

# SEASONAL AND DIURNAL VARIATIONS OF SURFACE OZONE ON THE MPUMALANGA HIGHVELD

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DEDICATED TO MY LATE YOUNGER SISTER  
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# LIST OF ACRONYMS AND SYMBOLS

ANN	Artificial neural network
AOT40	Accumulation over threshold of 40 ppb
ASL	Above sea level
BTA	Particulate matter less than 10 $\mu\text{m}$ in diameter
BVOC's	Biogenic volatile organic compounds
$^1\text{D}$	Electronically excited state
DEAT	Department of Environmental Affairs and Tourism
EC	European Commission
GC-EI	Gas chromatography coupled with Electron impact ionization
$\text{gcm}^{-2}\text{yr}^{-1}$	gram per square centimeter per year
$\text{g/mol}$	gram per mole
$\text{HO}_x$	Hydrogen-containing free radicals
$h\nu$	UV or solar radiation (photons)
MAC-value	Maximum acceptable concentration value
MDA	Multivariate data analysis
MLR	Multiple linear regression
MS	Mass spectrum
$\text{m/s}$	meter per second
NIST	National Institute of Standards and Technology
NMHC	Non-methane hydrocarbons
NO	Nitrogen or nitric oxide
$\text{NO}_2$	Nitrogen dioxide
$\text{NO}_2/\text{NO}$	Ratio of emissions of nitrogen dioxide to nitrogen oxide
$\text{NO}_x$	Nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ )
$\text{NO}_x$ -sensitive	A term to define a condition in which reducing $\text{NO}_x$ emissions most effectively reduces ozone concentrations
$\text{NO}_y$	Total nitrogen species
NNW	North of northwest
NW	North west
$^{\circ}\text{C}$	Degrees Celsius

OSHA	Occupational Safety and Health Agency
<sup>3</sup> P	Ground electronic state
PAH	Polyaromatic hydrocarbons
PAN	Peroxyacetyl nitrate
PCR	Principal component regression
PLS	Partial least squares
PM <sub>10</sub>	Particulate matter less than 10 μm in diameter
ppb	Parts per billion, or parts per 10 <sup>9</sup> , by volume
RO <sup>•</sup> <sub>2</sub>	Alkyl peroxy radical
SE	South east
SSE	South of southeast
SSW	South of southwest
SW	South west
T	Ambient temperature
VOC's	Volatile organic compounds
VOK'e	Vlugtige organiese komponente
VOC/NO <sub>x</sub>	Ratio of emissions of volatile organic compounds to nitrogen oxides
VOC-sensitive	A term to define a condition in which reducing VOC's emissions most effectively reduces ozone concentrations
W/m <sup>2</sup>	Watt per square meter
WNW	West of northwest
WSP	Wind speed
λ	Wavelength



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## ABSTRACT

Surface ozone concentrations are used to monitor changes and trends observed in the sources of both ozone and precursors, and they are also important indicators of possible health and environmental impacts. Urban and rural air quality can be improved by regular control of major air pollutants such as ozone, NO<sub>x</sub> and VOC's.

Air quality data (O<sub>3</sub>, NO and NO<sub>2</sub>) of two Eskom monitoring sites on the Mpumalanga Highveld, Elandsfontein (26°15'S, 29°25'E, 1742 m ASL) and Verkykkop (27°18'S, 29°53'E, 2047 m ASL), were analysed and compared, to evaluate the exceedances of air quality threshold values and the annual, seasonal and diurnal variations of air pollutants. The relationship between monitoring sites at higher altitudes and ozone concentrations was also investigated. Vertical profiles of volatile organic compounds were also sampled at Elandsfontein during a field campaign on the 30<sup>th</sup> and 31<sup>st</sup> August 2005 using a small aircraft, to investigate their abundance in the atmosphere.

The annual and seasonal trends were investigated between January 2000 and December 2004. High ozone concentrations, exceeding the DEAT human health hourly guideline value of 120 ppb were observed at both monitoring sites. High ozone exceedances at night were also observed at Verkykkop. Surface ozone concentrations were higher at Verkykkop compared to Elandsfontein, which were mainly due to transport of formed ozone and its precursors from upwind emission sources with persistent north-westerly winds during the period.

Higher NO<sub>x</sub> concentrations were observed at Elandsfontein than at Verkykkop because Elandsfontein is located near many industries, which contribute to their high emissions. They are also due to motor traffic emissions from nearby traffic highways situated to the West of this monitoring site. They contributed to lower ozone concentrations observed at this site. Elandsfontein is described as a VOC-limited region because it has high concentrations of NO<sub>x</sub>

and low concentrations of ozone, and Verkykkop is a  $\text{NO}_x$ -limited region with low  $\text{NO}_x$  concentrations and high ozone concentrations.

Seasonal and diurnal patterns of surface ozone on the Mpumalanga Highveld showed maximum values in spring, while those recorded during summer and autumn showed minimum values. Maximum values of ozone in spring are due to biomass burning which occurs mainly during the dry season.

Diurnal cycle of ozone concentrations exhibits maximum values in the afternoon and minimum in the early morning hours and evening. The afternoon maximum is due to photochemical formation of ozone and the evening minimum is partly due to surface deposition, the titration of  $\text{O}_3$  by  $\text{NO}$  and no photolysis of ozone precursors causing ozone production at night.

Meteorological variables (temperature, wind speed and direction, and solar radiation) were also monitored in order to determine if there is any correlation between ozone concentrations and weather conditions. The correlations that were observed were then statistically (using linear regression analysis or scatter plots) analysed to indicate which meteorological variables and ozone precursors influence the formation of ozone the most.

Temperature showed a direct relation with surface ozone at both sites because ozone increased with increasing temperature. Wind direction influences the formation of ozone at Verkykkop, which is downwind the source emission area. High concentrations of  $\text{NO}$  and  $\text{NO}_2$  reduced ozone concentrations at Elandsfontein due to titration of  $\text{O}_3$  by  $\text{NO}$  and reaction of  $\text{NO}_2$  and hydroxyl radicals to form  $\text{HNO}_3$ , which is eventually removed from the atmosphere by rain.

