ROLE OF SYNOPTIC WEATHER SYSTEMS IN SURFACE OZONE CONCENTRATION IN DURBAN REGION

BY

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PREFACE

The work described in this thesis was carried out in the Department of Geographical and Environmental Sciences, University of Natal, Durban, from May 1994 to December 1995, under the supervision of Professor Roseanne D. Diab.

This study represents original work by the author and has not been submitted in any form to another University. Where use was made of the work of others, it has been duly acknowledged in the text.

ACKNOWLEDGEMENTS

I wish to express my gratitude to all those who assisted me in producing this work. I take this opportunity to thank my supervisor, Professor Roseanne Diab for her guidance, devoted supervision and critical comments throughout the duration of this study.

I also wish to thank the Meteorological Office at the Durban International Airport for their assistance with relevant synoptic charts and meteorological data, and to the Durban Water and Air pollution management for loaning the Dasibi Ozone monitor to Atmospheric Research Group University of Natal Durban.

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I wish to thank my parents: Posi and Violet; brothers: Desmond, Bheki, Mhlanganyelwa, Bongani, Mandla and sisters: Anna, Eunice and Nelisiwe for their unwavering support throughout even during times of sadness.

I dedicate this work to the following member of my family who passed away: Fanyana Simon Langa.

The financial assistance of the Foundation for Research Development, University of Natal Graduation assistantship and Educational Opportunities Council is hereby acknowledged.

Lastly, to Almighty who carried me and my family through the years of difficulty and eventually gave us all the best things in life.

ABSTRACT

Measurements of surface ozone in Durban have been undertaken since September 1994 until August 1995 using a Dasibi ozone monitor model 1108. There is a seasonal variation in surface ozone with a small amplitude of 6.5 ppb. The mean maximum of 12.5 ppb is experienced in August and the minimum in December (6 ppb). The late winter peak and the sharp rise from June to July is possibly related to the greater accumulation of ozone at the surface due to the poor dispersion, higher frequency of inversions and lower mixing depth.

The study also focuses on the relationship between synoptic weather systems and daily ozone concentrations in an attempt to establish if any relationship exists. The analysis suggests that there is an increase in ozone concentration during the pre-frontal and established high pressure systems and a reduction in ozone under post-frontal conditions.

The mean diurnal variation in surface ozone depicts a maximum between solar noon and 14:00, which is typical of an urban-industrial environment, in which ozone precursor gases have built up during the morning. However, a secondary peak in the early morning during winter and autumn was more difficult to explain and is thought to be due to the transport of ozone from the interior in the mountain-plain wind systems.

Comparison of ozone values at Durban with results available from the other locations in South Africa such as Cape Point and the Eastern Transvaal Highveld has been undertaken. Ozone values at Durban are lower than Cape Point, which is a representative of a background monitoring station. It is hypothesised that those low ozone concentrations may be due

to high NO_x which in turn depletes ozone.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

Chapter One

General Background

CHAPTER ONE

INTRODUCTION

1.1 GENERAL BACKGROUND

Much concern has been expressed about the change in chemical composition of the earth's atmosphere. Of particular interest to this study is the increase in surface ozone concentration which is experienced, in particular, in large urban and industrial centres of the world (Logan, 1985). Such observations provide cause for concern and strong support for research into the behaviour of atmospheric ozone.

Ozone in the troposphere is increasing and although ozone is considered to be a trace gas, it plays a dominant role in determining the thermal structure of the atmosphere (Bojkov, 1995). In addition, ozone has a highly reactive chemical nature in the troposphere and as such, plays a significant role in global tropospheric chemistry. Near the surface it may be considered a pollutant, with many undesirable characteristics, and in the free troposphere it may contribute to global warming through its absorption of longwave terrestrial radiation.

Ozone has indeed become a global issue and has precipitated a great deal of research originating within a variety of disciplines. Short term, or day-to-day fluctuations in surface ozone have been examined in detail for many Northern Hemisphere cities (Liu, 1993). In particular, the relationship between surface ozone and daily weather patterns is well documented in the literature (Liu, 1993). Many subsequent studies have developed the understanding of this relationship further (for example, Orlanski, 1989). Due to the lack of meteorological data and ozone measurements in the Southern Hemisphere, short term ozone characteristics have not been as extensively studied as in the Northern Hemisphere. This is particularly true for southern Africa.

In recent years, greater attention has been focused on increasing global tropospheric ozone levels and the nature and causes of the observed long term, seasonal and daily variations (Logan, 1985; Crutzen, 1988). Traditionally, industrial and urban development has been blamed for the substantial increase in substances which pollute the atmosphere (Urone, 1986). Other less-well understood contributing factors, such as rural fire and biogenic emissions, are now being more carefully considered (Thompson, 1996a). In the last four years much attention

has been focused on the southern and central African region, and as a result, the transport of, and chemistry of tropospheric ozone and ozone precursors is better understood (Thompson, 1996c).

It is against this background that an investigation of surface ozone concentration in Durban is undertaken. Ozone is expected to vary as a function of season and time of day and to fluctuate in response to changing weather systems as well as long-term anthropogenic influences.

This evidence is documented widely in studies (for example, those done by Fujibi, 1985; Liu et al., 1990 and Liu et al., 1994). Although, it is acknowledged that surface ozone is constantly produced and destroyed by natural processes, causing a dynamic equilibrium in the ozone amount, the increase in ozone concentration that is observed, suggests that the equilibrium has been disturbed. In this context, it is of interest to examine the nature and characteristics of ozone concentration in a highly urbanised and industrialised city such as Durban.

Historically, there have been few measurements of ozone in Durban and certainly no analysis of any data has been undertaken. The measurements undertaken as part of this study have therefore provided an opportunity to make a

first assessment of ozone concentrations in the city.

1.2 OBJECTIVES OF THE STUDY

The main aim of the study is to examine the role of synoptic weather systems in the buildup of ozone in an industrialised environment, with a view to improving our skills in forecasting high ozone days.

To achieve this goal, the study aims to:

1. Describe and explain the seasonal variation of surface ozone;
2. Investigate surface ozone concentration as a function of time of day;
3. Examine the role of synoptic weather systems in the day to day variation in surface ozone concentration;
4. Study the relationship between ozone and meteorological variables.

The study hopes to test the following hypotheses:

1. Seasonal and diurnal patterns of ozone concentration are typical of an urban-industrial environment;
2. With high temperature and solar radiation, photochemical reactions will be enhanced leading to

high ozone concentration;

3. Under a pre-frontal synoptic weather situation, stable atmospheric conditions and high pollution concentration lead to ozone enhancement;
4. Under a post-frontal synoptic weather situation, unstable atmospheric conditions and low concentration of pollution lead to reduced ozone concentration.

1.3 THE SCOPE OF THIS STUDY

In order to contextualize the problems addressed in this dissertation, the background to the issues surrounding surface ozone is addressed. A detailed description of the methodology applied in the thesis, and the data sets and derived meteorological variables utilised are given in Chapter two. In Chapter three, the chemistry of ozone formation and destruction is described in detail. Chapter four pays particular attention to local climatology and its potential role in surface ozone concentration. Chapter five describes the seasonal, diurnal and daily variation of surface ozone and the relationship between surface ozone and meteorological variables and synoptic weather systems. Finally, chapter six presents a summary of the research.

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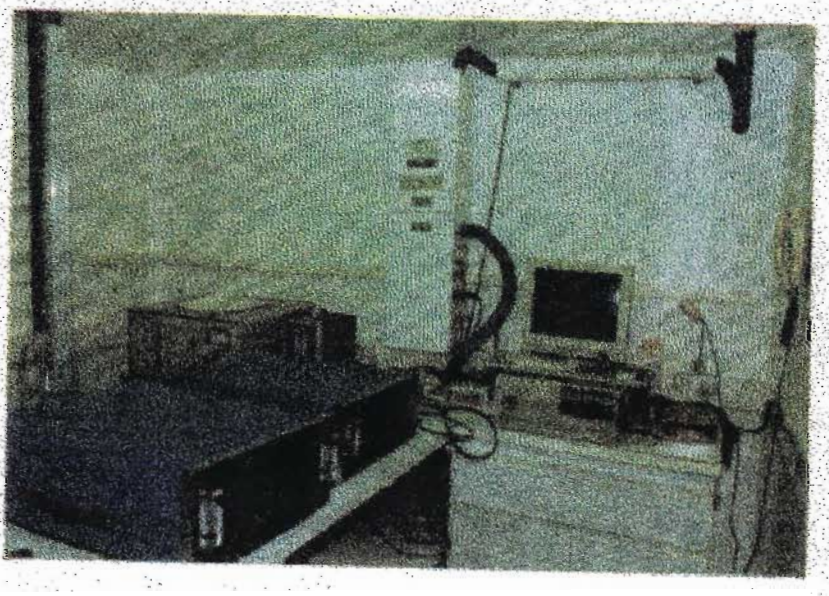
Now that the current research has been placed in a broader context, the succeeding Chapter is devoted to surface ozone monitoring in Durban.

Chapter Two

Surface Ozone Monitoring in Durban



CHAPTER TWO

DATA AND METHODOLOGY

2.1 INTRODUCTION

Continuous measurement of surface ozone was undertaken at the University of Natal in Durban. Radiosonde and surface meteorological data were obtained from the Durban International Airport for the period of study. The data included surface temperature, pressure, wind and humidity. The analysis of data will be undertaken in Chapter five.

2.2 OZONE DATA

2.2.1 LOCATION OF MONITORING INSTRUMENT

The monitoring station is located at the University of Natal in Durban at an elevation of 150 metres above sea level. The Dasibi ozone monitor is situated in a laboratory on the roof of the building in which the Physics department is located. It is approximately 20 metres above the surface (Plate. 2.1). It should be borne in mind that the monitoring station is located at a higher elevation than the main urban-industrial area of Durban and that the

2.2.2 PERIOD OF MEASUREMENT

Measurement of surface ozone has been undertaken since May 1994. For the first few months some problems were experienced with the instrument, but thereafter data are considered reliable. Hourly data for the period September 1994 to August 1995 have been utilized in the study. A few gaps exist in the data record due to the instrument being offline during calibration. Data availability on this period was 94 %.

2.2.3. INSTRUMENTATION

A Dasibi ozone monitor model 1108 was used to measure surface ozone (Plate. 2.2). The data are recorded as hourly mean values in parts per billion (ppb). The precision of the instrument is given as approximately 1 ppb (Dasibi Environmental Corporation, 1989). A second Dasibi was operated alongside the first instrument. Comparison between the results obtained from each of the instrument showed no significant or systematic differences.

The optical configuration of the Dasibi instrument comprises in sequence, a mercury-vapour lamp as the source of UV radiation, a window for the UV radiation to enter the absorption chamber, two mirrors within the absorption chamber for folding the radiation path, an exit window, and

a photodiode used to detect the reduction in the total intensity of the UV radiation by the ozone contained in the atmospheric sample placed in the absorption chamber (Fig. 2.1).

During the absorption the ozone measured is converted to ozone densities by means of the Bouguer Beer equation (Hagemeyer *et al.*, 1982). Since the technique is considered to be absolute in theory at least, the accuracy of the Dasibi should be good, provided the optical tubes are cleaned, calibration of the instrument is done regularly and no leaks are allowed to develop in the plumbing system.

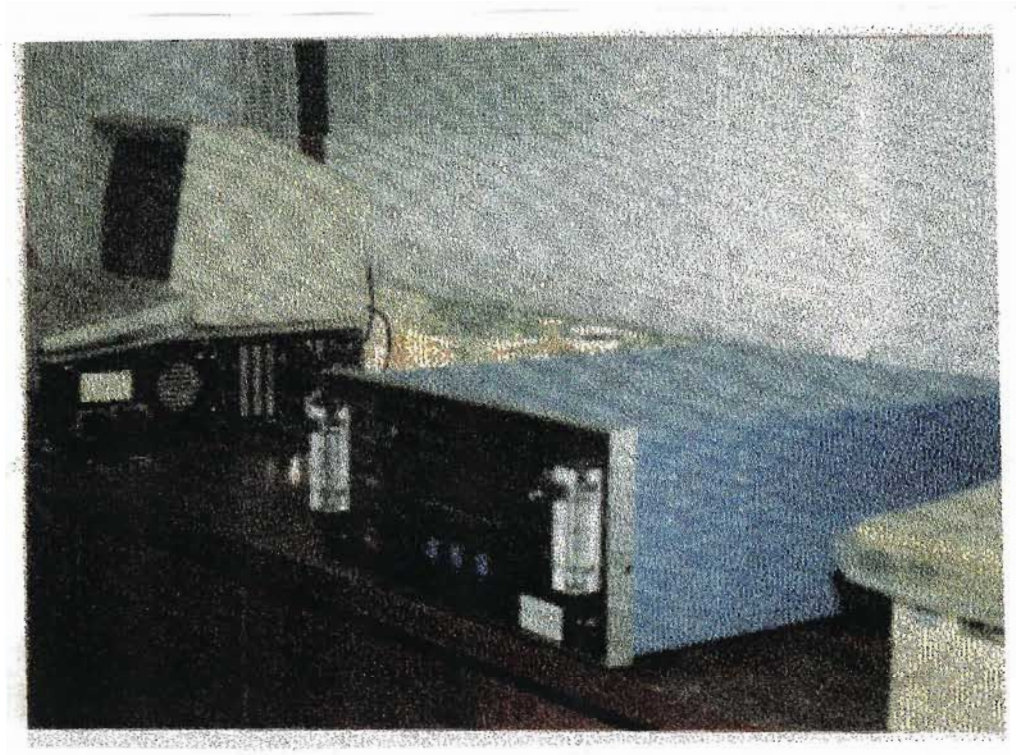


Plate 2.2 The Dasibi ozone analyzer in the laboratory.

The sample tube extends outside to a position approximately 0.5 metres above the rooftop. The inlet orifice is protected from insects by a fine metal screen and moisture is prevented from entering the tube by looping it downward. The tube runs to the ozone analyzer five metres below.

Data are transferred to a PC via an A/D card converter. The PC software package continuously logs concentrations on to the hard disk and transforms one-minute averages to the recorded ten-minute and hourly averages. Several times per

week corrective actions are taken to keep the instrument within specified ranges.

The instrument is reliable and easy to maintain and provides highly stabilised measurement capabilities for extended periods without repeated adjustments, and it operates over a wide range of ambient conditions without effects on measurement accuracy (Dasibi Environmental Corporation, 1989).

