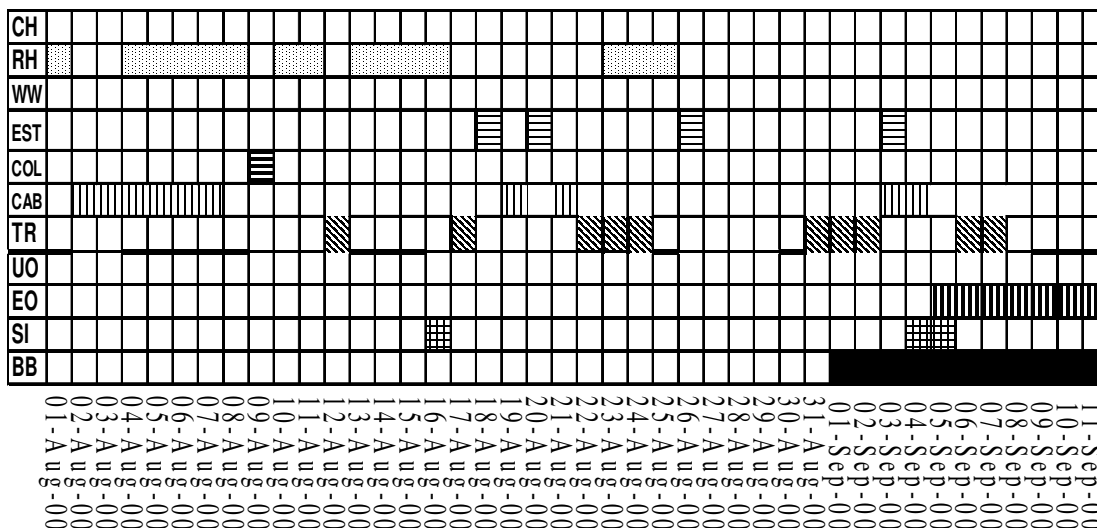


Figure 4.4　　Synoptic scale circulation classification over Lusaka at the surface between 1 August and 11 September 2000.

The mid-tropospheric levels (700 – 500 hPa) were dominated by a strong continental high-pressure system for most of the period (Figure 4.5). The stable

conditions created by the subsidence coupled with intense biomass burning in most parts of the tropical Africa resulted in the high levels of ozone reported. The highest ozone measured in the whole region was reported at Lusaka.
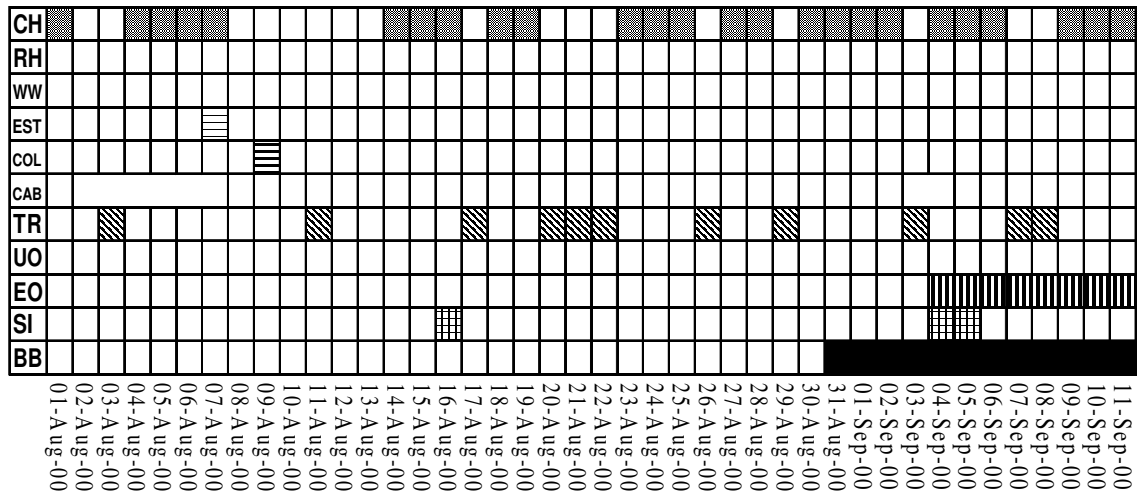


Figure 4.5    Synoptic scale circulation classification over Lusaka between 700 and 500 hPa between 1 August and 11 September 2000.  CH = Continental high, RH = Ridging High, WW = Westerly Wave, COL = Cut Off Low, EW = Easterly Wave, CAB = Congo air basin, TR = Trough system, UO = Unusual other, EO = Enhanced Ozone, SI = Smoke index, BB = Biomass burning