VOC concentrations were observed to be higher in the morning than in the afternoon and also higher at a lower altitude. Among VOC's that were quantified, toluene was found to be the most abundant VOC with high concentrations, which increase from the morning to the afternoon. Concentration ratios of toluene to benzene increase with the time of the day,



which indicate that toluene is emitted from most activities that take place during the day. Alkanes were the most abundant VOC's in the atmosphere among VOC's that couldn't be quantified because they are less reactive towards hydroxyl radicals and thus have a longer atmospheric lifetime.

## OPSOMMING

Oppervlakte osoonkonsentrasies is gebruik om veranderings en tendense wat in bronne van osoon en voorgangerverbindings te monitor. Dit is ook belangrike indikatore van moontlike gesondheid- en omgewingsimpakte. Stads- en plattelandse lugkwaliteit kan deur gereelde beheer van hoof lugbesoedelingsverbindings soos osoon, NO<sub>x</sub> en VOK'e verbeter word.

Lugkwaliteitdata (O<sub>3</sub>, NO en NO<sub>2</sub>) van twee Eskom moniteringstasies op die Mpumalanga Hoëveld, Elandsfontein en Verkykkop is geanaliseer en vergelyk om die oorskrydings van lugkwaliteitwaardes op 'n jaarlikse, seisoen en daaglikse basis te evalueer. Die verhouding tussen die moniteringstasies by hoër hoogtes bo seespieël en osoonkonsentrasies is ook ondersoek. Die vertikale profiel van vlugtige organiese verbindings is ook by Elandsfontein gedurende die 30<sup>ste</sup> en 31<sup>ste</sup> Augustus 2005 met behulp van 'n klein vliegtuig bepaal.

Die jaarlikse en seisoen tendense is ondersoek tussen Januarie 2000 en Desember 2004. Hoë osoonkonsentrasies, wat die voorgeskrewe DEAT standaard vir menslike gesondheid van 120 ppb per uur oorskry, is by beide stasies waargeneem. Hoë osoon oorskrydings gedurende die nag is ook by Verkykkop waargeneem. Hoër oppervlak osoonkonsentrasies is by Verkykkop in vergelyking met Elandsfontein, wat aan die transport van gevormde osoon en sy voorgangerverbindings vanaf wind-op emissiebronne uit 'n noordwestelike windrigting toegeskryf kan word.

Hoër NO<sub>x</sub> konsentrasies is by Elandsfontein in vergelyking met Verkykkop waargeneem omrede Elandsfontein naby baie industrieë is wat tot die hoë emissies bydra. Die hoër vlakke is ook te danke aan motor-emissies vanaf naby geleë vervoerroetes wat na die weste kant van hierdie moniteringstasie geleë is. Dit dra by tot laer osoonkonsentrasies wat by dié stasie waargeneem word. Elandsfontein kan as 'n VOK-beperkende gebied want dit het hoë konsentrasies van NO<sub>x</sub> en lae konsentrasies van osoon en Verkykkop

is 'n  $\text{NO}_x$ -beperkende gebied, met lae  $\text{NO}_x$  en hoë osoonkonsentrasies beskryf word.

Seisoen en daaglikse wisselings van oppervlakte osoon op die Mpumalanga Hoëveld het maksimum waardes in die lente seisoen getoon, terwyl die waardes wat gedurende somer en herfs waargeneem is, minimum waardes vertoon. Die maksimum osoonwaardes in die lente is te danke aan biomassa verbrandings, wat gedurende die droë seisoen voorkom.

Daaglikse variasies van osoonkonsentrasies vertoon maksimum waardes in die namiddag en minimum waardes in die vroeë oggendure en in die aand. Die namiddag maksimum is te danke aan fotochemies vorming van osoon en die minimum in die aand is gedeeltelik te danke aan oppervlak deposisie, die titrasie van  $\text{O}_3$  deur  $\text{NO}$  en geen fotoliese van osoon voorgangerverbindings in die aand voorkom nie.

Weerkundige parameters (temperatuur, wind spoed en rigting, en sonstraling) was ook gemonitor om vas te stel of daar enige korrelasie tussen osoonkonsentrasies en weerkondisies is. Die korrelasies wat genoteer is, word dan statistiese gebruik (met gebruik van lineêr regressie analise of verspreiding diagramme) om aan te dui watter weerkundige veranderlikes en osoon voorgangerverbindings die vorming van osoon die meeste beïnvloed.

Temperatuur het 'n direkte verband met oppervlakte osoon by beide meetstasies getoon want osoon het met verhoogde temperatuur verhoog. Windrigting beïnvloed die vorming van osoon by Verkykkop, wat wind af die meeste emissie bronne geleë is. Hoër konsentrasies van  $\text{NO}$  en  $\text{NO}_2$  het tot laer osoonkonsentrasies by Elandsfontein gelei wat aan die titrasie van  $\text{O}_3$  deur  $\text{NO}$  en die reaksie van  $\text{NO}_2$  en hidroksielradikale om  $\text{HNO}_3$  te vorm toegeskryf kan word.  $\text{HNO}_3$  word vanaf die atmosfeer deur reën verwyder.

Die vertikale profiel meetings van VOK'e het getoon dat hoër VOK-konsentrasies is in die môre as in die namiddag voorkom en ook dat die VOK-konsentrasies hoër naby die aardoppervlak is. Van die VOK'e wat

gekwantifiseer is, was die tolueenkonsentrasies die hoogste. Die tolueenkonsentrasie het ook van die môre tot die namiddag verhoog. Die konsentrasieverhoudings van toluen tot benseen verhoog met die tyd van die dag, wat daarop dui dat toluen afkomstig is van aktiwiteite wat gedurende die dag plaasvind. Alkane was die grootste groep verbindings wat nie gekwantifiseer kon word nie omrede hulle minder reaktief teenoor hidroksielradikale is en dus 'n langer atmosferiese leeftyd het.