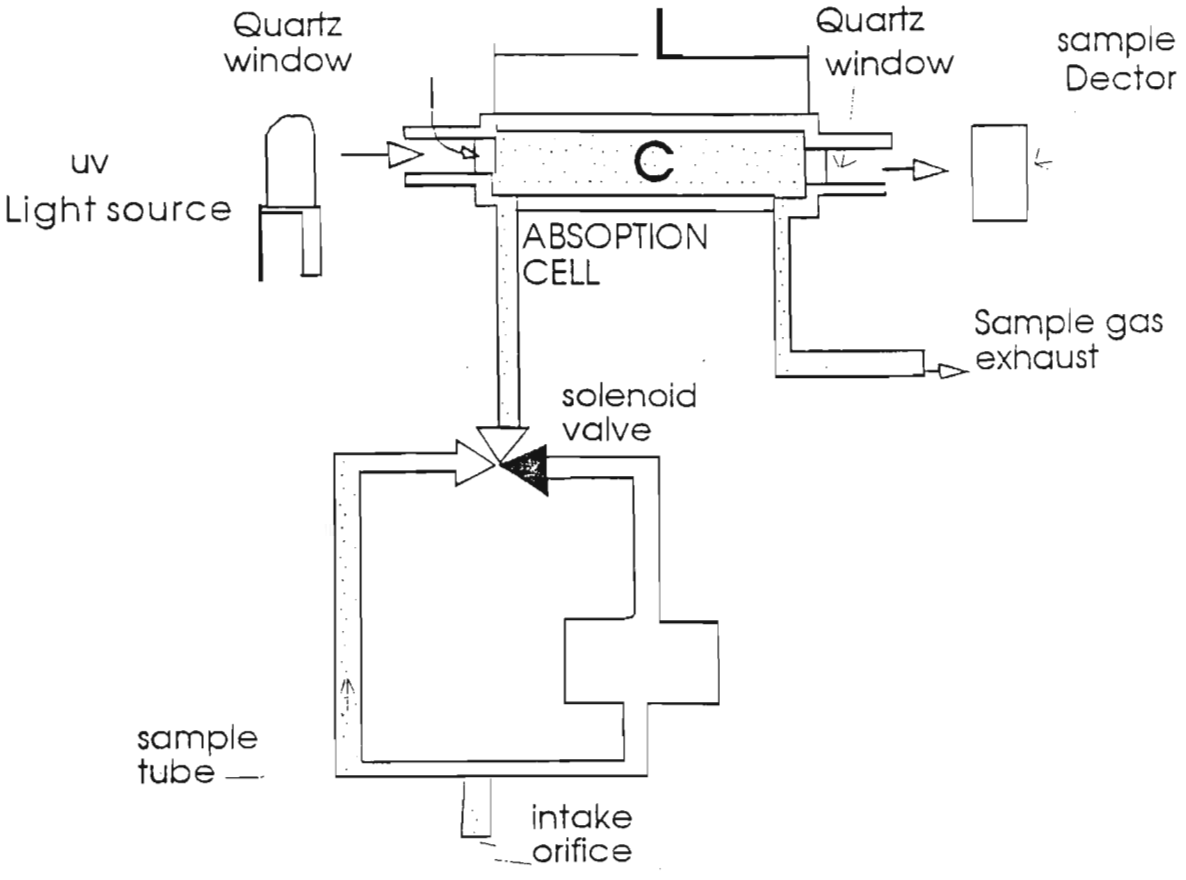


Figure 2.1 Diagram showing the internal structure of Dasibi ozone monitor (After Dasibi Environmental Corporation, 1989).

2.2.4 PRINCIPLES OF MEASUREMENT

The Dasibi analyser is based on the principle of absorption of ultraviolet radiation by ozone melecule. The degree to which the radiation is changed during the sample cycle depends on the absorption cell path length (L), the wavelength of the UV light and the concentration (C) of ozone in the sample gas (Dasibi Environmental Corporation, 1989). The functional relationship between these factors is given by Equations 2.1 and 2.2.

$$\frac{I}{I_0} = e^{-K_1 C} \qquad \text{Eqn.2.1}$$

(Dasibi Environmental Corporation, 1989)

The above equation is solved for the ozone concentration in ppm, including pressure and temperature corrections for conditions other than standard as follows:

$$C = \left[\frac{(10^6 P.T)}{(K_1 L.PT_0)}\right]\left[\ln\left(\frac{I}{I_0}\right)\right] \qquad \text{Eqn.2.2}$$

(Dasibi Environmental Corporation, 1989)

where:

C = ozone concentration (ppm)

I = intensity of UV radiation during sample measurement cycle with ozone present.

I_0 = intensity of UV radiation during reference cycle with ozone removed.

K_1 = absorption coefficient of ozone (308 cm^{-1} atm^{-1} at 0°C, 1 atmosphere and 253.7 nm wavelength)

L = Path length (71 cm for this analyzer)

P = Pressure of gas sample in absorption cell (hPa)

P_0 = Standard pressure (1 hPa)

T = Temperature of gas sample in absorption cell (K)

T_0 = Standard temperature 273 K

The ozone concentration from equation (2.2) above is calculated by a microprocessor which is contained in the analyzer for relative UV light intensities I and I_0 obtained during the sample measurements. The sample gas pressure and temperature are obtained from appropriate sensors in the sample flow path (Dasibi Environmental Corporation, 1989).

2.4 METEOROLOGICAL DATA

Daily (12:00 GMT) radiosonde data were obtained from the Durban International Airport for the period September 1994 to August 1995. Radiosonde data were used to calculate temperature inversion heights and mixing depths. The daily maximum mixing depth was estimated as the height at which the dry adiabat through the surface maximum temperature intersected the environmental lapse rate. The maximum

mixing depth is reached at the time of greatest surface heating (Diab, 1975). The mean hourly surface meteorological data, including temperature, wind speed, relative humidity and pressure were also obtained from the meteorological office at Durban International Airport. Daily (12:00 GMT) surface synoptic charts were used to establish the role of synoptic weather systems in ozone concentration over Durban.

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Recognising that there are several explanations for fluctuations in surface ozone levels, it is appropriate to investigate all possible causes. The next chapter explores those factors which are likely to cause such changes.

CHAPTER THREE

ATMOSPHERIC OZONE CHEMISTRY

3.1 GENERAL BACKGROUND

The sources of ozone in the troposphere can be loosely divided into two categories. One is the primary input of ozone gas, mainly stratospheric-tropospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere and the other is the photochemical formation of ozone within the troposphere (IPCC, 1994).

The sources and chemical formation and destruction of ozone in troposphere will be discussed in the following sections. The removal is accomplished through two competing processes: firstly, the transport to and removal at the earth's surface, and secondly *in situ* chemical destruction.

3.2 PRIMARY SOURCES OF OZONE IN THE TROPOSPHERE

The first such primary source, namely direct input of ozone from anthropogenic sources is generally not recognised as

$$O + O_2 \text{ -----> } O_3 + M$$

This ozone will in turn react with the newly formed nitric oxide (NO) to produce NO_2 and diatomic oxygen once more.

$$NO + O_3 \text{ -----> } NO_2 + O_2 \qquad \text{(eqn. 3.2)}$$

Thus a natural equilibrium concentration of ozone is allowed to exist, and can be represented by equation 3.3 (j and k representing the photolysis rate and rate constant respectively in order that the ratio of NO_2 to NO and background O_3 be determined).

$$[O_3] = \frac{j(NO_2)}{k(NO + O_3)} * \frac{[NO_2]}{[NO]} \qquad \text{(eqn.3.3)}$$

[ ] = concentrations

If the conversion (oxidation) of NO to NO_2 occurs by another route than by reaction with O_3, it would represent an increase in NO_2 and a decrease in NO. This, if applied in the last equation, would result in an increase in ozone concentration through accumulation (Penkett, 1988).

Such oxidation of NO to NO_2 other than by ozone can occur in a number of ways. The two examples that Penkett (1990) presents are described below.

The oxidation of carbon monoxide (CO) and hydrocarbons by

hydroxyl radicals (OH) results in the release of peroxy radicals (HO_2) which can take part in the oxidation of NO.

$$CO + OH \text{ --------> } CO_2 + H$$
$$H + O_2 + M \text{ ----> } HO_2 + M$$
$$HO_2 + NO \text{ --------> } NO_2 + OH \qquad \text{(eqn. 3.4)}$$

In the case of methane (CH_4), and for many peroxy radicals with different alkyl components formed from different hydrocarbons, the reaction will take the form:

$$CH_4 + OH \text{ -----> } CH_3 + H_2O$$
$$CH_3 + O_2 \text{ -----> } CH_3O_2$$
$$CH_3O_2 + NO \text{ -----> } CH_3O + NO_2 \qquad \text{(eqn. 3.5)}$$

The non methane hydrocarbons are more reactive than CH_4, but are less common in the free atmosphere and are thus not considered to have a great impact (Penkett, 1990).

A summary of the above two reaction sequences that produce NO_2 would be:

$$RO_2 + NO \text{ ---------> } RO + NO_2 \qquad \text{(eqn.3.6)}$$

The suggestion made by this analysis is that the formation

of, or more accurately the accumulation of ozone in the troposphere is influenced by the presence of peroxy radicals, and more importantly compounds such as CH_4 and CO which lead to their formation, and which henceforth will referred to as ozone precursor molecules, or more simply as ozone precursors (Wayne, 1990).

3.4 DESTRUCTION OF OZONE IN THE TROPOSPHERE

The destruction of ozone at the earth's surface is a major factor determining the ozone concentration in the lower troposphere. The global average tropospheric ozone concentration, the ozone concentration from urban source and the ozone concentration in the atmosphere boundary layer at night are all regulated by the ozone removal at the surface (Galbally *et al.*, 1980).

The conditions governing the destruction of ozone at the earth's surface are described by Galbally et al., (1980). The ozone destruction rate which is denoted by **F**, is proportional to the ozone concentration (Galbally, 1971). The constant of proportionality called the destruction constant **S** (Galbally, 1971), is invariant for a particular surface in a given condition. This constant can only vary

with varying humidity, temperature and surface structure

and composition of atmosphere (Galbally, 1978). The equation can be written as:

$F = S * (O_3)_o$ where subscript o indicates the height.

As expressed in the discussion concerning ozone formation in the troposphere, the presence of sufficient concentrations of NO_2 or NO that will oxidise to form NO_2, is essential for ozone formation. Should NO_2 concentrations not be sufficient, ozone destruction will occur by one of two means:

Firstly, destruction can occur due to photolysis into diatomic, and singlet oxygen:

$$O_3 + hv \text{ ---> } O_2 + O(^1D) \qquad \text{(eqn.3.7)}$$

and the singlet prevented from recombination with O_2 by alternative linkages with H_2O or N_2O (Reaction 3.9 takes place in the stratosphere) (Fig.3.1):

$$O(^1D) + H_2O \text{ -------> } OH + OH \qquad \text{(eqn.3.8)}$$

or

$$O(^1D) + N_2O \text{ -------> } N_2 + O_2 \qquad \text{(eqn.3.9)}$$

$$\text{-------> } NO + NO \qquad \text{(eqn.3.10)}$$

(after Fahey et al., 1990).

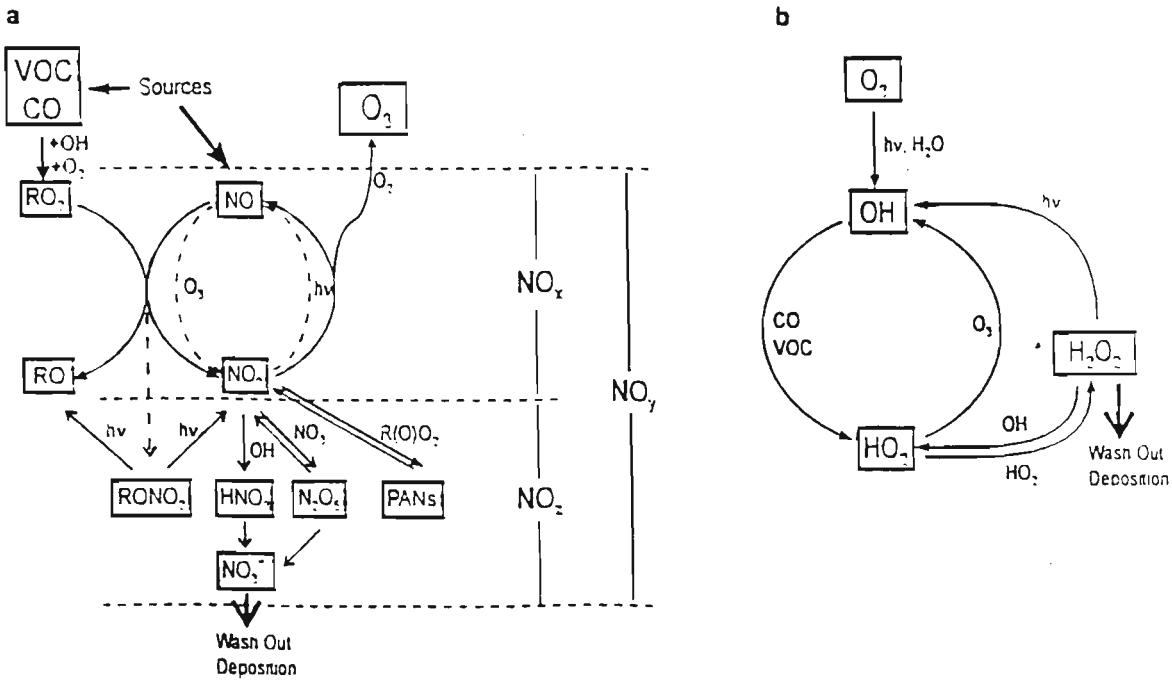

Figure 3.1 (a) Schematic view of cycles of NO_x and NO_y and their relation to the chemical ozone balance. The quantity NO_z is defined as NO_y - NO_x and represents the sum of all oxidation products of NO_x. (b) Primary formation of OH from O_3 photolysis. It shows the destruction of ozone that leads to the formation of hydrogen peroxide (after IPCC, 1994).