## General flow over southern Africa during SAFARI 2000

Westerly and easterly regimes dominated the trajectory airflow to Lusaka on 6 September. It is noted that the westerly airflow at the mid-troposphere originated from the Atlantic Ocean and traversed the western parts to Lusaka. The easterlies are mainly surface winds. The air masses passed through areas of intense biomass burning (Figure 3.13). The back trajectories ending at Lusaka on 6 September (Figure 4.6) illustrate the easterly wind regime on 6 September converging with the westerlies from the Atlantic Ocean at Lusaka at 500 hPa.
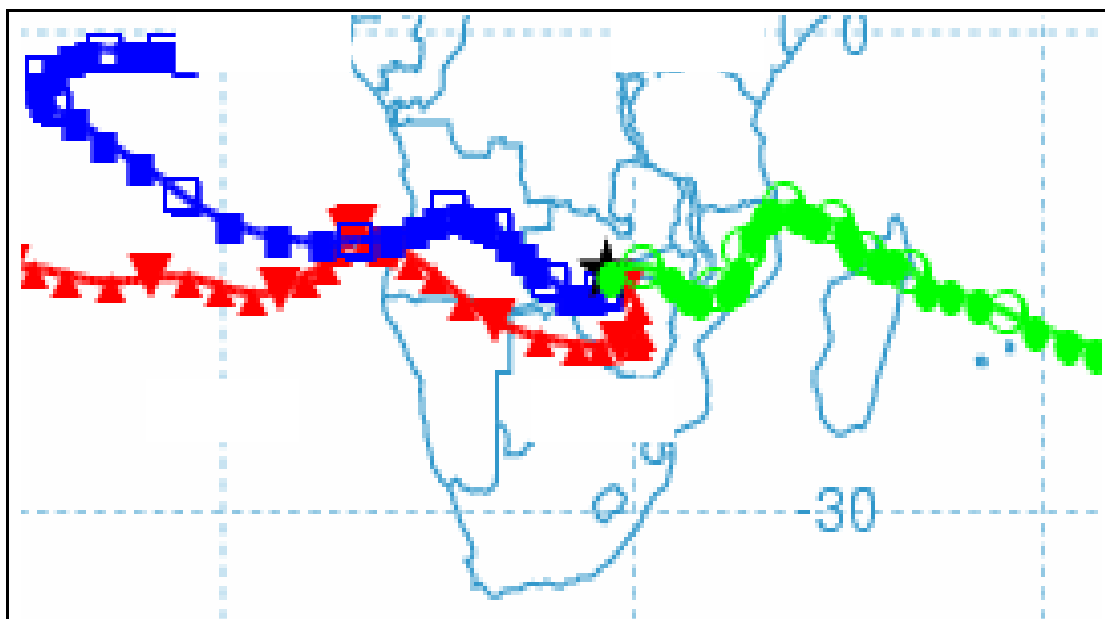
Figure 4.6    Ten-day back trajectories ending at Lusaka on 6 September 2000, colour codes: Red = 5 000m, Blue=3 000 m and Green-2 000 m.   Large markers indicate days (24h00) while smaller markers indicate 6 hour intervals.


The 500 hPa synoptic patterns of 6 September are explained using an upper air synoptic chart.   The circulation around the upper air anticyclone results in NW flow over the region exiting to the Indian Ocean over South Africa and Mozambique (Figure 4.7).
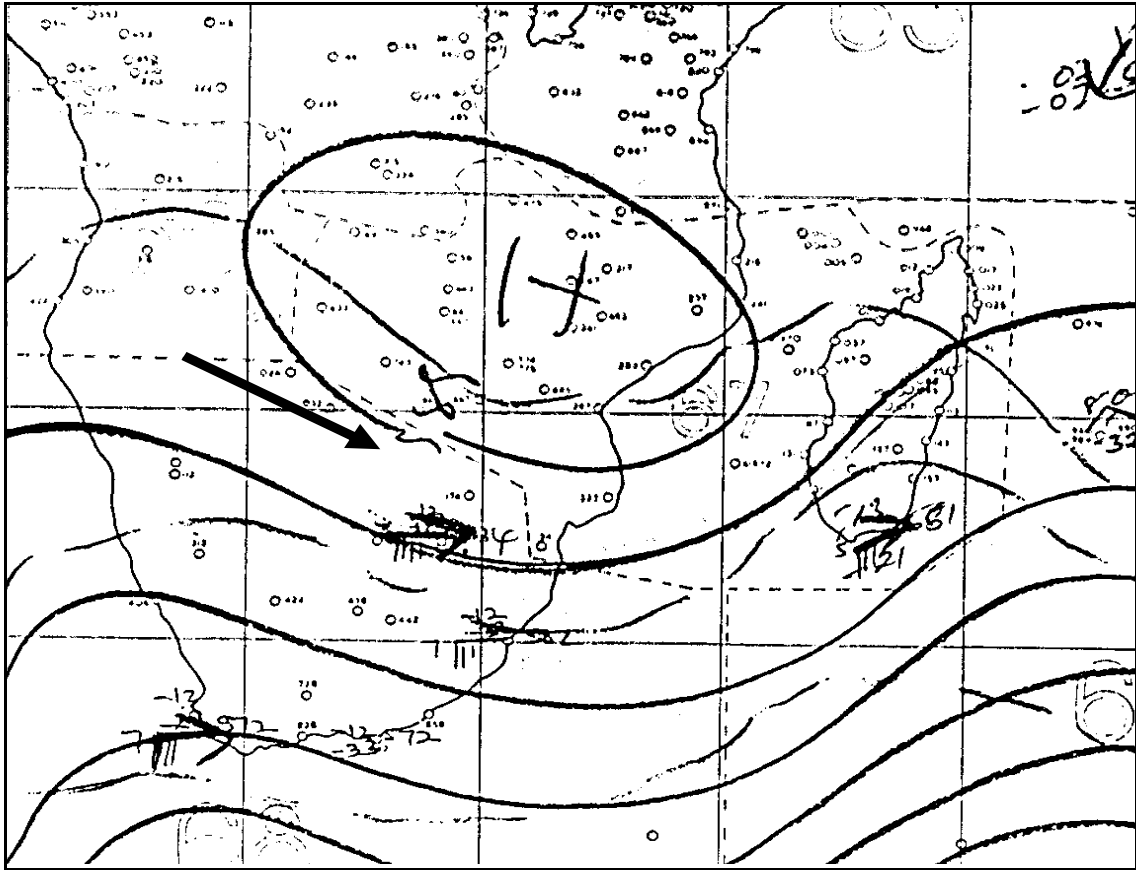
Figure 4.7     Synoptic chart at 500 hPa level on 6 September.