# CHAPTER 1

## INTRODUCTION AND OBJECTIVES

---

*This chapter gives an introduction of the project motivation, the aims and objectives of the project and lastly the geographical location and background of the monitoring stations.*

---

### 1.1 Introduction

Surface ozone (O<sub>3</sub>) concentrations are a major concern since the early 1900s because elevated concentrations have negative impacts on living organisms and materials [Ambroise *et al* 2001, Dueñas *et al* 2002, Elkamel *et al* 2001, Glavas *et al* 1999, Lazutin *et al* 1995, Syri *et al*, van Tienhoven *et al* 2004, Wang *et al* 1998, Yi *et al* 1996]. To be able to predict ozone concentrations, one must understand its chemistry and the conditions that contribute to the formation and destruction of it in the atmosphere [Dueñas *et al* 2002, Lengyel *et al* 2004].

Ozone is not emitted directly into the air but is a secondary pollutant that results from complex chemical reactions in the atmosphere [Elkamel *et al* 2001, Abdul *et al* 2002]. It can occur from natural and anthropogenic sources. Naturally, it is known to arise from the intrusion from the stratosphere and emitted from lightning. Anthropogenic pollution leads to the formation of ozone through complex reactions involving sunlight, nitrogen oxides (NO<sub>x</sub>), volatile organic compounds (VOC's) and carbon monoxide (CO) [Parrish *et al* 1999].

Volatile organic compounds are emitted from various natural sources such as trees, mainly isoprene and monoterpenes, and anthropogenic sources such as automobile engines. Nitrogen oxides are released into the atmosphere by soils, automobile engines, combustion of fossil fuels, and combustion of coal in electric power stations and naturally by lightning. Carbon monoxide is emitted from exhausts of automobile engines and from burning coal [Combrink *et al* 1995].

Meteorological parameters have a large influence on the efficiency of the photochemical reactions leading to surface ozone formation and destruction, therefore the variation in ozone concentration is related to meteorological parameters such as temperature, wind speed and direction, rainfall, cloud cover and solar radiation [Debaje *et al* 2003, Dueñas *et al* 2002, Helmig *et al* 1999, Lengyel *et al* 2004].

Ozone is a highly reactive chemical compound that is influenced in various ways by its sources, sinks and chemical reactions, and thus has variability in both spatial and temporal distributions [Lin *et al* 2002, Ribas *et al* 2004]. The concentration of ozone in any area results from the combination of formation, transport, destruction and deposition. Elevation also affects ozone concentrations, with higher concentrations typically observed at areas located at higher altitude (or free troposphere) [Vingarzan 2004]. A good way of unraveling the dynamics of ozone is to examine its daily and seasonal cycles, since ozone is not static and its spatial and temporal distributions have shown to exhibit cycles that have different patterns at different latitudes and altitudes [Riga-Karandinos *et al* 2005, Vingarzan 2004].

## **1.2 Objectives**

The objectives of this study are:

- To execute statistical analysis of ozone and its precursor data collected at the Eskom sites at Elandsfontein and Verkykkop.

- To determine the vertical profile of volatile organic compounds on the Mpumalanga Highveld during an early spring season.
- To explain the observed ozone concentrations with meteorological parameters and ozone precursors.

To achieve these goals, the study aims to:

- Analyze a 5-year surface ozone data set obtained at the Eskom sites at Elandsfontein and Verkykkop.
- Explain the interaction between ozone concentrations and its precursors at Elandsfontein and Verkykkop in terms of their annual, seasonal and diurnal variations.
- Compare ozone concentrations with meteorological parameters to determine if there is any correlation and to identify the most important factors in determining ozone levels.
- Evaluate the influence of the elevated site at Verkykkop on the diurnal pattern and number of exceedances recorded above the DEAT 1 hour guideline value of 120 ppb.
- Obtain the vertical profiles of volatile organic compounds during a field campaign in August 2005.

This study will specifically focus on ozone precursors and meteorological parameters such as:

- Nitrogen dioxide (NO<sub>2</sub>)
- Nitric oxide (NO)
- Particulate matter (PM<sub>10</sub>)
- Solar radiation (W/m<sup>2</sup>)
- Temperature (°C)
- Wind speed (m/s)
- Wind direction (degrees)

### 1.3 Study area

For this study, the data from two monitoring stations, namely, Elandsfontein and Verkykkop situated on the Mpumalanga Highveld are selected since Mpumalanga is an area of intense urban and industrial activity and the main coal-producing region of South Africa [Combrink *et al* 1995]. There are a number of activities that may cause poor air quality in Mpumalanga, including industry, power generation, petrochemical plants, coal dumps, agriculture, mining, veld fires and motor vehicle use [Mpumalanga state of the Environment Report 2003, Tyson *et al* 1988].

The power stations are potentially a major source of air pollution in the Mpumalanga Highveld [Tyson *et al* 1988] since Eskom has located ten out of a total of thirteen coal-fired power stations in this region. More than three quarters ( $\approx 75\%$ ) of South Africa's energy comes from burning coal, approximately half (53%) of which is used to generate electricity, 33% for petrochemical industries (Sasol), 12% used by metallurgical industries (Mittal and Highveld steel) and 2% in homes for heating and cooking [Generation Fact Sheet 2006]



## CHAPTER 2

### LITERATURE SURVEY

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*In this Chapter...*

*A brief introduction to ozone ( $O_3$ ) is given in section 2.1. Section 2.2 provides an overview of the properties of ozone and the adverse impacts of high concentrations of ozone on human health, vegetation and materials, while section 2.3 is about the locations of the Earth's total ozone. The precursors of surface ozone and their natural and anthropogenic sources are discussed in section 2.4. Section 2.5 gives an overview of the chemistry of the troposphere, that is, the formation of the HO radical in the atmosphere, and the formation and destruction of ozone in the troposphere. The relation between  $O_3$ ,  $NO_x$  and VOC's is discussed in section 2.6. Section 2.7 focuses on the spatial and temporal variability of surface ozone, as well as temporal variations of the ozone precursors. Section 2.8 gives a brief summary of meteorological conditions that enhance or hinder surface ozone formation and section 2.9 concludes the chapter by summarising briefly the statistical models that are used for ozone forecasting.*

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#### 2.1 Introduction

Although ozone chemistry has been thoroughly investigated in many experiments and in photochemical modelling studies, there are still difficulties in predicting precisely the ozone concentrations as well as its spatial distribution, behaviour and associated trends. It is believed that there are more parameters than just precursor concentrations which lead to ozone formation or destruction processes in the atmosphere [Dueñas *et al* 2002, Zwoździak *et al* 2001]. To improve urban air quality, major air pollutants such

as O<sub>3</sub>, CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, particulate matter, hydrocarbons, non-methane hydrocarbons (NMHC) and volatile organic compounds should be controlled and regulated [Riga-Karandinos *et al* 2005].