The second destruction mechanism would be through direct reaction of ozone with peroxy radicals which were themselves a product of the oxidation of a carbon compound:

$$HO_2 + O_3 \text{ ------> } OH + 2O_2 \qquad \text{eqn. 3.11}$$

summarised as

$$RO_2 + O_3 \text{ --------> } OH + 2O_2 \qquad \text{eqn.3.12}$$

3.5 LIFETIME OF OZONE

The seasonal variation of lifetime of ozone has been calculated (Liu, et al., 1987). The lifetime of ozone is equal to the sum of the concentration of all odd oxygen species (O_x) divided by the photochemical loss of odd oxygen (Levy, et al., 1985). NO_2 is considered to be one of the odd oxygen species because to larger extent the photolysis of NO_2 balance the reaction of ozone with NO and does not result in either production or loss of ozone. The lifetime of ozone is about a factor of 10 longer in winter than in summer (Liu, et al., 1987). It is believe that the long lifetime in winter is due to reaction 3.7. The long lifetime of ozone in winter implies that ozone will be transported over long distances. The estimated winter lifetime of ozone in midlatitude is greater than 200 days (Liu, et al., 1987).

It is believed that the cloud cover should increase ozone lifetime in the boundary layer. In addition, above the boundary layer, the ozone lifetime is substantially longer because of lower H_2O mixing ratio (eqn. 3.8).

3.6 SOURCES OF PRECURSORS TO THE TROPOSPHERE

3.6.1 INDUSTRIAL AND URBAN SOURCES

The precursors (hydrocarbons, co, CH_4 etc.) result from the combustion processes in motor car engines and industries (Giacomo *et al.*, 1993; Logan, 1985; and Morgan *et al.*, 1993). Complete oxidation during combustion does not occur, and the exhaust contains gases other than CO_2 and H_2O (Logan, 1985). Some of these exhaust products are hydrocarbons that have not been burned or oxidized at all. Other exhaust products include hydrocarbons that have undergone incomplete combustion. The most prevalent partially oxidized gas is carbon monoxide (CO) (Logan, 1985).

The oxidation process now continues to take place in the atmosphere and not just within the combustion chamber. These peroxy radicals (RO_2) originating from the incomplete combustion of the hydrocarbons are necessary precursors of the efficient production of photochemical ozone (Logan,

1985).

To detail the sources of all the different precursors of ozone would prove to be a great task, but some indication must be made as to the nature of some of these in order that it be realised that rural and urban areas alike are generally not pristine or unpolluted as concerns the availability of such trace gasses.

3.6.2 BIOMASS BURNING

Biomass burning takes many forms; among them, forest and savanna fires, burning of agricultural wastes, and the use of biomass fuels as a domestic energy source are the most important.

Mention has already been made as to the contribution of biomass burning to global concentrations of NO_2 and attention drawn to its possible influence on tropospheric ozone concentrations. Empirical evidence of the relevance of biomass burning is available from the results of a Brazilian study by Kirchhoff *et al.*, (1991). They claim that the burning of sugar cane foliage has a pollution source strength per unit area comparable to well-known biomass burning sources in Amazonia. Brazilian data from

aircraft measurements (2 km altitude) in cane areas in the dry burning season showed ozone values peaking at 80 ppbv, while in the wet season, concentrations were much lower at 30-40 ppbv. The suggestion that the higher ozone concentrations were a result of photochemical reactions were in this instance supported by the fact that ground based diurnal variation of rural sites during burning echoed that of the urban area Sao Jose dos Campos which showed daytime values of 45- 60 ppbv (Levine, 1991).

Biomass fires release a mixture of gases containing the same ozone precursors emitted from fossil fuel combustion: NO*x*, CO, CH*4* and non methane hydrocarbon including a large proportion of alkenes (Delay *et al.*,1985; Andreae *et al.*, 1989, 1992; Kirchhoff and Marinho, 1994). The emissions of ozone precursors from biomass burning have been estimated in a recent review by Andreae (1993) to be comparable in magnitude to the emissions from fossil fuel burning. Thus a strong possibility exists that areas in South Africa might be strongly influenced by biomass burning sources. Certainly, the results of SAFARI-92 experiment in southern Africa (Thompson, 1996a) emphasise the importance of biomass burning in ozone concentration.

3.6.3 PRECURSOR GASES

3.6.3.1 NITROGEN DIOXIDE

Nitrogen dioxide (NO_2) is critical to the photochemical processes in the troposphere. Since nitrogen is a key element in the earth's atmosphere and in many biological functions, it is not surprising to find it, or one of its oxides, as a product of natural processes. This is evidenced in Table 3.1 which shows considerable quantities of NO_x being emitted by lightning, stratospheric injection, ammonia oxidation, biomass burning, and emissions from soil.

It is apparent from this table that there is considerable disagreement between scientists as to the quantities of NO_x emitted globally from these sources. One reason for this may be the fact that the sources are spatially extensive and not easily measurable. There does ,however, seem to be some agreement as to the relative importance of each.

Table 3.1 draws attention to, and places in perspective, the fact that anthropogenic activities such as the combustion of fossil fuels, in the form of gasoline, coal, and diesel oil is a major sources of NO_x, much larger than any natural source. This suggests that anthropogenic

activities (including much of the biomass burning) are likely to be the major influence on tropospheric ozone photochemistry.

Table 3.1 Estimated sources of NOx (Tg/yr)

(After IPCC, 1994)

SOURCES	RANGE	LIKELY
Natural soil	5-12	7
Lightning	3-20	7
Biomass burning	3-13	8
Subsonic aircraft	0.2-1	0.4
Fossil fuel	21-25	24
agricultural soil	?	?

3.6.3.2 METHANE

Methane, for which the linkage to ozone has been detailed in this chapter, is one precursor that is claimed to be increasing in concentration globally. Penkett (1990) mentions concentrations estimated from analysis of ice

cores by Stauffer, *et al.*, (1975), who point to the methane concentration of the undisturbed atmosphere as having been 700 ppbv, and compare this to current concentrations that exceed 1600 ppbv. The majority of this increase is claimed to have occurred in the last four decades.

The major sources of methane are emission from wetlands, oceans, and termites, and fossil fuel and biomass burning. The quantities of each are detailed in Table 3.2.

Natural wetlands are the major source of methane and in recent years considerable new data on methane flux from these ecosystems have been published. The recent flux data from the Amazon region suggest that a large fraction of CH_4 is emitted from tropical wetlands, with a global estimate of 60 Tg/yr (Bartlett, *et al.*, 1990).

The evaluation of the ocean source was performed by Lambert, *et al.*, (1993). According to them only about 3.5 Tg/yr are emitted by open oceans, but emissions from methane rich areas could be considerably more important, producing the total oceanic source of the order of 50 Tg/yr.

A recent estimate of termite emissions to global methane made by Martius, *et al.*, (1993) agrees well with the value 20 Tg/yr given by IPPC, (1992) .

From studies of the carbon 14 content of atmospheric CH_4, it was established that about 20% (100 Tg/yr) of total annual methane emission originates from fossil carbon sources (IPPC, 1992). Other new values of 25 Tg/yr (CIAB, 1992), 17 Tg/yr (Muller, 1992), 43 Tg/yr (Beck, 1993), 49 Tg/yr (Subak, *et al.*, 1993) and 45.6 Tg/yr (Kirchgessner, *et al.*, 1993) were measured.

The new global estimates for the biomass burning source are 30.5 Tg/yr (Hao and Ward, 1993) and 43 Tg/yr (Andreae and Warnek, 1994).

Methane is mainly removed through chemical reactions in the troposphere. A growing number of studies have also shown that methane is consumed by soil microbial communities in the range between 20 and 60 Tg/yr (Reeburg, *et al.*, 1994).

Table 3.2 Estimated sources and sinks of methane (Tg/yr) (After IPCC, 1994)

SOURCES	RANGE	LIKELY	TOTALS
NATURAL			
WETLANDS			
TROPICS	30-80	60	
NORTHLATITUDE	20-60	40	
TERMITES	10-50	20	
FRESHWATER	1-25	5	
OCEAN	5-50	10	
ANTHROPOGENIC			
FOSSIL FUEL		100	
COAL MINES	15-45		
NATURAL GAS	25-50		
PETROLIUM	5-30		
COAL COMBUSTION	7-30		
LANDFILLS	20-70	30	
BIOMASS BURNING	20-80	40	
SINKS			
REACTION WITH OH	330-560	445	
REMOVAL BY SOIL	15-45	30	
TOTAL SINK			475

3.6.3.3 NON METHANE HYDROCARBONS (NMHCs)

Most non methane hydrocarbons have an atmospheric lifetime of less than a week (IPCC, 1994). NMHC with anthropogenic sources exhibit a maximum in winter, reflecting the seasonality of the removal by hydroxyl radicals (Fehsenfeld *et al.*, 1992). The sources of NMHCs are vegetation, oceans,

biomass burning, and technological sources eg gasoline. The amount of each source is shown in Table 3.3.

Table 3.3 Estimated sources of NMHC (Tg/yr)

(After IPCC, 1994)

SOURCES	RANGE	LIKELY
Vegetation	230-800	500
Oceans	20-150	?
Biomass burning	30-90	40
Technological	60-100	70

3.6.3.4 CARBON MONOXIDE (CO)

The estimated carbon monoxide sources and sinks are summarised in the Table 3.4. It has been mentioned in this chapter that the sources include transport, combustion, industrial processes, and refuse incineration. The sinks include reaction with the hydroxyl radical (OH) and soil uptake which is a minor sink.

Table 3.4. Estimated sources and sinks of carbon monoxide (Tg/yr) (After IPCC, 1994)

SOURCES	RANGE	LIKELY
Technological	300-900	500
Biomass burning	400-700	600
Oceans	20-190	?
Methane oxidation	400-1000	600
NMHC oxidation	300-1300	600
Biogenic	60-160	100
SINKS		
OH reaction	1400-2600	2100
Soil uptake	250-640	250

3.7 OZONE EFFECTS

3.7.1 EFFECTS ON HUMAN HEALTH

As discussed by Spengler (1993), exposure to ozone causes many adverse reactions in humans. For example, it causes irritation to the pulmonary airways, leading to inflammation and increased permeability in lung tissues. The elevated levels of daily ozone are associated with restricted activities, asthma symptoms, and respiratory problems.

Hammer *et al.*, (1974) attempted to quantify thresholds for health effects. They found that concentrations of 0.05 ppm were responsible for causing headaches, 0.27 ppm gave rise to coughs and 0.29 ppm caused chest discomfort.

Elsom *et al.*, (1992) pointed out that the odour threshold for ozone is approximately 80 ppb and that the threshold for adverse health effects on population is about 0.10 ppm. Based on a number of experiments it was shown that eye irritation occurs when ozone ranges between 0.10 ppm to 0.15 ppm, with the intensity of eye irritation increasing as concentration exceeds these values.

3.7.2 EFFECTS ON MATERIALS AND VEGETATION

Ozone causes cracking of stretched rubber at concentrations of only 0.01 to 0.02 ppm (Elsom, 1992). Elsom (1992) mentioned that although ozone inhibitors are built into rubber products such as motor vehicle tyres and rubber, ozone can still degrade it.

The increase in the amount of ozone in urban areas can retard tree growth and damage some crops (Logan, 1985). When plants are exposed to ozone, photosynthesis is reduced (Morgan, 1993). The typical signs of ozone effects are

CHAPTER FOUR

ATMOSPHERIC CIRCULATIONS OVER DURBAN REGION

4.1 INTRODUCTION

The atmospheric circulation over KwaZulu-Natal and South Africa at large, has been well documented in the literature. The objective here is not, however, to outline the atmospheric circulation over South Africa, but to pay particular attention to the aspects of the circulation which are important to the topic under investigation, that is the role of synoptic weather systems in relation to ozone concentrations over Durban. The air pollution climatology of an area is determined by the particular topographic setting and by the weather and climate of the area. All these factors will contribute to variations in air pollution concentration in the atmosphere.

Durban is situated in a coastal environment which is complicated by local small scale winds. The effect of these small scale winds may be very important in the dispersion of pollution. Air circulation is important in this study because it provide conditions necessary for air pollution accumulation. When air is stagnant, it is

possible that air pollution is high, because of poor dispersion. Synoptic weather systems such as high and low pressure systems are important because of their role in ventilation and or stagnation of the atmosphere which, in turn influences air pollution concentration.

4.2 MACROSCALE CIRCULATION

The mean atmospheric circulation over South Africa, as has been documented by Jackson (1952) and Taljaard (1953), is anticyclonic. According to Preston Whyte and Tyson, (1988), this anticyclonic airflow is conducive to the subsidence of air which produces adiabatic warming, drying of the atmosphere, increasing atmosphere stability, suppression of precipitation and the occurrence of dry spells. This is significant in dispersion terms, as it creates conditions favourable for the formation of surface radiation temperature inversions, surface drainage wind inversions and elevated subsidence inversions, all of which inhibit the dispersion of atmospheric pollutants.

The adiabatic warming of subsiding air in high pressure systems is the primary cause of subsidence or elevated inversions over southern Africa (Preston-Whyte *et al.*, 1977). Subsidence inversions occur throughout the year, but most frequently from June to December. The dry, stable

2^{0}C. Surface inversions over Durban occur with a frequency exceeding 70% from May to August (Preston-Whyte and Diab, 1980).

4.3 **SYNOPTIC CIRCULATION**

It is necessary, to outline the effect that the synoptic weather systems have on the accumulation or dispersion of pollution over the east coast of KwaZulu-Natal, especially Durban. Air pollution potential, according to Diab, (1976), refers to the set of meteorological conditions which are favourable for the accumulation of pollution.

Air pollution potential at any given time, is a function of the vertical and horizontal components of motion. Vertical motion depends on the stability structure of the atmosphere, such that the greater the wind speed, the greater the dispersion. The relationship according to Diab, (1976) is not that straight forward. Sometimes a strong wind may lead to stack downdrafting which can increase the concentration of pollution on the ground. It is also important to note that light wind can transport pollution for great distances with no dispersion taking place (Diab, 1976). The nature and characteristics of vertical mixing over Durban are under strong seasonal control (Preston-

Whyte and Diab, 1980). During winter, slow moving intensified high pressure systems are responsible for an increase in the average incidence and duration of clear skies, lowered humidity and weak winds.

The passage of mid-latitude frontal systems and accompanying coastal lows along the east coast leads to a distinctive weather sequence. Associated with this weather sequence are well defined patterns of APP, which are summarised in Figure 4.1.