## Vertical distribution of ozone and long range transport

The three sites, Lusaka, Irene and Nairobi where ozonesonde measurements were made simultaneously on 6 September 2000, provide good opportunity for comparison of trajectory patterns for very diverse localities. The transport flow pattern for Lusaka is from the eastern parts of Angola and western parts of Zambia as already discussed (Figure 4.6).

The ozone vertical profile plotted for Irene on 6 September, a day with fairly high ozone pollution (Figure 4.8), reveals enhanced ozone concentrations at 3.4 km above the ground.
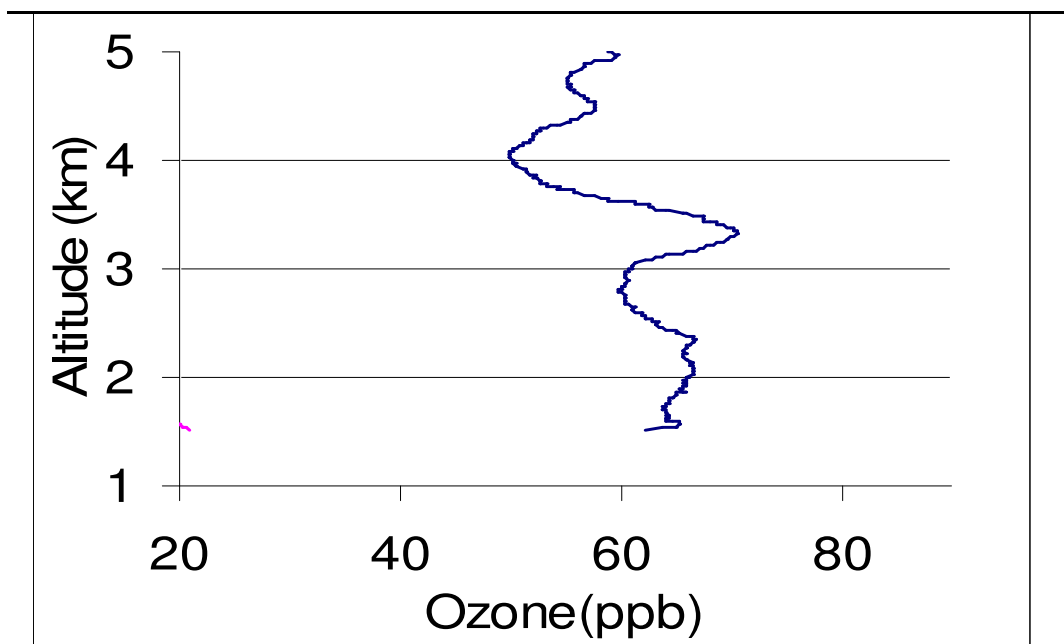


Figure 4.8    Vertical ozone profile over Irene, 6 September 2000.

The back trajectories on 6 September ending at Irene on the other hand are mainly from the South Atlantic Ocean through parts of southern Namibia (Figure 4.9). These pathways were removed from the main biomass burning areas in southern Africa. This explains why ozone values over Irene were lower than over Lusaka on 6 September. Although not indicated in the figure, the ten day backward trajectory analysis indicates that air originated over South America, possible bringing secondary products from Biomass burning emissions.
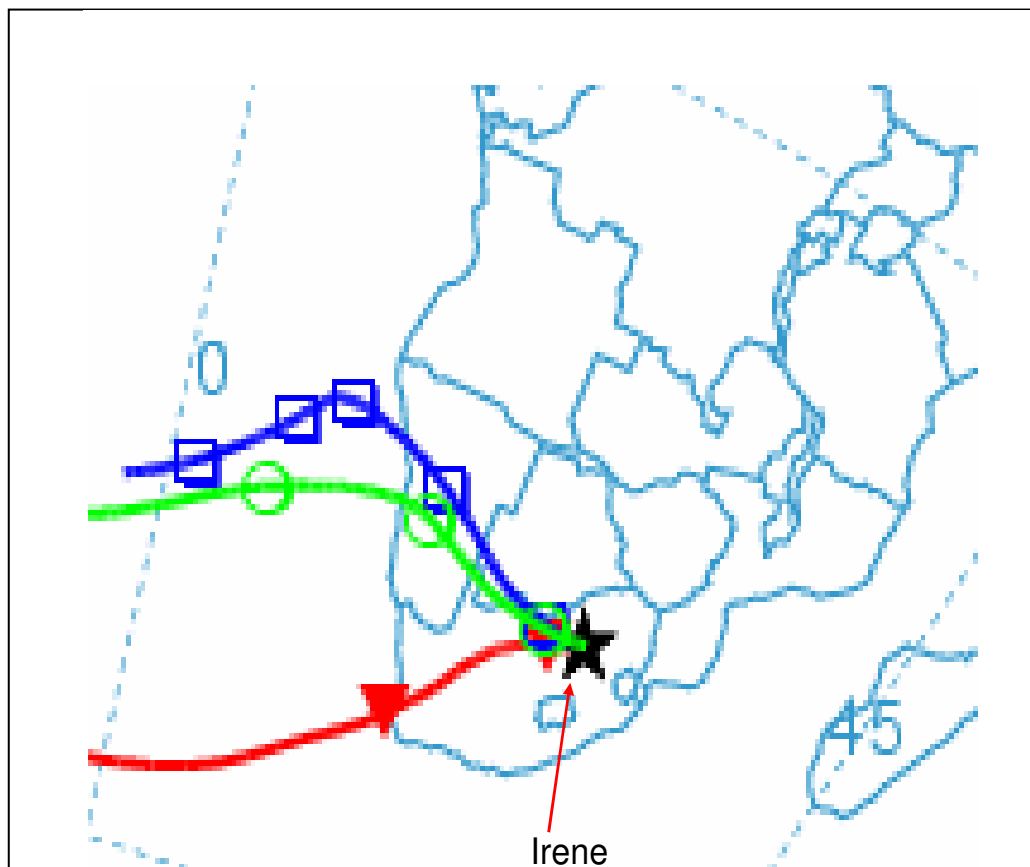


Figure 4.9    Back trajectories for Irene on 6 September 2000. Red = 5 000 m, Blue = 3 000 m and Green = 2 000 m.  Markers indicate days (24h00).