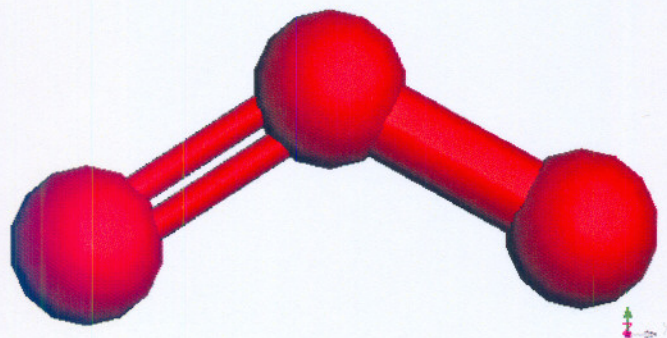
Surface ozone concentrations are strongly related to meteorological parameters. The meteorological parameters include temperature, solar radiation, cloud cover, rainfall, dust, relative humidity, wind speed and direction [Dueñas *et al* 2002, Lengyel *et al* 2004]. Clear skies, warm temperatures, solar radiation and soft winds are believed to have a great influence on surface ozone concentrations [Dueñas *et al* 2002].

Vertical profiles through the boundary layer can reveal the inversion layers and also whether emissions originate close to the monitoring site or are transported from a source upwind of the location [Helmig *et al* 2000]. The vertical transport of ozone and its precursors between the boundary layer and higher altitudes, including the exchange of air with the stratosphere, has a strong influence on surface ozone. The decrease of ozone in the mixed layer and towards the earth's surface indicates a significant removal of ozone near the surface. [Helmig *et al* 2002].

Statistical methods can also be applied to correlate surface ozone concentrations with its precursors and meteorological parameters [Dueñas *et al* 2002, Pastor-Bárcenas *et al* 2005]. Successive generations of models for ozone forecasting have been developed over the past years to understand the factors controlling tropospheric ozone and to formulate emission control strategies [Jacob 2000] The assessment of air quality in urban ecosystems, using the available air quality data will help to generate information that will aid in planning pollution control strategies to keep pollutant concentrations within acceptable limits [Pastor-Bárcenas *et al* 2005, Riga-Karandinos *et al* 2005].

## 2.2 Properties of ozone

Ozone is chemically defined as an allotrope of dioxygen ( $O_2$ ), the molecule with an extra oxygen atom added, having the chemical symbol  $O_3$  [Möller 2004] and a molecular weight of 48 g/mol. The three oxygen atoms are linked at an angle of  $116^\circ$  with a distance of 1.278 Å (or picometer) [Möller 2004] between the atoms (Figure 2.1). Ozone is a bluish and diamagnetic gas at room temperature and pressure. It becomes a blue liquid below  $-112^\circ\text{C}$  and a deep blue-violet solid below  $-192.5^\circ\text{C}$  (80K) [Möller 2004]. At atmospheric pressure, it dissolves partially in water but at standard temperature and pressure, the solubility is 13 times more than that of  $O_2$  [Lenntech 2005]. It can be characterized by a smell that can be detected around high voltage discharges such as television, photocopy machine, welding and printers or even during a thunderstorm [Möller 2004, Takeuch *et al* 1995].

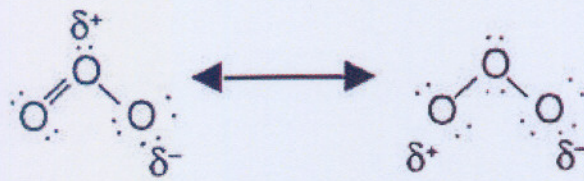


**Figure 2.1:** The modelled structure of ozone

Ozone is electrically defined as oxygen with a high energy level. The symbols  $\delta+$  and  $\delta-$  indicate that the  $O_3$  molecule is short of or has an excess of electrons in the locations where the symbols occur, see (Figure 2.2). This means that it is a dipolar molecule. Ozone is very unstable and highly reactive. For example, it reacts with a rubber band and damages it as it starts to develop a hard crusty surface with cracks. Elastic materials can become



brittle and crack, while paints and textile dyes fade easily when exposed to high ozone levels.



**Figure 2.2:** Resonance structures of ozone [Lenntech 2005]

Due to the potential harmful effects, maximum atmospheric ozone concentrations are proposed in several countries. In Europe, the current information threshold for the protection of human health is a one-hour average of 180  $\mu\text{g}/\text{m}^3$  and an hourly alert threshold of 240  $\mu\text{g}/\text{m}^3$  [[http://ec.europa.eu/environment/air/documents/pos\\_paper.pdf](http://ec.europa.eu/environment/air/documents/pos_paper.pdf)], (1 ppb O<sub>3</sub> is equivalent to 2  $\mu\text{g}/\text{m}^3$ ). The Occupational Safety and Health Agency (OSHA) has proposed the maximum acceptable concentration (MAC)-value for ozone a human is allowed to be exposed to for a certain time. The MAC-value for ozone is 60 ppb (120  $\mu\text{g}/\text{m}^3$ ) for 8 hrs a day, 5 days a week [Lenntech 2005, Riga-Karandinos *et al* 2005]. In South Africa, the Department of Environmental Affairs and Tourism (DEAT) ambient air quality standards Document 39 of 2004 stipulates an instant peak of 250 ppb and a one-hour average of 120 ppb as current guideline values for the protection of human health [South Africa 2005]. However, these values are presently being reviewed and are likely to be reduced to more stringent values inline with European Commission standards. At higher concentrations, ozone is harmful for human health after inhalation. It reduces the lung function and inflames the lining of the lungs and also damages respiratory tissues through inhalation [Abdul-Wahab *et al* 2005, Ambrose *et al* 2001, Nicholson *et al* 2001].