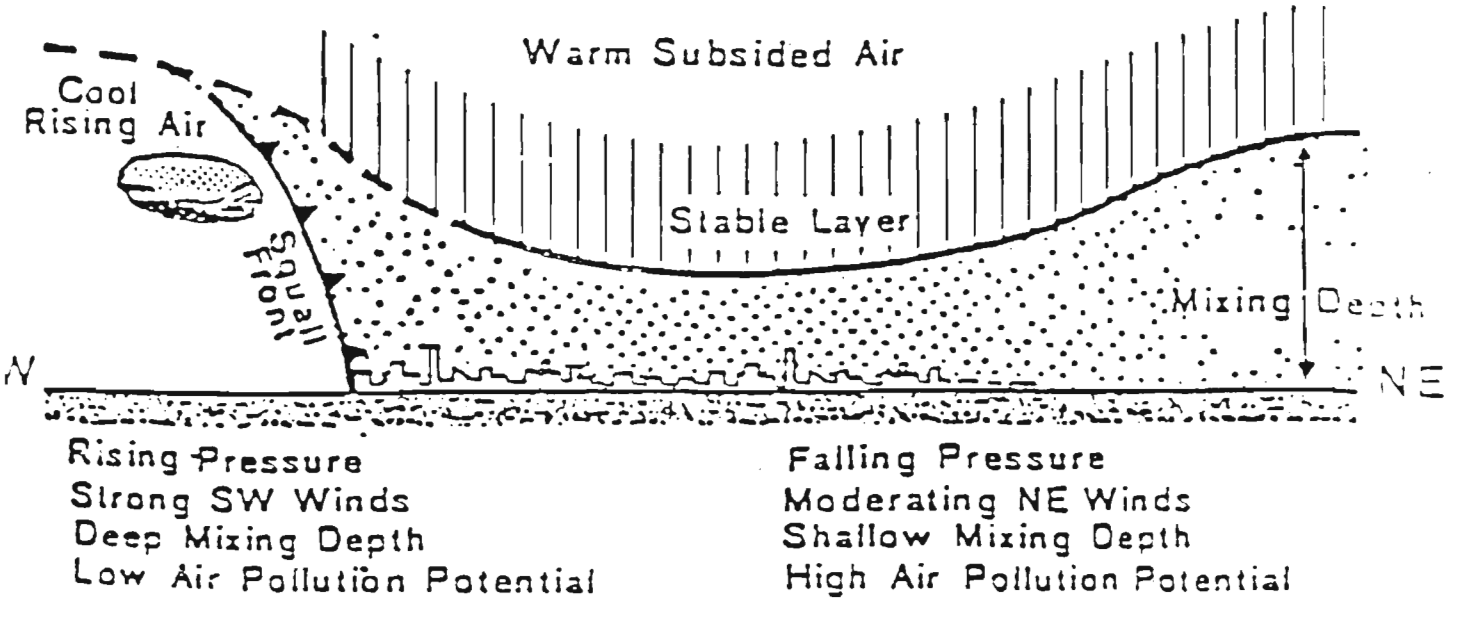

Figure 4.1 Schematic diagram showing the fluctuations in air pollution potential with the passage of a frontal disturbances. (after Preston-Whyte and Diab, 1980)

Diab, (1976) discuss three synoptic regimes, each of which is characterised by a distinct air pollution potential discussed below.

4.3.1 ESTABLISHED HIGH PRESSURE SYSTEM

The first synoptic situation is that of the established high pressure system (Fig.4.2). It is characterised by light north-easterly winds and low mixing depths caused by the existence of an upper atmosphere subsidence inversion. The development of nocturnal surface inversions is common, thus the dispersal capacity of the atmosphere is poor and air pollution potential high.

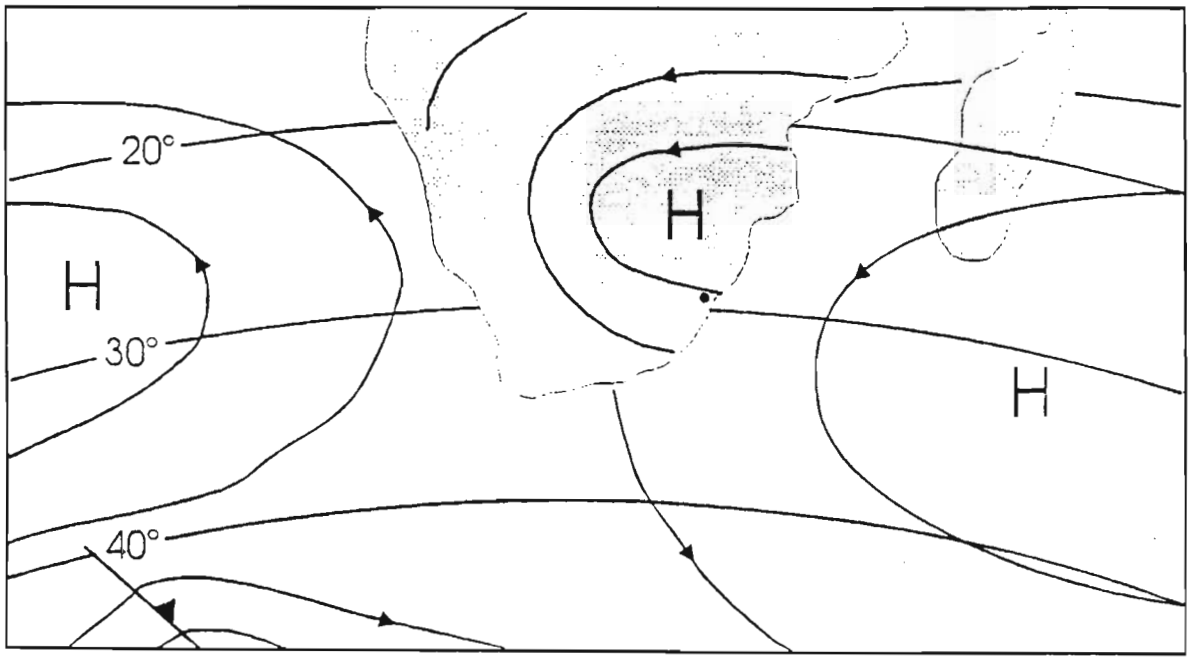

Figure 4.2 Dominant high pressure system (After Preston-Whyte and Tyson, 1988)

4.3.2 PRE-FRONTAL SYSTEM

The approach of a coastal low is accompanied by lowering of the subsidence inversion, which reaches its lowest level immediately before the wind reversal from north east to south west that is often associated with the passage of a low pressure system. It usually succeeds a dominant high pressure system and takes place just before the passage of cold front or coastal low. Under these conditions the air pollution potential increases even further as the subsidence inversion dips towards the surface ahead of the low (Diab, 1976) (Fig.4.3)

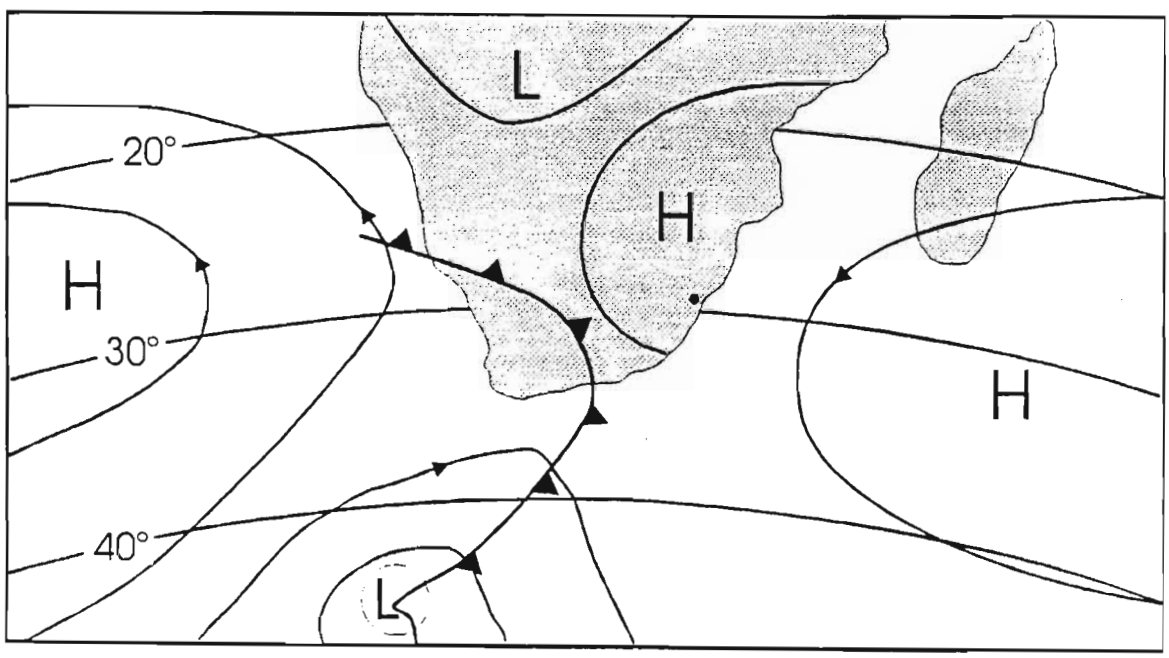

Figure 4.3 Pre-frontal conditions (After Preston-Whyte and Tyson, 1988)

4.3.3 POST-FRONTAL SYSTEM

The final synoptic regime is the post-frontal condition. It is characterised by the presence of strong winds, the uplifting of the subsidence inversion, and is often accompanied by rain. This gives rise to rapid dispersal and removal of pollutants. With the passage of the low, the subsidence inversion either disappears or is displaced to higher levels. With the passage of the low,the wind switches to south-westerly and increases in strength (Diab, 1976). During this stage mesoscale circulations are inhibited because, it is cloudy and strong winds are being experienced. Air pollution is low under these conditions (Fig.4.4).

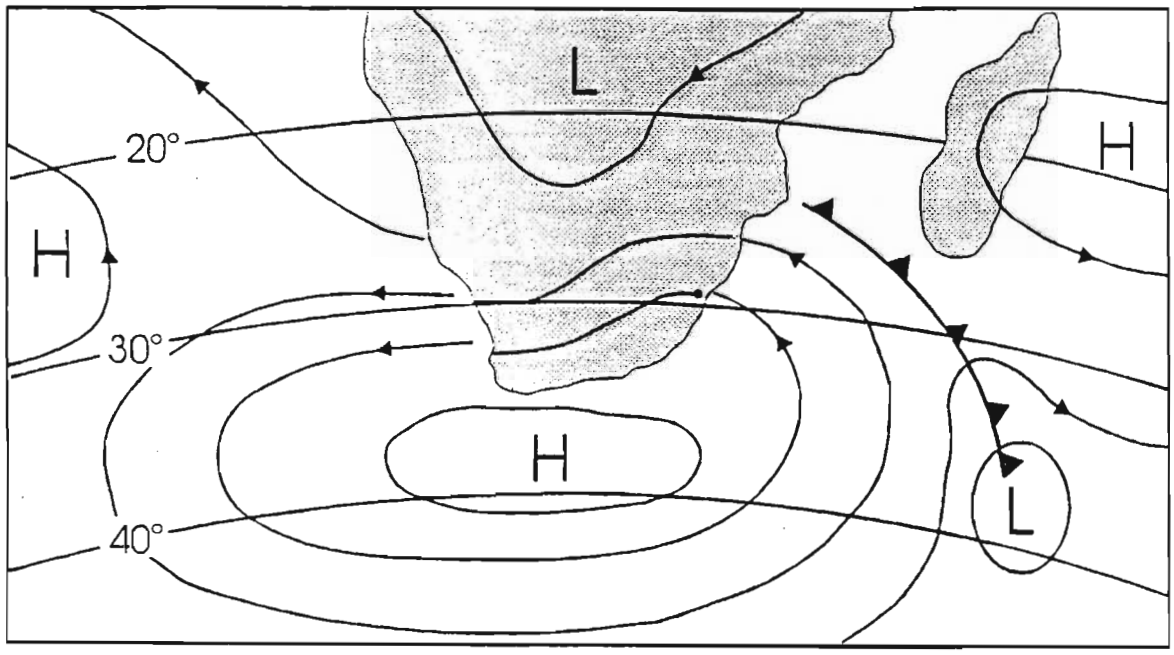

Figure 4.4 Post-frontal conditions (After Preston-Whyte and Tyson, 1988)

4.4 LOCAL CIRCULATION

4.4.1 LAND-SEA BREEZE

Mesoscale circulations in the form of land and sea breezes cause diurnal fluctuations in circulation characteristics. Nocturnal, non-turbulent land breezes occur under stable condition near the surface, while day time sea breezes prevail under conditions of instability (Tyson *et al.*, 1976). Land and sea breezes and have a significant influence on stability and consequently on the dispersion efficiency of the atmosphere.

The generation of land and sea breezes may be attributed to the discontinuity in terms of heat, roughness and moisture which exists along the land-ocean boundary. During the day, sea breezes blow onshore, advancing inland as they strengthen (Preston-Whyte and Tyson, 1988). The sea breeze is most common in summer, when moist, relatively cool air over the sea is advected almost daily over the Natal coast. When deflected by the Coriolis force they become north-easterly winds (Preston-Whyte, 1969).

By night, with radiational cooling of the land, an offshore land breeze develops as a separate circulation. The growth of the land breeze circulation and the development of cold air drainage are closely linked to the macroscale weather patterns. Calm, clear weather is required to facilitate the

strong nocturnal cooling of the land. Such weather is associated with anticyclones which are displaced to lower latitudes in winter thus increasing atmospheric stability over the Natal coast bringing warm dry weather (Preston-Whyte, 1968).

Due to atmospheric stability near the ground the ventilation is poor. At night, the radiational cooling produces a temperature inversion. The surface inversion persists for some time after sunrise. The land breeze is too weak thus the ventilation of the area is left to the sea breeze which is weak and of short duration during winter. Thus adequate ventilation only takes place with the arrival of a depression and unstable weather.

A significant aspect of the land breeze is its ability to transport atmospheric pollutants. Contaminated air would be moved seawards by the land breeze and then parallel to the coast by gradient winds. Pollutants could thus be carried a considerable distance from their source and may even be returned to land by the returning sea breeze (Preston-whyte et al., 1988).