Low ozone values were measured in Nairobi on 6 September (Figure 4.10) as indicated by the vertical ozone distribution in the lower troposphere. The highest ozone concentration was only 40 ppbv at an altitude of ~2 km above the surface. These values are extremely low compared to the ozone pollution observed over Lusaka and Irene.
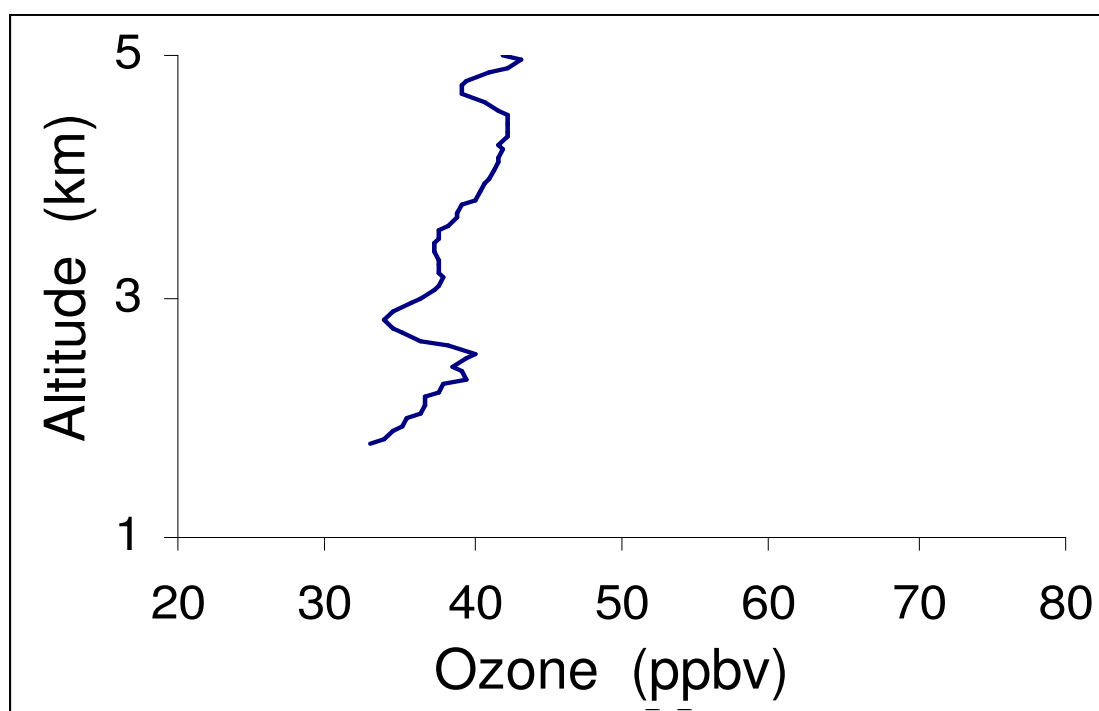


Figure 4.10    Vertical ozone distribution over Nairobi on 6 September 2000.

The trajectories for Nairobi on 6 September (Figure 4.11) indicate that a marine air mass from the Indian Ocean reached Nairobi. This explains why Nairobi had very low ozone concentrations on this particular day.
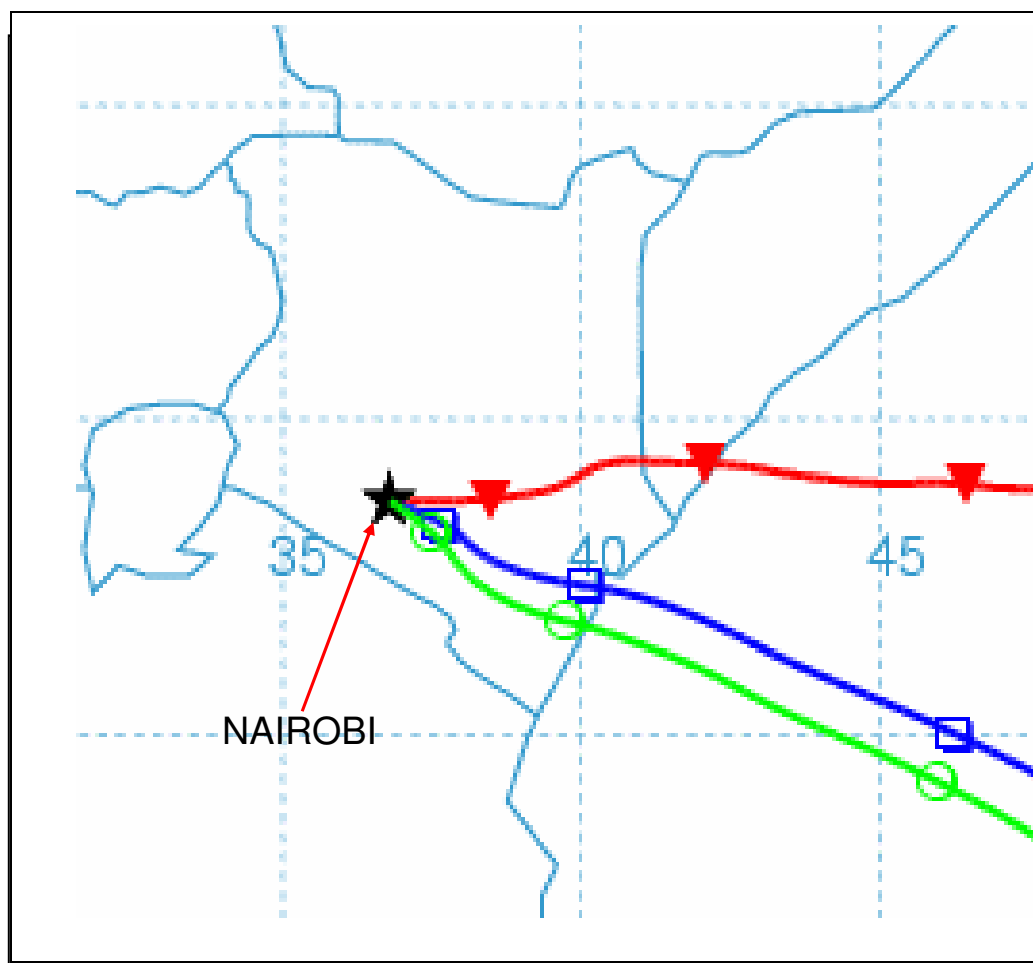