Primary air pollutants, particularly NO<sub>2</sub> and SO<sub>2</sub>, together with ozone, are important threats to plants [Riga-Karandinos *et al* 2005]. Damage of



agricultural crops, such as maize, and commercial forest yield can be observed at high ozone concentrations [Nicholson *et al* 2001, Riga-Karandinos *et al* 2005, Ribas *et al* 2003]. Ozone damages the foliage of trees and other plants [Yi *et al* 1996] by closing their stomata and damaging the internal cells, thus decreasing the rate of photosynthesis and growth. Visible injury occurs as small flecks between the leaf veins, therefore, leafy plants lose the entire crop if the foliage is seriously damaged [van Tienhoven *et al* 2004]. For vegetation protection, the accepted threshold value is 80 µg/m<sup>3</sup> (40 ppb) for 24 hr average concentration [Ribas *et al* 2003, van Tienhoven *et al* 2004]. The accumulated exposure thresholds such as AOT40 (accumulation over threshold of 40 ppb), during daily hours (08:00 to 20:00) for three consecutive months (growing season) are commonly used to determine the potential ozone damage to agricultural and semi-natural vegetation [Ribas *et al* 2003, van Tienhoven *et al* 2004]

**Table 2.1** Thresholds for ozone concentrations in the air, set by the current Directive 92/72/EEC

[\[http://ec.europa.eu/environment/air/documents/pos\\_paper.pdf\]](http://ec.europa.eu/environment/air/documents/pos_paper.pdf).

Description	Based on	Value
Population information threshold	1 hr average	180 µg/m <sup>3</sup> <sup>a</sup> 120 ppb
Population alert threshold	1 hr average	*240 µg/m <sup>3</sup> <sup>a</sup> 250 ppb
Health protection threshold	Max daily 8 hr mean	110 µg/m <sup>3</sup>
Vegetation protection threshold	1 hr average	200 µg/m <sup>3</sup>
Vegetation protection threshold	24 hr average	65 µg/m <sup>3</sup>
Vegetation protection threshold	AOT40 calculated from 1 hour values of May to July	**6000 µg/m <sup>3</sup>

<sup>a</sup>SA DEAT guideline values (2004)

\*Limit value came into force in 2004

\*\*Limit value comes into force in 2010 [John Delaney 2004]

## 2.3 Global distribution of ozone

Ozone is found in two locations, the stratosphere, which is between 15 km and 25 km above the earth's surface [Combrink *et al* 1995] and the troposphere, which is between 0 km and 7 km above the surface [Monks 2000]. About 90% of the total ozone is found in the stratosphere and only 10% in the troposphere [Crutzen *et al* 1998].

### 2.3.1 Stratosphere

In the stratosphere, the strong solar radiation splits the oxygen molecule into two atomic oxygens, which in turn, react with molecular oxygen in the atmosphere to form ozone [de Paula *et al* 2004].



where M is any unreactive air molecule, usually N<sub>2</sub>, O<sub>2</sub> or argon, which absorbs the vibrational energy that might disrupt the ozone molecule [Brimblecombe 1996, de Paula *et al* 2004] and thereby stabilizes the formed ozone molecule [Seinfeld 1986]. This ozone forms a layer in the atmosphere known as ozone layer, which protects all life forms from the strong, harmful ultra-violet radiation,  $\lambda$  between 240 nm and 320 nm, which can cause skin cancer and damage vegetation [Department of Environmental protection, 2006] and the reason why stratospheric ozone is sometimes termed "good" ozone [Ozone Science Assessment report 1999].

### 2.3.2 Troposphere

Ozone near the earth's surface can occur from natural and anthropogenic sources. It is known to arise from two basic processes: [Crutzen *et al* 1998,



Dueñas *et al* 2002, Möller 2004, Roussel *et al* 1995, Vingarzan 2004, Wang *et al* 1994]

- i. Transport of ozone from the stratosphere to the troposphere
- ii. Photochemical reactions of ozone precursors in the troposphere

In the stratosphere, ozone is continually produced from reactions initiated by the short-wavelength UV radiation during very hot and sunny periods and since ozone is heavier than air, it begins to fall towards the earth's surface [Ozone Science Assessment report 1999]. Ozone is also produced through complex reactions of sunlight with nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), volatile organic compounds (VOC's), which are largely hydrocarbons and methane (CH<sub>4</sub>), emitted from anthropogenic sources [Ambrose *et al* 2001, Bell *et al* 2004, Elkamel *et al* 2001, Mauzerall *et al* 2005, Parrish *et al* 1999]. Therefore surface ozone is sometimes termed "bad" ozone since it is the major component of the urban and rural photochemical smog [Ambrose *et al* 2001, Elkamel *et al* 2001, van Tienhoven *et al* 2004, Yi *et al* 1996].

## 2.4 Surface ozone precursors and their emissions

Surface ozone precursors are trace gases such as nitric oxide, nitrogen dioxide, carbon monoxide, volatile organic compounds, (including hydrocarbons) and non-methane hydrocarbons. These air pollutants are sometimes characterized into two groups [Mayer 1999, Möller 2004].