4.4.2 MOUNTAIN-PLAIN AND PLAIN-MOUNTAIN WINDS

The characteristic topography of KwaZulu-Natal, especially the eastern part, consists mainly of deeply incised river

valleys running perpendicular to the coast. This topography gives rise to some well developed regional winds systems which affect air pollution on the coast of KwaZulu-Natal (Fig.4.5).

During the night, cooling takes place which lead to the development of mountain winds which blow down the longitudinal axes of the valleys (Diab, 1976). During the night when conditions are suitable, mountain plain winds combine with the land breeze near the coast and the nocturnal offshore wind at the coast may be very stable. The results from such a stable layer of air is very important in air pollution concentration (Diab, 1976).

The pollution released in such condition under stable air layer may not be mixed upwards. By day, the reverse is true, because plain-mountain winds are said to develop, which flow from the coast to the interior.

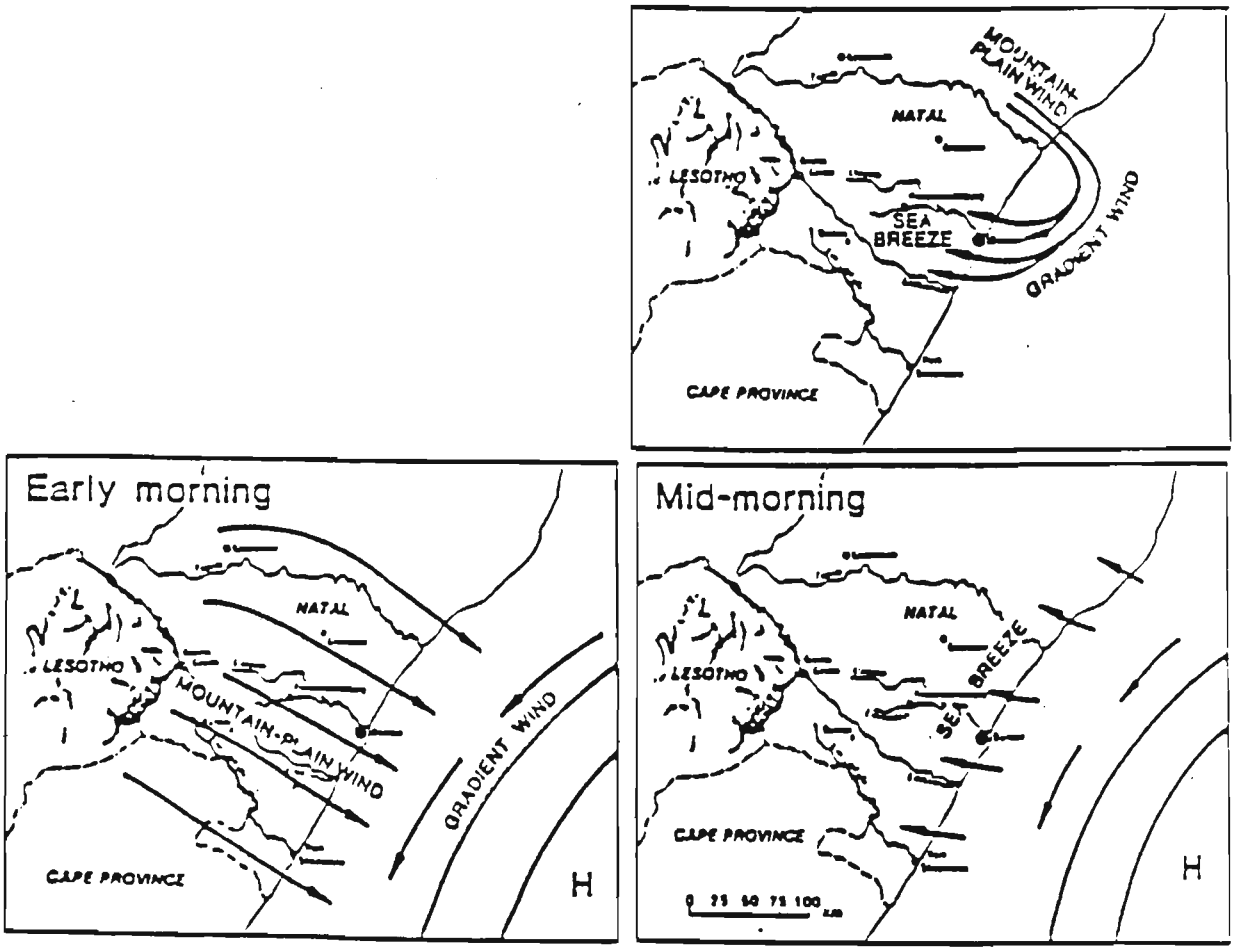

Figure 4.5 Early morning surface and local gradient winds over Natal. Recirculation of pollution may occur as a consequence of such airflow patterns. (After Preston-Whyte and Tyson, 1988.)

SUMMARY

The continuous procession of eastward moving, high and low pressure systems is according to Preston Whyte and Tyson ,1988, largely responsible for wind and other weather

changes over the study areas. High and low pressure systems are influenced firstly by climatic controls imposed by the Drakensberg Escarpment which separates the interior plateau from the narrow coastal margin and secondly by contrasting temperatures of the ocean current adjacent to the shores of the subcontinent.

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Having described the air circulation and its implication in surface ozone concentration, it is now necessary to consider the analysis of data that were collected.

Chapter Five

Temporal Variations in Surface Ozone

CHAPTER FIVE

TEMPORAL VARIATIONS IN SURFACE OZONE

5.1 INTRODUCTION

The data are evaluated with regard to their diurnal and seasonal behaviour. A statistical analysis of the relationship between ozone and meteorological variables is also presented. The analysis shows that surface ozone concentrations vary with time of the day, season, temperature, wind speed, humidity and the passage of synoptic weather systems.

Mean ozone concentrations in Durban are unexpectedly low. In fact they are lower than those measured at Cape Point, which is representative of a background monitoring station. Mean monthly Cape Point values lie between 13 and 28 ppb, with a maximum in winter (Combrink, et al., 1995). It is hypothesised that the low ozone concentration in Durban may be due to high NO_x which in turn would deplete ozone. However, in the absence of NO_x measurements at Durban, this hypothesis could not be tested. Also, in a marine environment, methyl iodide released from the ocean may provide an additional sink for ozone (Chemidies and Walker,

1973).

In the absence of measuring of other chemical species, the focus of this chapter is on temporal variations of surface ozone rather than an actual magnitudes.

5.2 SEASONAL VARIATION IN SURFACE OZONE

Mean monthly ozone concentrations for the period of study are shown in Figure 5.1. There is a clear annual cycle with a small amplitude of 6.5 ppb. The mean monthly maximum value (12.5 ppb) is experienced in August and the minimum in January (6.4 ppb) (Table 5.1). The daily mean maxima and minima are also shown in Table 5.1.

The annual cycle observed at Durban is qualitatively similar to that of Southern Hemispheric baseline stations. In this respect, reference is made to equation 3.7 which describes the photolytic destruction of ozone in the free troposphere, which would account for the annual ozone cycle (Maximum in winter [low hv] and minimum in summer [maximum hv]).

Although the similarity may be fortuitous, it should not be excluded altogether that the chemical processes characteristic for clean maritime air masses also make their mark on the annual cycle observed at Durban in

addition to conditions brought about by poor dispersion during winter.

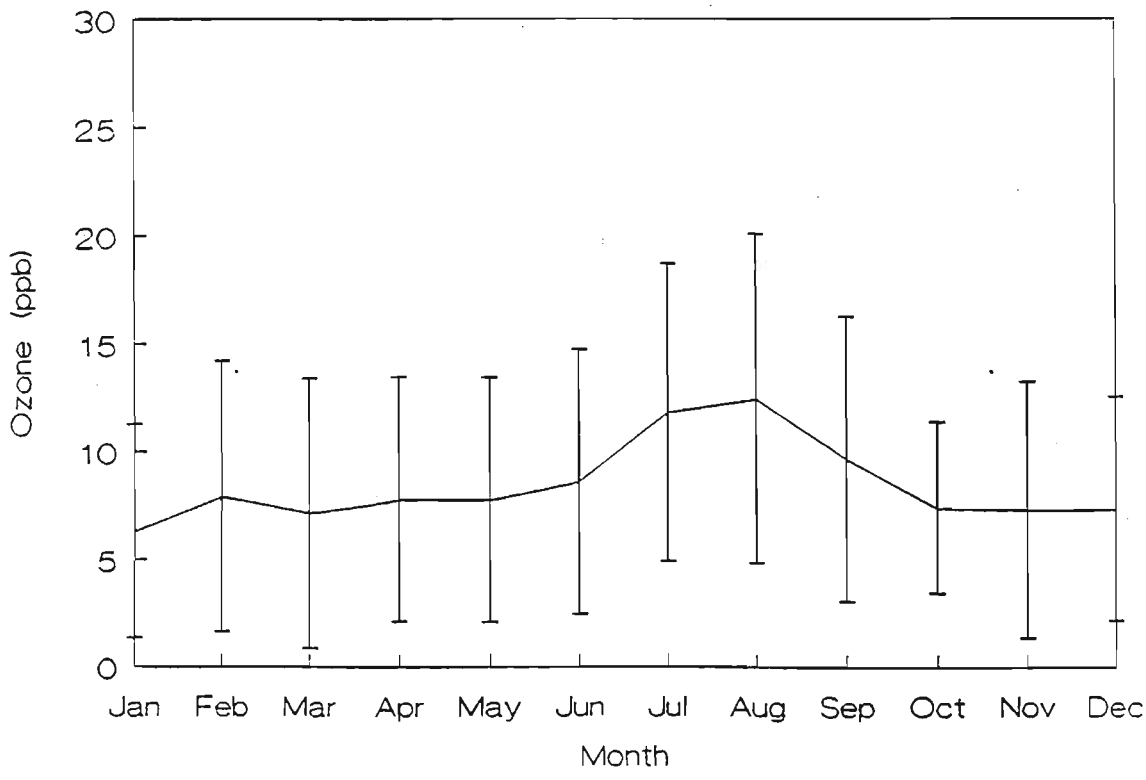

Figure 5.1 Mean monthly variation of surface ozone (ppb) at Durban. Standard deviations for each month are shown as vertical bars

The late winter peak and the sharp rise from June to July is possibly related to the greater accumulation of ozone at the surface due to the poor dispersion, higher frequency of inversions and lower mixing depth at this time (Diab, 1976). There is no evidence of a summer peak, which is typical of a highly polluted urban-industrial environment, such as has been found at stations in the Eastern Transvaal Highveld (ETH) (Combrink, *et al.*, 1995). The lower ozone concentration during summer may also be influenced by a higher frequency of precipitation which causes wash out (Donley, *et al.*, 1979; U.S. Department of State, 1988).

As pointed out that highly polluted urban-industrial environments generally give rise to summer maxima, since this is not observed at measuring site, this could imply the following: (i) that the presence of ozone precursors is generally low (augers against heavy industry in the region). (ii) that the maritime influence is stronger than originally anticipated. (iii) that the predominance of ozone destruction processes (nocturnal temperature inversions) even in summer is fairly high.

The standard deviation bars in Figure 5.1 show that the variability about the mean is large. This is re-emphasised in Figure 5.2 which presents mean daily values throughout the year. Background levels lie between 5 and 10 ppb, but

the enhancement in the late winter months is evident. Not only is there an enhancement which is evident in the mean, but both the minimum and maximum values are higher in winter (Tables 5.1 and 5.2). The maximum values, in particular, are higher. Possible underlying factors will be addressed in Section 5.3.

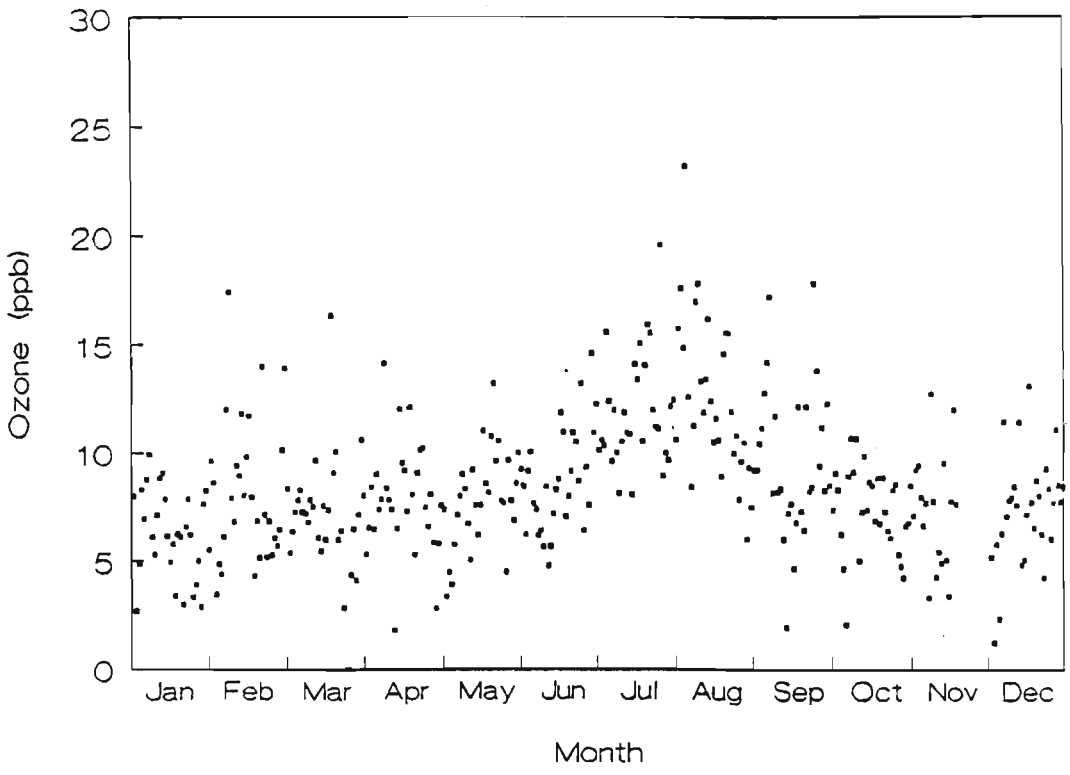

Figure 5.2 Daily mean values of ozone (ppb) at Durban.