Figure 4.11    Back trajectories for Nairobi on 6 September 2000. Red = 5 000 m, Blue = 3 000 m and Green = 2000 m.  Markers indicate days (24h00).

Lusaka recorded a high ozone value of 91 ppbv at 2166 m above the ground on 6 September. In the mid-troposphere, much higher values were observed (135 ppbv) at 5 km level (Figure 3.3). The high ozone values were observed within the two stable layers at the respective altitudes in the vertical profile (Figure 4.12).
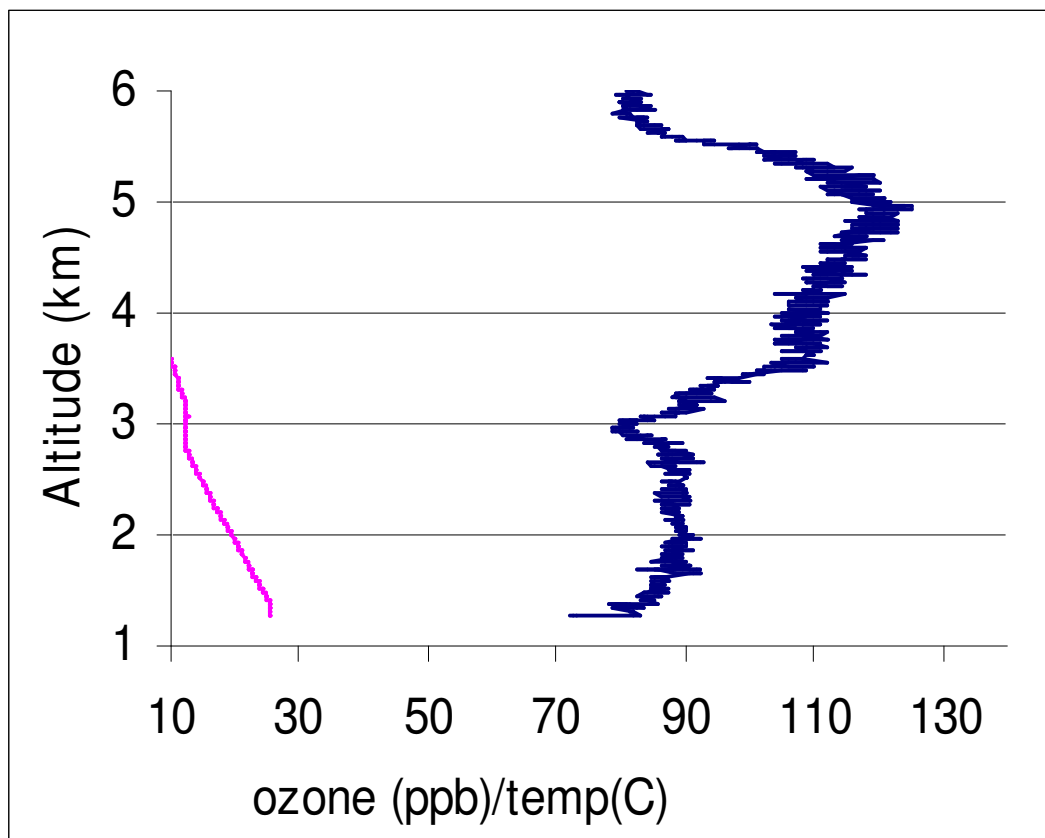
Figure 4.12    Vertical ozone distribution over Lusaka on 6 September 2000.

The general transport pattern to Lusaka has been discussed and illustrated in Figure 4.6.

**Monthly ozone variations and associated transport**

The annual austral spring mid-tropospheric ozone maximal over southern Africa occurs in the months of July, August and September. Tropospheric ozone column amounts show that in general, there is more tropospheric ozone between June and November than at other times of the year, with minimum ozone between January and May (Thompson *et al.*, 2002).

To be able to compute mid-troposphere back trajectories for both Nairobi and Irene sites during their respective seasonal maximum ozone days, monthly ozone variation for the year 2000 was established. The corresponding vertical ozone profile was plotted to pick the altitude of the ozone peak. The trajectory origins of the ozone pollution were then computed using HYSPLIT Model. Figures 4.13 and 4.14 show ozone seasonal peaks for Irene and Nairobi with their corresponding back trajectories in Figure 4.9 and 4.11.