"Classical" air pollutants (SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub>)

"Special" air pollutants (VOC's and other carcinogenic compounds)

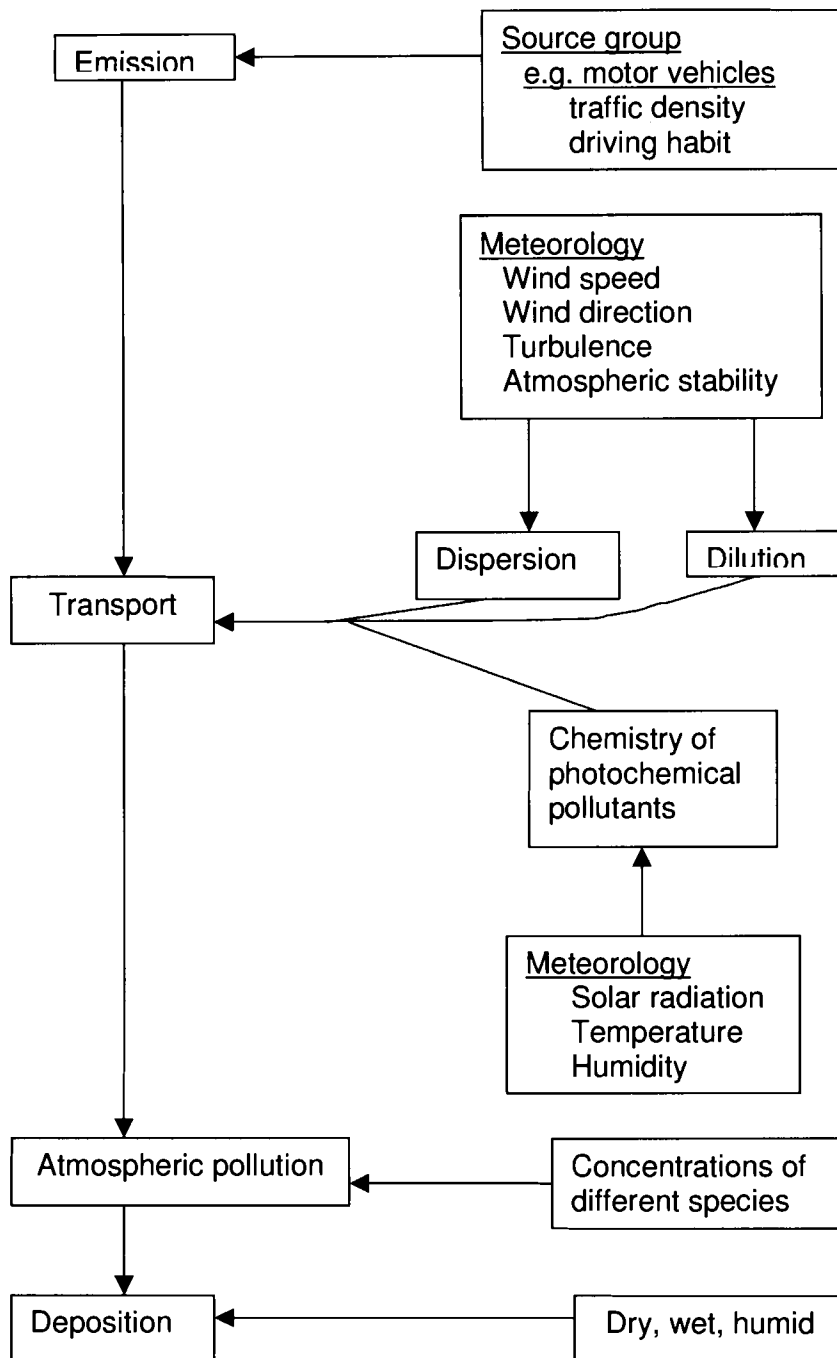
Emission of air pollutants is caused by a number of anthropogenic processes, which can be classified into source groups such as motor traffic, industry, power plants, trade and domestic fuel. Of these sources, motor vehicle traffic seems to be the most contributing source group to air pollution [Lal *et al* 2000,

Mayer 1999, Nicholson *et al* 2001, Ozone Science Assessment report 1999]. Emissions of air pollutants by motor vehicles depend on many factors such as traffic intensity and the driving habits [Mayer 1999].

Emitted air pollutants are dispersed and diluted in the atmosphere. Photochemical reactions that produce surface ozone occur frequently during this transport process. Dispersion and dilution of these emitted air pollutants are influenced strongly by meteorological parameters, specifically wind speed and direction, turbulence, and atmospheric stability [Mayer *et al* 1999, Tyson *et al* 1988]. To assess atmospheric dispersion, it is essential to have information relating to general climate of the area, terrain characteristics and the nature of the diurnal and seasonal variations of the boundary layer [Tyson *et al* 1988]. Chemical processes are also dependent on meteorological conditions such as solar radiation, temperature and humidity. Therefore dispersion, dilution and chemical reactions, all result in atmospheric pollution, which shows concentrations of different trace gases varying with regard to time and space. The temporal variation of the trace gases can be characterized by time course (annual, weekly and diurnal) [Mayer 1999].

A schematic illustration of the air pollution pathways in the atmosphere is given in Figure 2.3.





**Figure 2.3:** Schematic illustration of the atmospheric air pollution path  
[Adapted from Mayer 1999]

The following primary pollutants,  $\text{NO}_x$ , CO and hydrocarbons, are considered to be the major ozone formation precursors and their emission sources are therefore discussed below.

## Nitrogen oxides (NO<sub>x</sub>)

Besides the motor vehicles, nitrogen dioxides are emitted by biomass burning, coal-fired electric power plants and combustion of fossil fuels in certain industries [Bell *et al* 2004, Parrish *et al* 1999]. NO<sub>x</sub> also result in small percentages from natural sources in soil microbial activity, forest fires and lightning [Bell *et al* 2004, Ozone Science Assessment report 1999, Vingarzan 2004].

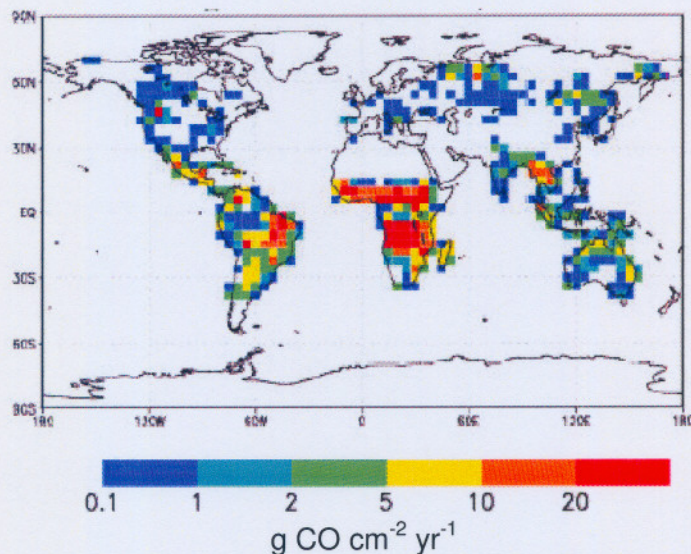
**Table 2.2:** Estimates of tropospheric sources of NO<sub>x</sub> (million tons N/year)  
[Adapted from Crutzen 1998].