Table 5.1 Monthly mean values and monthly mean daily maxima and minima of surface ozone concentration (ppb) at Durban.

Month	MONTHLY MEAN	DAILY MEAN MAX	MIN
JANUARY	6.4	9.9	2.7
FEBRUARY	7.9	17.4	3.5
MARCH	8.0	16.3	4.1
APRIL	7.8	14.1	1.8
MAY	7.8	13.2	3.3
JUNE	8.6	14.6	4.7
JULY	11.8	19.6	8.0
AUGUST	12.5	23.2	6.0
SEPTEMBER	9.7	17.3	4.3
OCTOBER	7.4	10.7	2.1
NOVEMBER	7.3	12.7	3.3
DECEMBER	7.3	13.1	1.2

TABLE 5.2. Seasonal mean values and seasonal mean daily maxima and minima of surface ozone concentrations (ppb) at Durban.

	SUMMER	AUTUMN	WINTER	SPRING
MAXIMUM	13.8	14.6	18.7	12.3
MEAN	7.2	7.9	11.0	7.3
MINIMUM	3.7	3.1	5.2	3.8

5.3 DIURNAL VARIATION OF OZONE

The mean diurnal cycle in surface ozone at Durban is characterised by a minimum in the morning (8:00) and a maximum in the afternoon (14:00) (Fig. 5.3). The strong mean diurnal cycle is typical of that found in polluted urban environments (Oltmans, 1981). It reflects the relationship between the buildup of ozone precursor gases in the early morning and the subsequent photochemical formation of ozone. Throughout the night the values remain fairly steady, at about 6-8 ppb.

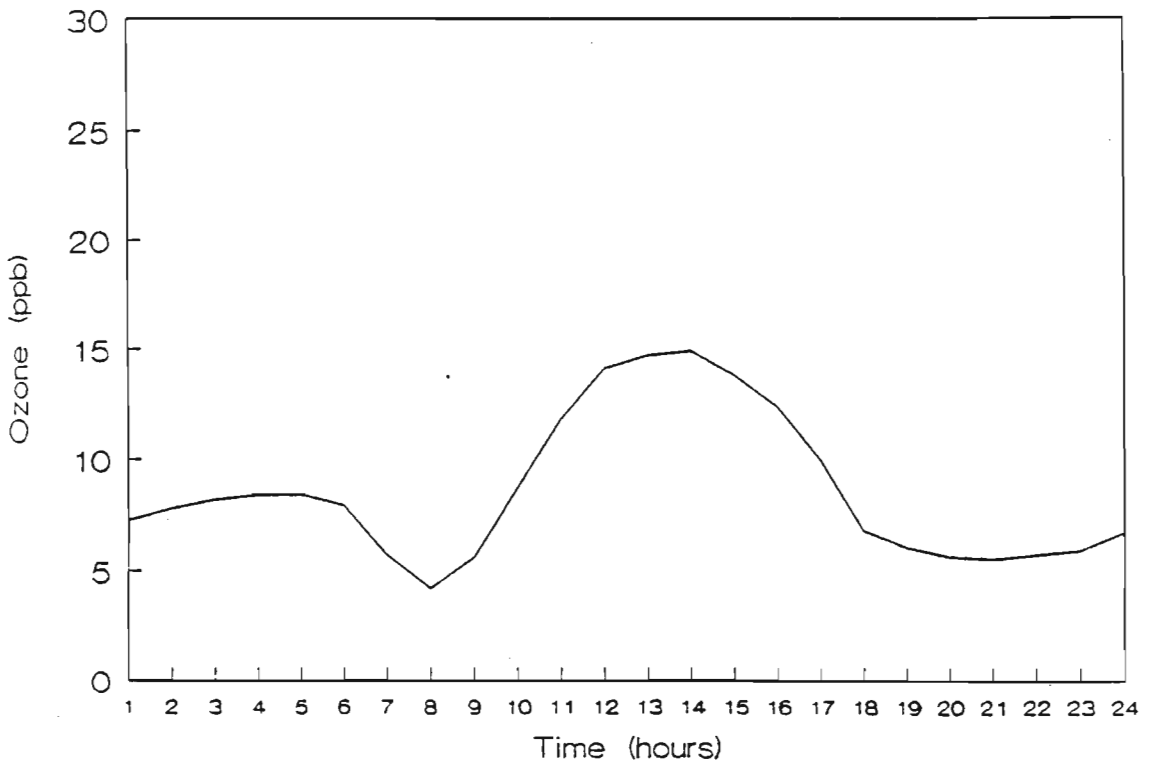

Figure 5.3 Mean diurnal variation of surface ozone (ppb) at Durban (Sep 94- Aug 95).

The pronounced daytime peak is due to photochemical generation of ozone as a result of higher temperatures and insolation at this time of the day. Increased photochemistry within the polluted layer may also be due to the relatively high concentrations of ozone precursors (NOx and hydrocarbons) produced from industries or transported into the region during the morning. The photochemistry is not the only control but other mechanisms such as nighttime deposition and vertical mixing during the day (seasonally dependent) is the strongest prevelent mechanism.

The diurnal pattern of ozone values is seasonally variable and values are higher in winter and autumn than in spring and summer (Fig.5.4). In all seasons the time of minimum ozone is 8:00, with the exception of summer when the minimum occurs one hour earlier. Spring and summer maxima are experienced at 12:00, where winter and autumn maxima are experienced at 14:00. These differences are clearly related to seasonal differences in the time of sunrise and the period of sunshine hours. There are also seasonal differences in the magnitudes of maxima and minima. A nighttime ozone elevation is observed around 4:00 in winter and autumn. It is acknowledged that there can be no nighttime formation of ozone, hence it is concluded that these peaks result from ozone imported into the region. The mechanism for transporting relatively ozone-rich air into the study area is not known, but is hypothesized to be the mountain-plain wind, which is described in detail by Tyson

and Preston-Whyte (1972). This circulation develops after midnight in the early hours of the morning, and could transport air from the higher altitude regions which are known to be richer in ozone concentration (Janach, 1989). Furthermore, the mountain-plain wind is best developed in the winter season when this phenomena is observed.

It is also likely that the seasonal differences in the diurnal pattern of ozone are related to seasonal contrasts in the occurrence of nocturnal temperature inversions which are prevalent in this region (Fig.5.5). The frequency of nighttime surface inversions on the east coast is high in winter (70 %) whereas in summer, the frequency is below 30 percent (Tyson et al., 1976). These inversions would trap ozone near the surface and prevent dilution into a greater volume of air.

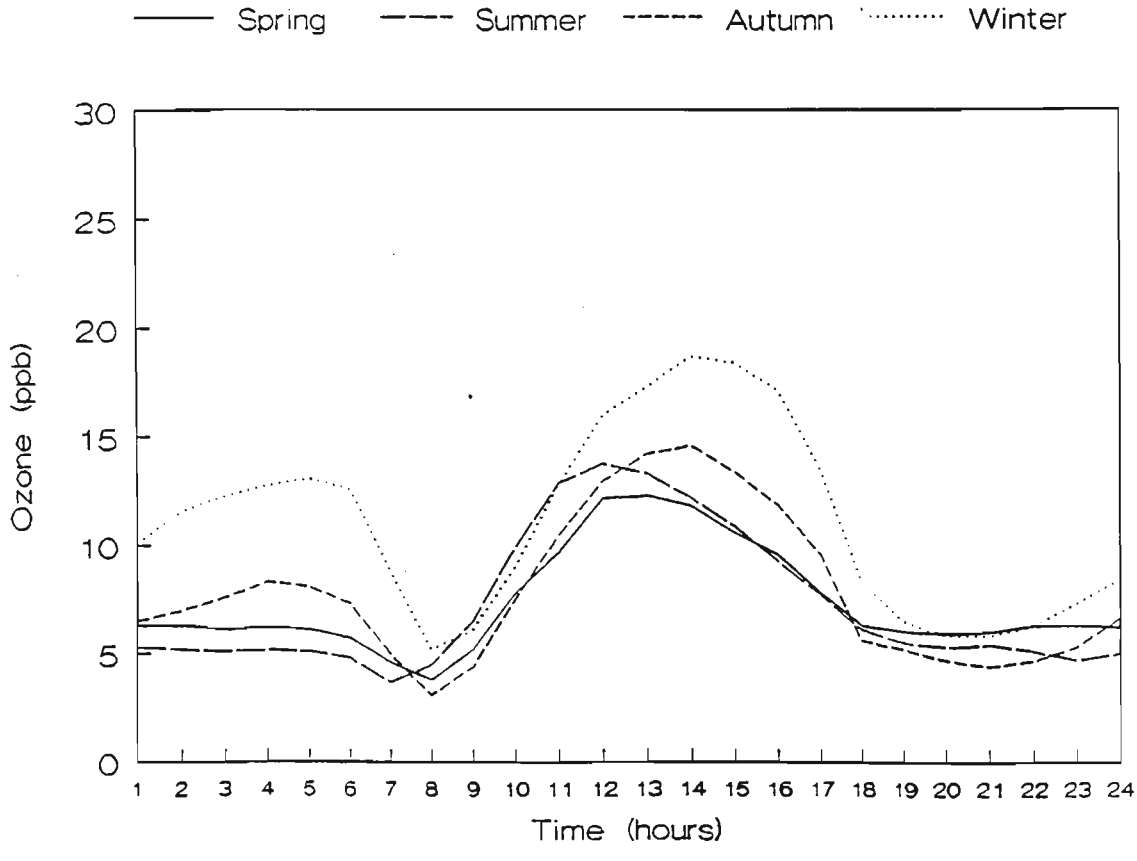

Figure 5.4 Mean diurnal variation of surface ozone (ppb) in Durban by season

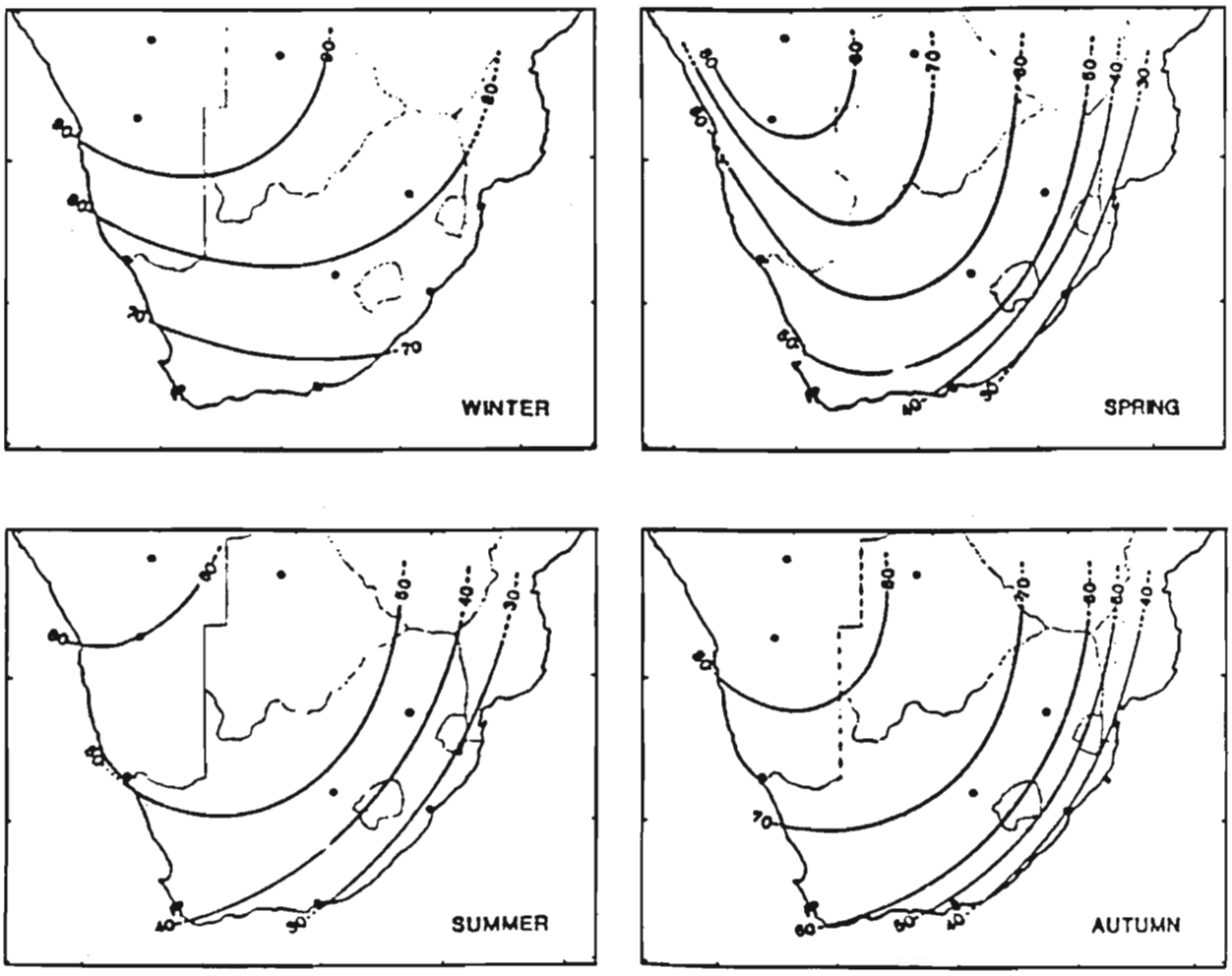

Figure 5.5 Seasonal percentage frequencies of midnight inversions over southern Africa (After Tyson, et al., 1976)

5.4 INFLUENCE OF SYNOPTIC WEATHER SYSTEMS ON OZONE CONCENTRATION

In accordance with the synoptic weather classification outlined in Chapter four, days during the study period have been classified into 3 categories. This was achieved by examination of surface synoptic charts. The frequency of occurrence of the three synoptic categories over the study area was determined as being 69.3% for pre-frontal, 24% for post-frontal and 6.3% for established high pressure systems.

The mean diurnal ozone concentration for each of the 3 categories is illustrated in Figure 5.6. All display a minimum at 08:00 and the characteristic early to mid-afternoon ozone maximum. Means and maximum and minimum values for each synoptic category are summarised in Table 5.3.