The monthly ozone variation in Irene shows seasonal ozone maximal between August and November. The highest single concentration value of ozone ~ (80 ppb) was recorded on 11 October 2000. The corresponding vertical ozone profile (Figure 4.13) shows elevated mid-tropospheric ozone of ~97 ppbv at 4.5 km. This is significant ozone pollution compared to the background ozone of ~30 ppbv in the region.
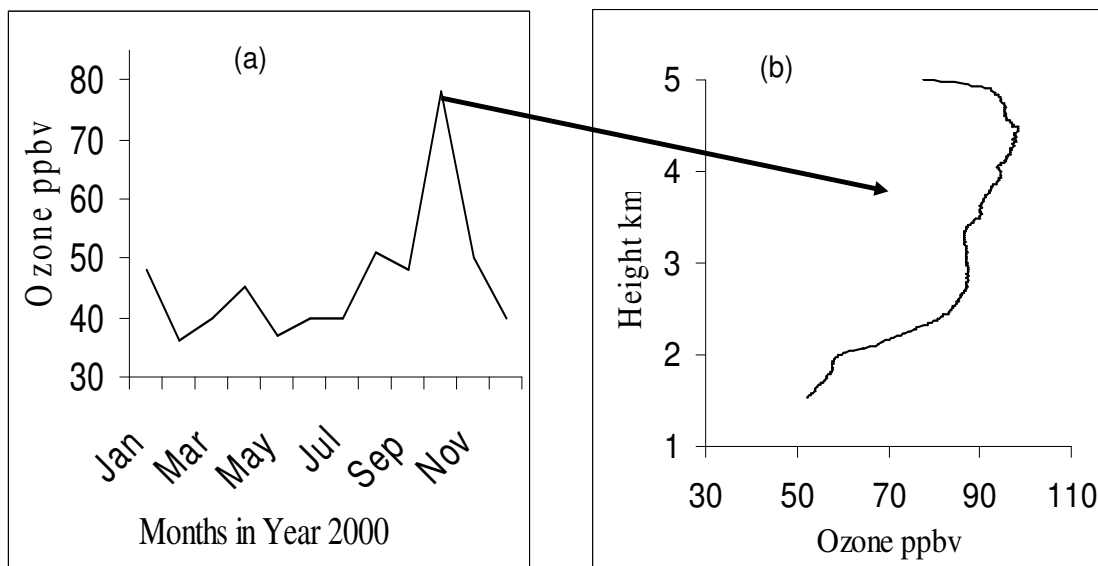
Figure 4.13    (a) Monthly ozone variation over Irene; and (b) Vertical ozone distribution over Irene on 11 October 2000.

Back trajectories ending at Irene site (Figure 4.11) indicate air transport emanated from the biomass burning areas of Zimbabwe and Mozambique, as well as from the southern Atlantic Ocean. The precursor gases from these areas contributed to the build up of ozone over Irene on 11 October 2000.

The seasonal ozone maximum for Nairobi precedes the Irene maximum by about two months as illustrated in Figure 4.14a. The ozone maximum was observed in July and August, with the highest mid-tropospheric ozone concentration of 58 ppbv on 10 August at 5 km altitude over Nairobi (Figure 4.14b).
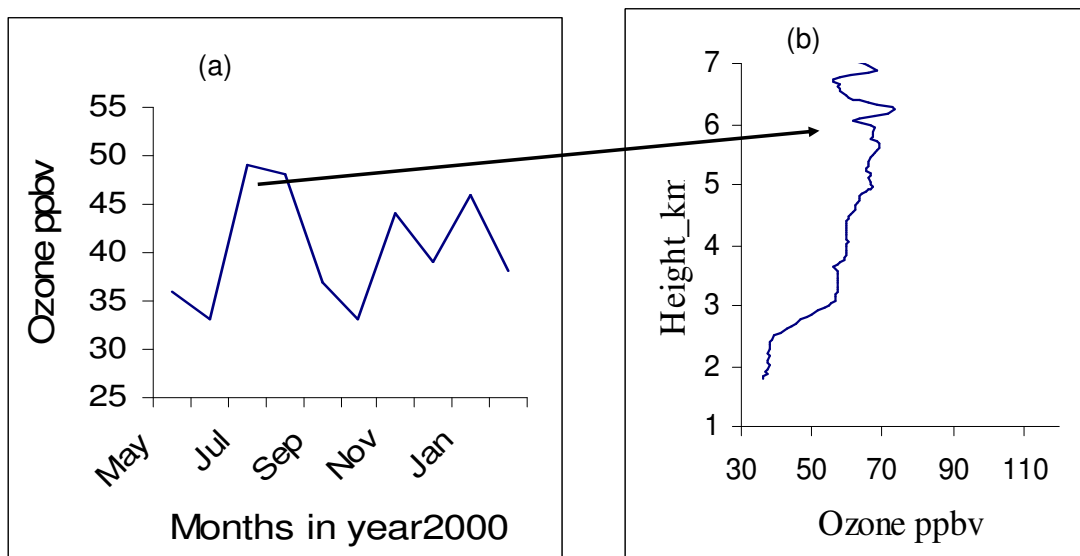
Figure 4.14     (a) Monthly ozone variation over Nairobi; and (b) vertical ozone distribution over Nairobi, 10 August 2000.