	<b>Sources</b>	<b>Millions of tons</b>	<b>Total</b>
Natural	Soils	5 - 20	
	Lightning	2 - 15	Σ7.5 – 35.5
	Stratosphere	0.5	
Anthropogenic	Industrial	21	
	Biomass	5 – 10	Σ26.6 – 31.6
	Air craft	0.6	

## Carbon monoxide (CO)

The other sources of carbon monoxide, other than motor vehicle exhausts, include fossil fuel combustion and biomass burning. Apart from direct surface emissions, the only chemical source of CO is the oxidation of methane and non-methane hydrocarbons by HO radicals, producing formaldehyde (CH<sub>2</sub>O), which is then photolyzed to carbon monoxide [Bahm *et al* 2004, Holzinger *et al* 2002, Lal *et al* 2000, Wang *et al* 1998].

Biomass burning contributes largely to the emitted atmospheric CO in Southern African countries. A typical example is given in Figure 2.4 below. Biomass burning is presently the main source of air pollution in the tropics, which takes place mainly during the dry season. There are several activities that involve biomass burning, that is, the burning of crops to enrich the soil, burning of forests and dry grass to clear the land, and burning of wood for cooking and heating [Crutzen 1998].



**Figure 2.4:** Basis function illustrating the amount of CO emitted yearly by biomass burning in African countries compared to other countries [Arellano jr. AF 2003]

## Hydrocarbons (methane and non-methane hydrocarbons)

Volatile organic compounds are emitted from anthropogenic sources including incomplete combustion of fossil-fuels, industrial processing of waste and chemicals, evaporation of fuels, natural gas leakage, biomass burning and savanna burning in southern Africa. They are also emitted from natural sources mainly vegetation, usually in the warmer growing seasons [Ozone Science Assessment report 1999, Padhy *et al* 2005]. Among the various species of VOC's emitted, isoprene from deciduous forests and monoterpenes from coniferous forests are the abundant VOC emitted from leaves of green plants and are major precursors of surface ozone, especially in heavily forested regions. They are highly reactive and have a high photochemical ozone formation potential. Biogenic VOC's also leads to the formation of organic acids, which contribute to environmental acidification and acid rains [Padhy *et al* 2005].

The contribution of NMHC's to the formation of photochemical O<sub>3</sub> is related to their reaction with hydroxyl radicals in the complex reactions. Several methods have been proposed to estimate the contribution of an individual compound to the formation of photochemical ozone, methods such as HO-reactivity-based and carbon-based [Na *et al* 2003]. The HO-reactivity-based method is useful because it ranks the reaction rate and concentration of a compound. There are NMHC's that are abundant in the atmosphere but are not important contributors in O<sub>3</sub> formation. In other words, a compound with a higher concentration is not necessarily an important precursor if it is less reactive, but a compound with a small concentration can be important if it is extremely reactive towards hydroxyl radicals [Na *et al* 2003]. Estimated tropospheric lifetimes of selected VOC's due to reaction with HO<sup>\*</sup>, O<sub>3</sub> and NO<sub>3</sub><sup>\*</sup> are listed in Table 2.3.



**Table 2.3:** Estimated lifetimes of organic compounds in the troposphere  
 [Adapted from Fowler *et al* 1997].

VOC	Lifetime due to reaction with		
	HO <sup>•(a)</sup>	O <sub>3</sub> <sup>(b)</sup>	NO <sub>3</sub> <sup>•(c)</sup>
<b>Alkanes</b>			
Ethane	29 days		65 years
Propane	6.3 days		5.6 years
Butane	2.9 days		1.9 years
2-methyl propane	3.1 days		1.1 years
Pentane	1.8 days		1.1 years
2-methyl butane	1.9 days		11 months
<b>Alkenes</b>			
Ethene	20 hours	9.7 days	5.2 months
Propene	6.6 hours	1.5 days	3.5 days
1-butene	5.5 hours	1.6 days	2.5 days
2-butene	2.9 hours	2.4 hours	2.1 hours
2-methyl propene	3.4 hours	1.4 days	2.4 hours
1-pentene	5.5 hours	1.5 days	2.5 days
2-pentene	2.6 hours	2.4 hours	2.1 hours
2-methyl-1-butene	2.8 hours	1.4 days	2.4 hours
3-methyl-1-butene	5.5 hours	1.6 days	2.5 days
2-methyl-2-butene	2.0 hours	55 minutes	5.1 minutes
1,3-butadiene	2.6 hours	2.4 days	7.9 hours
Isoprene	1.7 hours	1.2 days	1.2 hours
<b>Aldehydes</b>			
Formaldehyde	18 hours		1.9 months
Acetaldehyde	11 hours		12 days
<b>Aromatics</b>			
Benzene	5.7 days		
Toluene	1.2 days		1.3 years
Ethylbenzene	23 hours		

**Table 2.3:**Continue

VOC	Lifetime due to reaction with		
	HO <sup>•</sup>	O <sub>3</sub>	NO <sub>3</sub> <sup>•</sup>
o-xylene	12 hours		2.9 months
m-xylene	7.1 hours		4.7 months
p-xylene	12 hours		2.4 months
<b>Sulphur-containing organics</b>			
Dimethyl sulphide	1.5 days		43 minutes
Dimethyl disulphide	46 minutes		1.1 hours

(a) [HO] =  $1.6 \times 10^6$  molecule/cm<sup>3</sup> (0.06 ppt)

(b) [O<sub>3</sub>] =  $7.5 \times 10^{11}$  molecule/cm<sup>3</sup> (30 ppb)

(c) [NO<sub>3</sub>] =  $3.5 \times 10^8$  molecule/cm<sup>3</sup> (15 ppt)

Methane is the most abundant species in the atmosphere but is of less importance in the formation of ozone in urban areas since it is extremely less reactive than other hydrocarbons [Na *et al* 2003].