Table 5.3. **Mean ozone concentrations and mean maxima and minima (ppb) for pre-frontal, post-frontal and established high pressure systems.**

	PRE-FRONTAL	POSTFRONT	EST. HIGH
MAXIMUM	15.2	10.2	14.8
MEAN	8.5	7.3	7.3
MINIMUM	4.1	3.7	2.5

The mean ozone concentration was the highest in the presence of pre-frontal conditions. This is most likely due to reduced atmospheric dispersion as a result of a lowered subsidence inversion (Preston-Whyte and Diab, 1980), which gives rise to a mean maximum concentration of 15.2 ppb (Table 5.3). Similar, though slightly lower, values were associated with an established high pressure system.

Air masses associated with post-frontal conditions in Durban contain the lowest mean ozone concentration (Table 5.3). The associated weather is generally cool and cloudy with precipitation. Atmospheric dispersion is good. As such conditions are unfavourable for the photochemical formation

of ozone (Comrie and Yarnal, 1991), which explains the low

to moderate ozone values. The amplitude of the diurnal curve under a post-frontal situation is much lower than the other categories . The nighttime and daytime maxima are of similar magnitude. The lower daytime peak is probably related to reduced photochemical formation as a result of greater cloudiness.

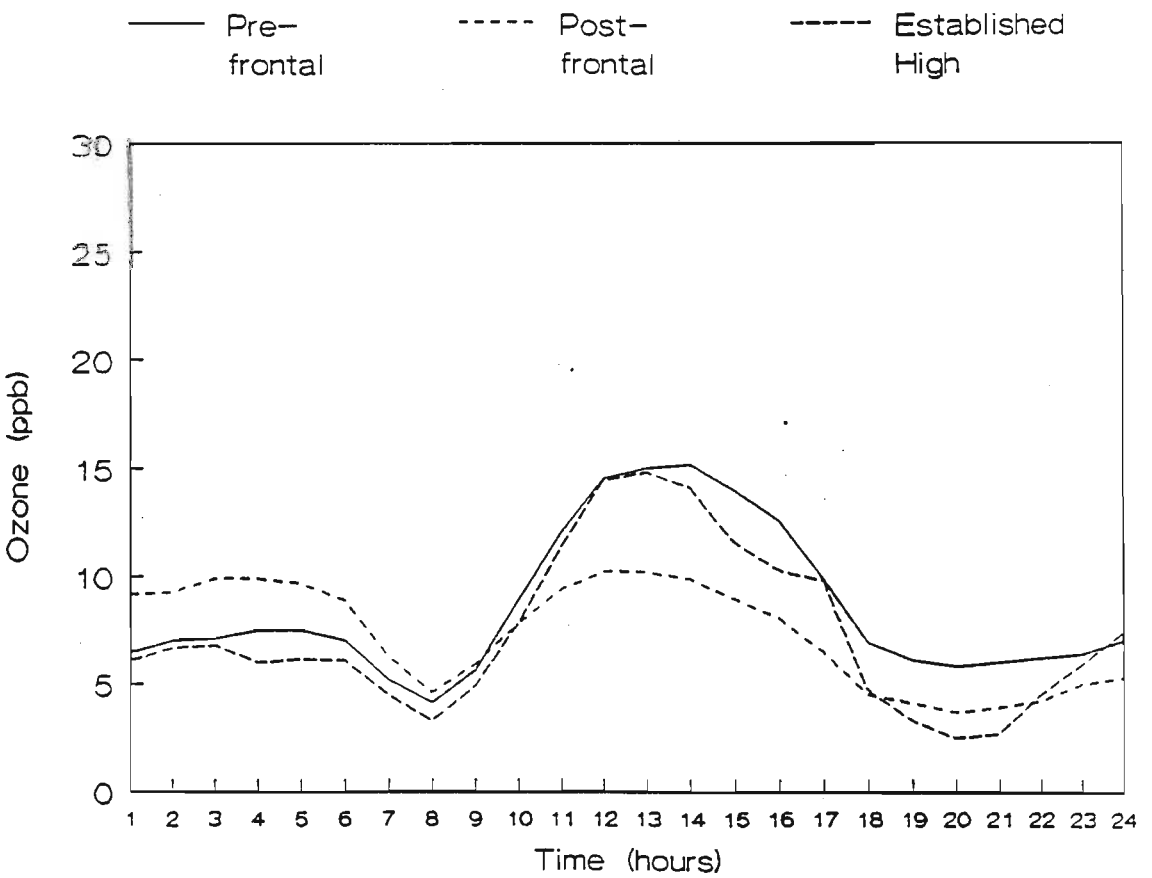

Figure 5.6. Mean diurnal variation of ozone (ppb) by synoptic weather category.

5.5 THE INFLUENCE OF METEOROLOGICAL VARIABLES ON OZONE CONCENTRATION

5.5.1 RELATIONSHIP BETWEEN OZONE AND WIND DIRECTION AND SPEED

The relationship between mean hourly wind speed is shown in Figure 5.7. There is a positive clear relationship of ozone, most likely reflecting higher daytime photochemical buildup of ozone which coincides with higher daytime wind speed. The outliers in figure 5.7 coincide with low wind speed.

Ozone concentration is also shown to be a function of surface wind direction. Figure 5.8 displays mean ozone concentration for each wind direction. Lowest values occur in air motion with west and north offshore winds which usually occur at night. Higher values of the order of 10 ppb, are associated with all other sectors and most likely reflect the location of the monitoring station in relation to urban-industrial areas of Durban. Winds from these sectors would pass over heavily polluted areas before reaching the monitoring station.

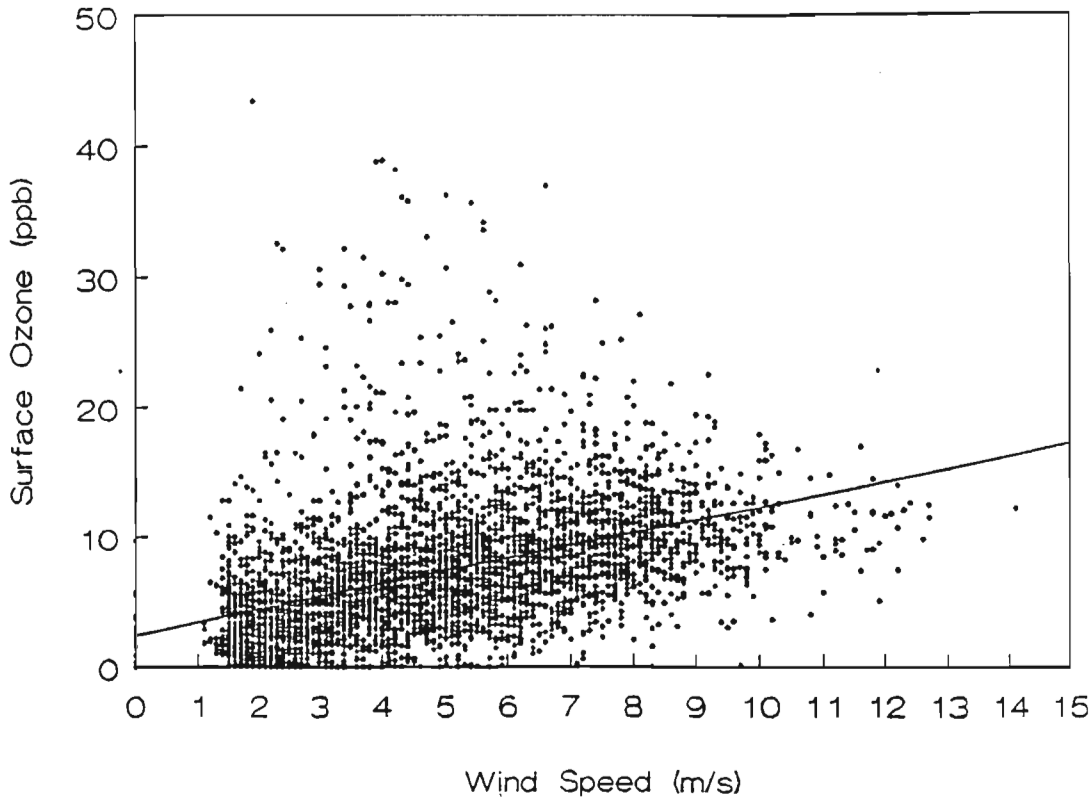

Figure 5.7. Plot of mean hourly ozone (ppb) against hourly mean surface wind speed ($m.s^{-1}$).

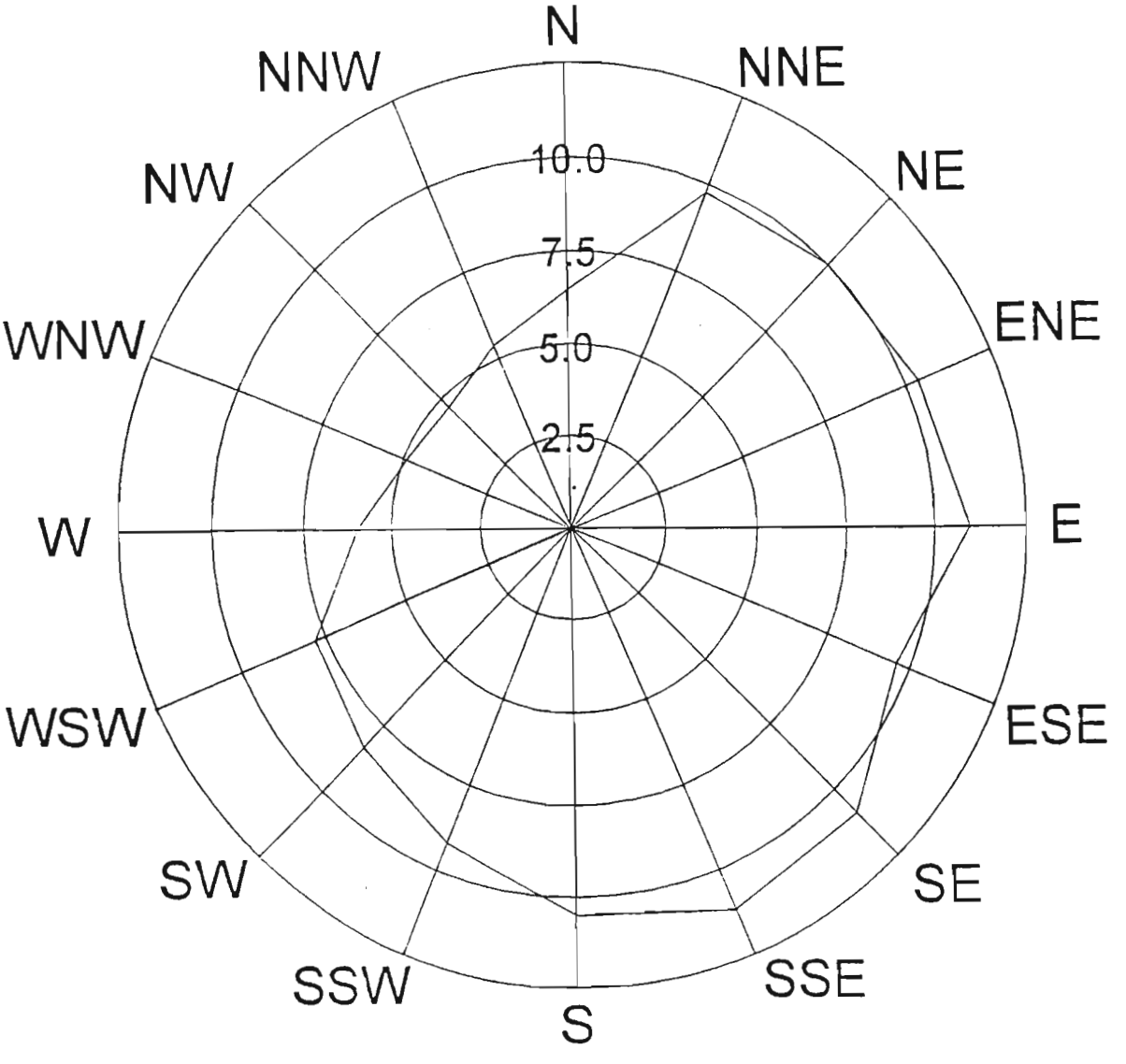

Figure 5.8 Mean surface ozone (ppb) according to wind direction.

5.5.2 RELATIONSHIP BETWEEN OZONE, HUMIDITY, TEMPERATURE AND PRESSURE

An analysis of the relationship between humidity and surface ozone was undertaken. The association between relatively high humidity and low ozone and vice versa indicates that a supply of water vapour reduces ozone concentration (Liu, *et al.*, 1992) (Fig.5.9). Temperature shows a positive correlation with ozone (Fig.5.10), whereas, there is no clear relationship between ozone concentration and surface pressure (Fig. 5.11). This relationship between temperature and ozone probably signifies that the diurnal temperature cycle coincides with maximum photochemical activity at noon.