The corresponding back trajectory ending in Nairobi (Figure 4.15) on 10 August reveals that north-easterly winds were prevalent. This fact agrees with the Kenyan air circulation climatology (Gatebe, 1999). The high ozone observed between 3 km and 5 km is likely to be a product of biomass burning in some parts of India and transported by north-easterly winds.
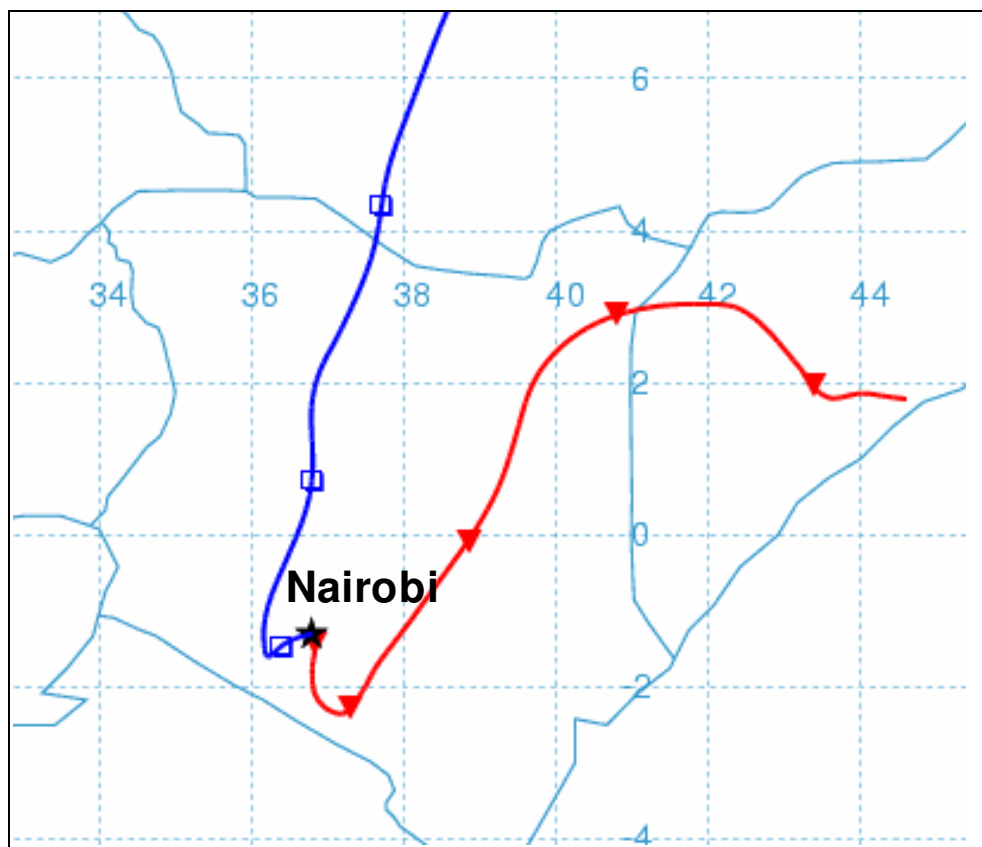
Figure 4.15    Typical back trajectories ending in Nairobi during seasonal ozone peak in the month of August, Red = 5 000 m and Blue = 3 000 m.  Markers indicate days (24h00).

# CHAPTER FIVE

# SUMMARY AND CONCLUSIONS

While ground based measurements are invaluable for health and environmental impact assessments, these may fail to capture information on the concentrations, chemical species and transport of pollutants within layered air masses. To overcome this limitation, a series of airborne atmospheric measurements, SAFARI 2000 campaign, was undertaken as a follow-up of the SAFARI-92, during the burning season in southern Africa.

The purpose of the SAFARI 2000 was to identify and understand the relationship between the physical, chemical, biological and anthropogenic processes that underlie the biogeophysical and biogeochemical systems of southern Africa. In this work, particular emphasis was placed on the characterisation, quantification and pollutant transport in the troposphere.

The flights were conducted under different meteorological conditions, for example, cloudy, foggy, hazy and at times clear conditions to assess the levels of ozone and other trace gases. Kirkman *et al.* (2000) demonstrated existence of enhanced levels for trace gases during the fire season of September 1992. Helas had similar observations (Helas *et al.,* 1995) though during a non-fire season.

This research has particularly addressed both spatial and temporal distributions of tropospheric ozone over the southern African region during the fire season. A number of important findings have emerged from the study relating to ozone characterization, regional air transport and circulation patterns with their associated meteorological conditions.

## Ozone characteristics and distributions

Combined aircraft, ozonesonde and satellite data show evidence of elevated ozone concentrations north of 20°S (Kirkman *et al.,* 2000). However, in this study relatively high ozone concentrations (> 80 ppb) were encountered within the mixed layer further south than anticipated (25°S). Therefore, this study has demonstrated that elevated

ozone levels, are present in areas further south (25°S) due to transport of precursor gases.

Ozonesonde measurements at regional sites during the month of September 2000, revealed that near tropical sites, like Lusaka had higher ozone concentrations than sites south of 20°S. Irene at 25.5°S is a good example as it depicts lower ozone levels. These observations attributable to biomass burning, indicate a northwards increasing trend in ozone levels for the region during Southern Hemisphere Spring, 2000, in agreement with findings by Thompson and colleagues, who implied latitudinal dependent gradient in tropospheric ozone by higher integrated concentrations at Brazzaville (4°S) and Ascension Island 8°S, than at Okuakujo 19°S and Irene 25°S (Thompson *et al.,* 1997; Diab *et al.,* 1996). However, at certain times, for example during the "River of Smoke" (Kanyanga *et al*., 2003) the influence of biomass burning on ozone was evident over Irene and Polokwane, thus contradicting the assertion that biomass burning influence is not felt south of 20°S latitude.

The Nairobi site (Kenya) at the equator had much less ozone concentration in September. The highest value at 3 - 4 km was ~40 ppbv on 6 September 2000. This was clear indication that Nairobi was not under the influence of biomass burning.

The gradual temporal accumulation of ozone in the August-September period corresponded with the period biomass burning activities were picking up in the region. This scenario was observed at Polokwane during the study period. This demonstrated the influence of biomass burning coupled with transport regime on ozone concentrations at distant sites with no discernable fires.

Large vertical variations were observed over most places. Frequent peaks of ozone at the boundary layer were evident over areas with no discernable biomass activities. It has been shown by use of back trajectories that most of the ozone peaks and eventual accumulations were determined by transport regimes.