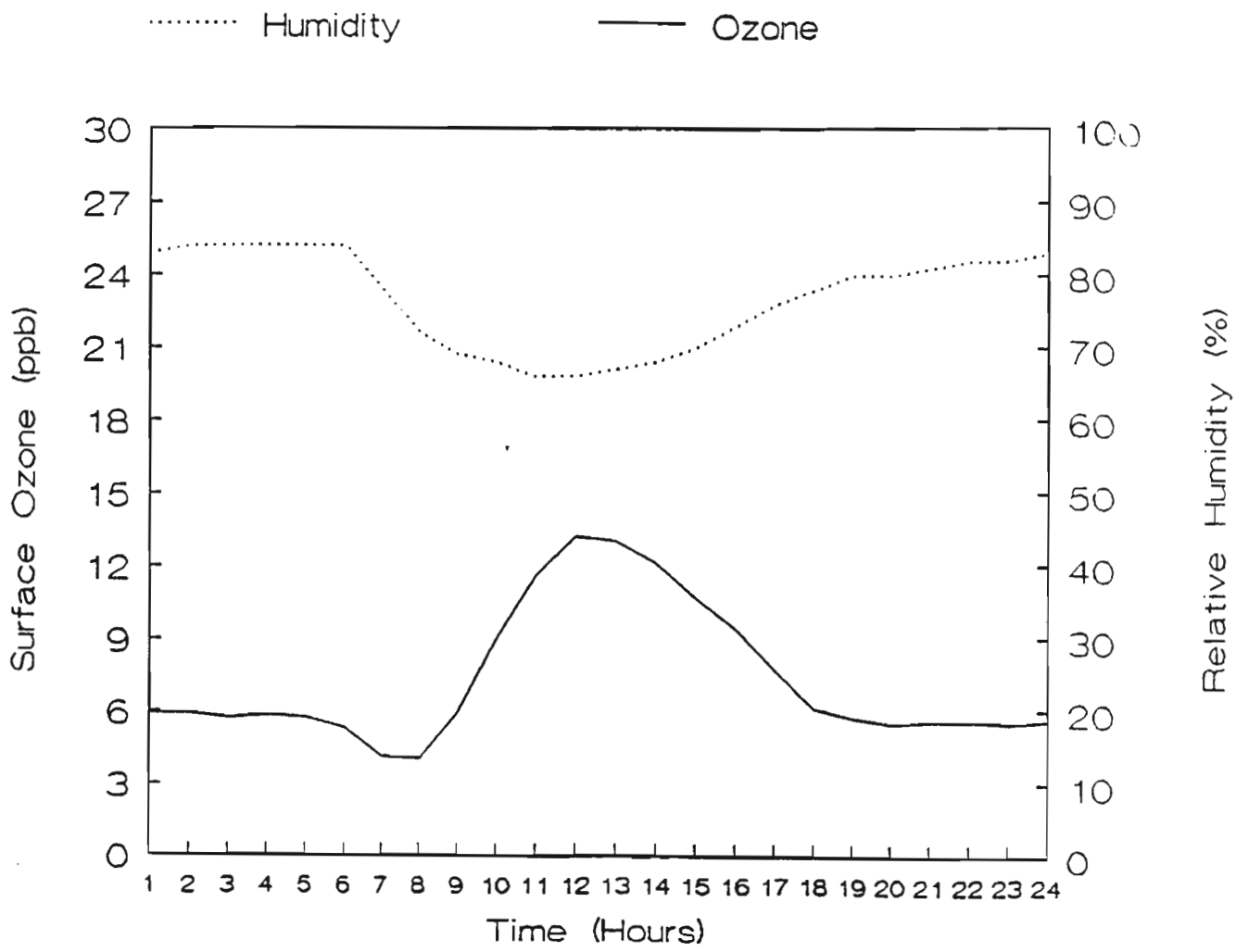

Figure 5.9 Diurnal variation of mean surface ozone (ppb) with mean surface humidity (%).

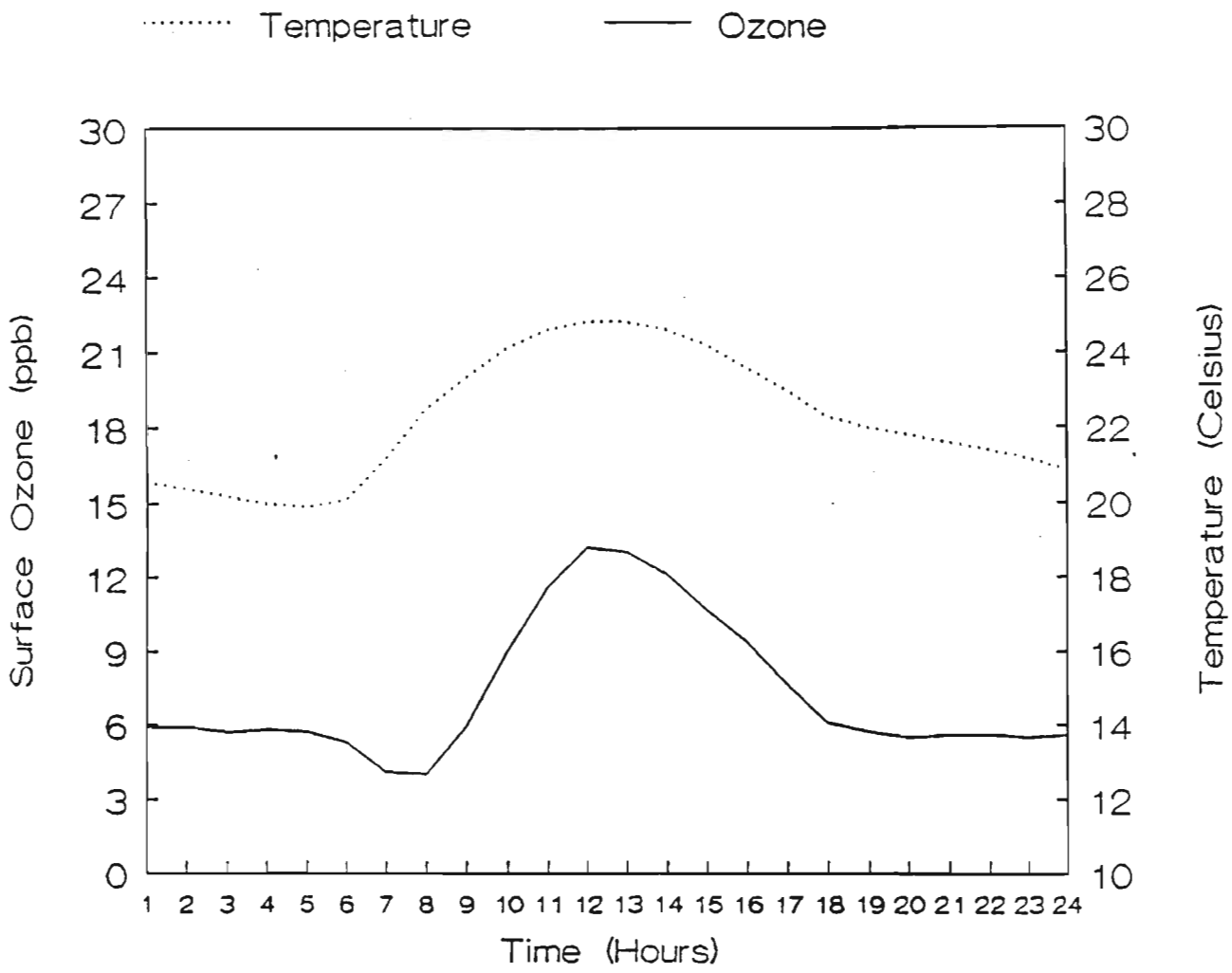

Figure 5.10 Diurnal variation of mean surface ozone (ppb) with mean surface temperature (^{0}C).

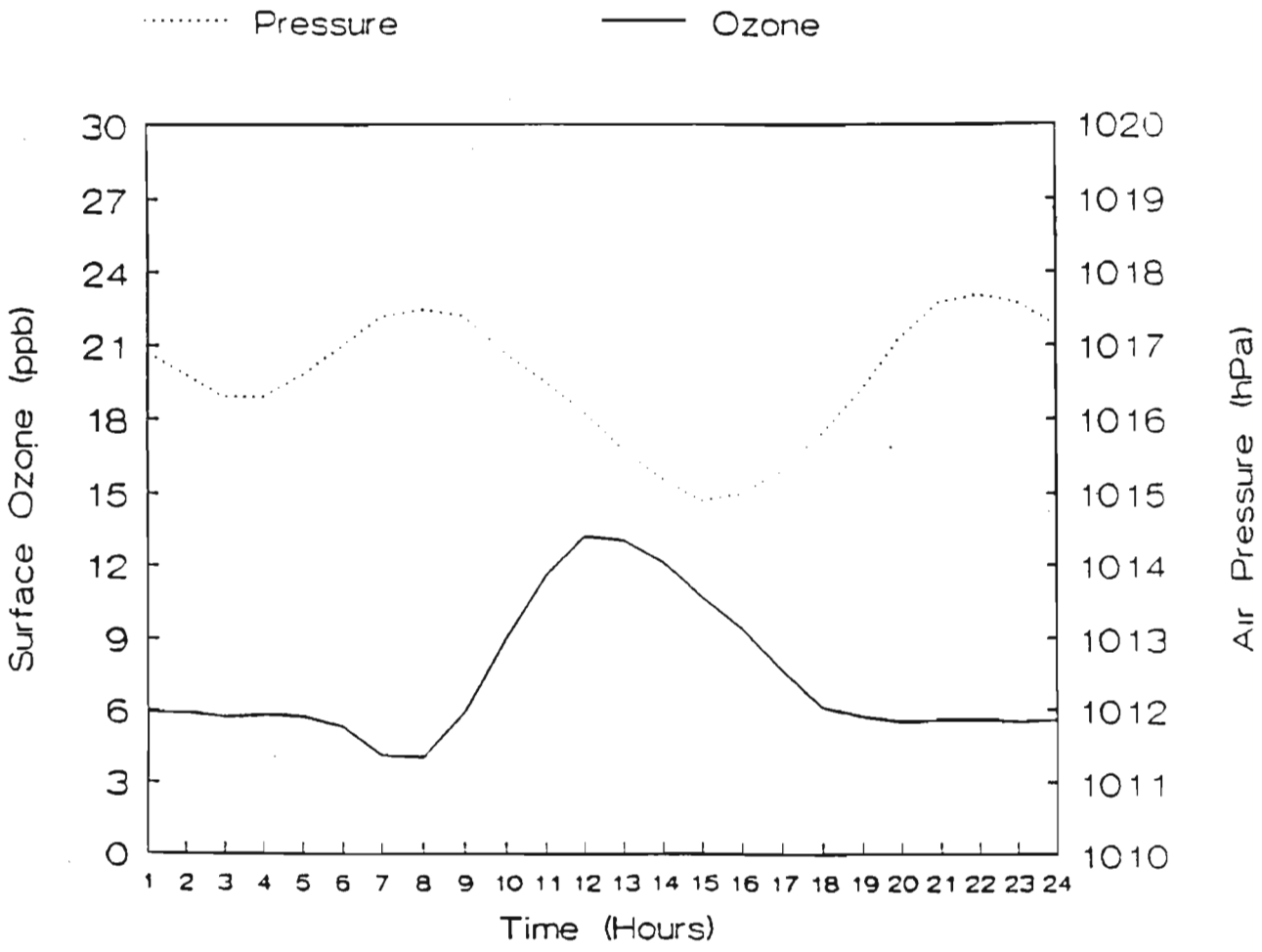

Figure 5.11. Diurnal variation of mean surface ozone (ppb) and surface pressure (hPa).

5.5.3 CORRELATION BETWEEN OZONE AND METEOROLOGICAL VARIABLES

The relationship between ozone and meteorological parameters during the period of study was analysed statistically using a linear multiple regression equation. The results are presented in Table 5.4).

It appears that temperature and wind speed are the most important factors. Positive correlations of 0.61 and 0.66 were observed between ozone and temperature and ozone and wind speed respectively. Ozone formation is clearly dependent on the high temperatures and wind speeds experienced during the day. The relationship between ozone and relative humidity and surface pressure is weakly developed.

Table 5.4 Multiple regression analysis of ozone and meteorological factors.

MODEL FITTING RESULTS FOR OZONE USING FOUR VARIABLE

Indep variable	coeff	std error	t-value	sig.level
WIND SPEED	0.666	0.045	14.65	0.0000
TEMPERATURE	0.615	0.054	11.32	0.0000
PRESSURE	0.059	0.017	3.37	0.0008
HUMIDITY	0.006	0.010	0.58	0.5557

R - SQ. = 0.39
STANDARD ERROR = 3.23

The multiple regression analysis using four independent meteorological variables yielded an R^2 value of 0.39. The approximately 40% of the variance in surface ozone is experienced by these four variables. However, the contribution of humidity and pressure is minimal. Wind speed and temperature account for approximately the same percentage variance. With addition of humidity and pressure as independent variable, there is little variation in R^2 value.

5.6 SUMMARY

The mean diurnal and seasonal surface ozone variations have been described for Durban. The relationships between surface ozone, meteorological variables and synoptic weather systems have also been investigated. The seasonal cycle shows a winter maximum, which coincides with season with highest frequency of surface inversions. The mean diurnal cycle in surface ozone reflects the relationship between the buildup of ozone precursor gases in the early morning and the subsequent photochemical formation of ozone. The nighttime ozone maximum in the autumn and winter is explained by the transport of relatively ozone rich air from higher altitude regions in the mountain plain circulation. Mean ozone concentration is also highest in association with pre-frontal synoptic weather conditions, most likely due to reduced atmospheric dispersion as the

Chapter Six

Conclusion

CHAPTER SIX

CONCLUSION

6.1 SUMMARY

Measurements of surface ozone at Durban from September 1994- August 1995 provided an understanding of the relationship between surface ozone variation and synoptic weather systems, meteorological variables and the variation of surface ozone with season and time of the day.

The mean ozone concentration in Durban is lower than that measured at Cape Point, which is representative of a background monitoring stations. It is hypothesised that the low ozone concentration in Durban may be due to high NO_x which in turn would deplete ozone.

Further investigation of surface ozone seasonal behaviour, shows a winter season maximum which is attributed to a high frequency of surface inversions which lead to the accumulation of precursor gases at the surface. The diurnal ozone maximum is experienced around solar noon to mid-

afternoon and is typical of urban-industrial environment.

The diurnal variation in surface ozone is also strongly related to synoptic weather systems. A nighttime ozone elevation occurs around 4:00 in winter and autumn. It is acknowledged that there is no nighttime formation of ozone, hence it is suggested that these elevations result from ozone imported into the region.

Relatively higher ozone concentrations are associated with pre-frontal synoptic weather conditions. Similar, though slightly lower, values are associated with an established high pressure system whereas, air masses associated with post-frontal conditions contain the lowest mean ozone concentrations. The associated weather is generally cool and cloudy with precipitation which minimize photochemical activities and ozone formation.

6.2 LIMITATIONS OF THE STUDY

- It should be borne in mind that the monitoring station is located at a higher elevation than the main urban-industrial area of Durban and that the readings may not necessarily be representative of ozone concentrations in an urban area. It is anticipated that, on days when the mixing depth is very shallow, the data will reflect lower ozone concentrations than

those areas situated at a lower elevation.

- There were no other species (for example NOx) measured during the period of study, which limits the conclusion which are able to be drawn.

- Data were available for a period of only one year and so the results may not necessarily be representative of longer period.

6.3 RECOMMENDATIONS

- Monitoring should continue so that data collected over a period longer than a year can be analyzed.

- The hypothesis of ozone transport from inland areas during the night should be tested by doing comparable measurements inland during the winter period.

- The reasons for the low ozone values in Durban should be explored by monitoring other species concurrently with ozone.

- Additional ozone monitoring stations should be installed in the Durban area to determine the

representativeness of the station at the University.

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