## Synoptic conditions

Episodes of high ozone concentrations were observed during periods of strong continental anticyclones features in the tropical belt (0° - 15°S) over southern Africa. Lusaka is a good example where a strong continental anticyclone prevailed from 3 to 11 September between 700 to 500 hPa layer. The period was characterised by intense biomass burning in the tropical belt with resultant high ozone episodes over Lusaka. Subsidence coupled with biomass burning enabled precursor gases to undergo chemical reactions that produced high ozone concentrations observed over Lusaka.

In the same period, high ozone episodes were observed at sites further south in the sub-tropics like Polokwane and Inhaca Island (15°S - 25°S), with no evidence of biomass burning in the vicinity. A deep trough prevailed at 700 to 500 hPa level. The high ozone concentrations can therefore be attributed to the "river of smoke", which was a large scale transport regime from Zambia, through Zimbabwe and finally exiting through the south east coast of South Africa.

A similar occurrence of high ozone episode in non-biomass fire site was encountered over Beira. Back trajectories reveal that a recirculation of air through biomass burning areas in the sub-continent through the coastal sites accounted for the enhanced ozone levels observed.

This finding concurs with work that showed that certain meteorological conditions and high values of ozone tend to occur concurrently or with a range of 1 - 2 days (Renate *et al.,* 2002). This suggests that ozone variations were associated with large-scale meteorological fluctuations.

The synoptic features studied over the southern Africa revealed that the continental anticyclonic pressure system and the south Indian Ocean frontal systems had the greatest influence on the ozone concentrations in the region. Therefore, high accumulation of ozone pollution lingered over the region as long as the anticyclone was in existence especially in the case of Lusaka, Zambia.

Therefore, these findings confirm the hypothesis that "particular synoptic conditions link the most intense biomass fire region, in the tropical belt (0° - 15°S), leading to enhanced ozone concentrations to the sub-tropical belt (15°S - 25°S)".

## Existence of two ozone maxima

Two ozone maxima were observed in the boundary layer over the western sector, adjacent to the Atlantic coastal areas of Angola; and over the eastern sector including northern Zimbabwe and Mozambique and extending to Indian Ocean. Both Lusaka and Polokwane vertical profiles reveal the existence of enhanced ozone pollution on 6 September 2000.

The horizontal and vertical ozone distributions showed two ozone peaks near Lusaka and close to Polokwane, thus confirming the results of the TOMS/Earth probe imagery for August-September period which revealed accumulations of ozone both in the western and eastern sectors of the sub continent.

The Lusaka ozonesonde vertical profile on 6 September show elevated ozone in the boundary layer of ~135 ppbv (at ~4000 m altitude) thus providing an indication of the amount of ozone pollution within the maxima. Thompson *et al.* (2002) in her work over Lusaka confirms the existence of the elevated ozone, with two peaks, below 5 km and the other below 10 km. Both peaks exceeded 100 ppbv.

The origins of these heavily polluted ozone layers over Lusaka were established through trajectory analysis to have emanated from western areas through westerly winds and from the Indian Ocean via easterly transport regime. The 500 hPa synoptic patterns support the trajectory flow ending at Lusaka.

A further feature of the ozone concentration observed over the highly polluted areas was existence of vertical layering triggered by temperature inversions. In addition it was noted that the changes in the vertical ozone concentrations were very large compared with the horizontal variations.

These findings provide further evidence of the linkage between enhanced ozone, biomass burning and transport regimes.

## N − S ozone gradient over the sub-region

The concentrations of ozone during the Polokwane − Bethlehem flight decreased gradually from ~60 to 30 ppbv. A similar observation obtained during the flight from Polokwane to Inhaca Island on 24 September, with ozone values varying from 200 ppbv to 50 ppb. The enhanced ozone observed over the Highveld conforms with similar findings by Freiman (2001) indicating that the industrial activities contribute to some of the ozone pollution observed.

The hypothesis that there exists a N - S ozone latitudinal gradient was confirmed.

## Seasonality of tropospheric ozone over southern Africa

The monthly ozone variation in the year 2000 shows seasonal ozone maxima for Irene between August and November. The highest concentration of ozone for the season was ~80 ppbv on 11 October 2000.

The seasonal ozone maxima for Nairobi lag the Irene maximum by about two months. The ozone maximum was observed in July and August, with the highest mid-tropospheric ozone concentration of 58 ppbv on 10 August over Nairobi.

Irene had suppressed levels of ozone for the rest of the seasons in 2000. However, Nairobi had another less pronounced seasonal peak in January - February, which is another very dry period in Kenya. This implies possibility of incursion of biomass burning plumes from the northern hemisphere. An inter-seasonal comparison for other years is really necessary, but this is beyond the scope of this current work.

## General conclusions

In tying together the findings from the results, a number of general conclusions can be made regarding the spatial and temporal distributions of tropospheric ozone over southern Africa. From the study, two regions of ozone maxima were found to be present in the western and eastern sectors of the sub-region. Both sectors had accumulations of ozone pollution significantly attributed to seasonal regional biomass burning.

The existence of a N - S ozone spatial gradient was established using both the aircraft flight and ozonesonde data sets.

A regional temporal ozone variation revealed a general increasing trend from August to September 2000 corresponding to the pattern of biomass burning.

The observed high ozone levels over areas far removed from the biomass fires was attributed to transport pathways influenced by synoptic conditions.

In this study, therefore, the major source of tropospheric ozone during SAFARI 2000 has been demonstrated to be the seasonal biomass burning coupled with transport regimes. This disapproves the hypothesis that 'enhanced high ozone levels over southern Africa are due to biomass burning'. On the contrary, transport regime and prevailing synoptic conditions have to be taken into account as well.

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