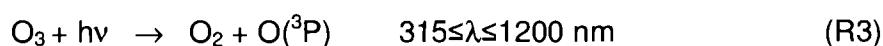
**Table 2.4:** Natural and anthropogenic sources of methane (in millions of tons = 10<sup>12</sup> g) [Crutzen 1998]

Sources	Total
Natural	270
Anthropogenic	630 – 270 ± 360
Ruminants	80 ± 20
Animal waste	20 ± 10
Biomass burning	40 ± 20
Natural gas leaks and oil production	65 ± 15
Coal mines	35 ± 10
Landfills	40 ± 20
Rice fields	80 ± 60

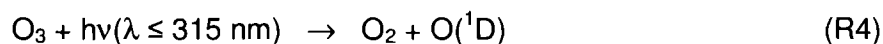
## 2.5 Chemistry of the troposphere

### 2.5.1 Formation of the hydroxyl radical

When ozone is dissociated by solar photons having wavelengths between 315 and 1200 nm, it produces an oxygen atom in its ground electronic state O(<sup>3</sup>P) [Seinfeld 1986].



When ozone absorbs a photon in the near-ultraviolet region with the wavelengths shorter than 315 nm, it forms an electronically excited singlet oxygen atom, O(<sup>1</sup>D), which in turn reacts with water vapour in the atmosphere and results in the formation of the hydroxyl radical (HO<sup>•</sup>) [Bahm *et al* 2004, Crutzen 1998, Helmig *et al* 2002, Naja *et al* 1996, Seinfeld 1986].



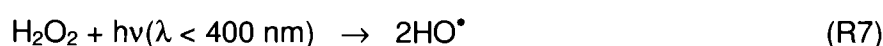
The hydroxyl radical is unreactive towards oxygen and nitrogen, but it reacts with most atmospheric trace species such as hydrocarbons, aldehydes, sulphur dioxides and carbon monoxide [Seinfeld 1986]. It plays an important role in the atmospheric chemistry during daytime. Photolysis reactions of ozone are considered to be the "trigger" of all the atmospheric oxidation reactions [Seinfeld 1986]

Other sources of hydroxyl radicals are [Ozone Science Assessment report 1999, vanLoon *et al* 2005]:

- Photolysis of nitrous acid



- Photolysis of hydrogen peroxide



- Reactions of hydroperoxyl radicals with nitric oxide



Hydroxyl radicals control the oxidizing power of the atmosphere [Abdul-Wahab *et al* 2005] since they reduce the concentrations of pollutants such as NO, CH<sub>4</sub>, CO, by oxidizing them to NO<sub>2</sub>, HCHO and CO<sub>2</sub> and control their flux into the stratosphere [Naja *et al* 1996]. The actual atmospheric concentration of hydroxyl radical is very small and difficult to measure, but has estimated to be on the order of 10<sup>7</sup> molecules cm<sup>-3</sup> in a polluted urban environment compared to a concentration of 2.5x10<sup>5</sup> molecules cm<sup>-3</sup> in a relatively clean rural area in a temperate zone [vanLoon *et al* 2005]. Other factors that contribute to enhanced hydroxyl radical concentration are high temperature and intense sunlight, so values tend to be higher in tropical compared to temperate regions [Ozone Science Assessment report 1999].

## 2.5.2 Photochemical formation of ozone in the troposphere

Ozone formation from NO<sub>x</sub> emitted in power plant plumes varies depending on the availability of hydrocarbons, the magnitude of the NO<sub>x</sub> emission rate and meteorological parameters. A power plant plume contains large quantities of NO<sub>x</sub>, little CO and practically no VOC's [Mauzerall *et al* 2005].

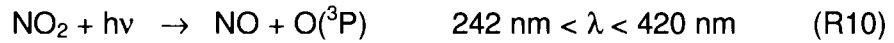
### 2.5.2.1 Photolysis of nitrogen dioxide

Nitric oxide (NO) formed during combustion of fossil fuels in automobile exhausts and industries or combustion of coal at a power station is oxidized by molecular oxygen to form nitrogen dioxide (NO<sub>2</sub>) [Seinfeld 1986]. The greatest increase in ozone occurs in the urban areas, where NO levels are the highest and solar radiation is strong [Sloane *et al* 1991].





Nitrogen dioxide absorbs a photon in the ultraviolet and visible regions,  $242 \text{ nm} < \lambda < 420 \text{ nm}$ , and photodissociates to form nitric oxide and atomic oxygen in its ground electronic state, which is reactive towards  $\text{O}_2$  [Brönnimann *et al* 1996]. The oxygen atom rapidly reacts with molecular oxygen in the atmosphere to form ozone and the only source of  $\text{O}(^3\text{P})$  atoms in the troposphere is the photolysis of nitrogen dioxide [Möller 2004].



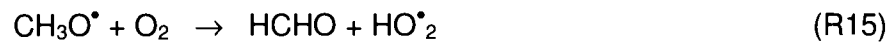
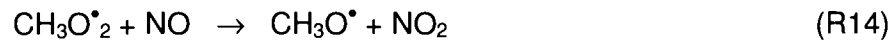
Reactions R10, R11 and R27 by themselves, in the absence of CO or organic compounds, do not produce ozone because these reactions only recycle  $\text{O}_3$  and  $\text{NO}_x$  [Guicherit *et al* 2000].

### 2.5.2.2 Oxidation of organic compounds

Ozone production in the troposphere can also be described as a  $\text{HO}_x$  ( $\text{HO}_x = \text{HO} + \text{HO}_2$ )-catalysed chain oxidation of CO and organic compounds such as methane and non-methane volatile organic compounds (NMVOC), in the presence of  $\text{NO}_x$  [Guicherit *et al* 2000, Jacob 2000]. A chain of reactions is initiated by the production of HO radicals, mainly from the photolysis reaction of ozone. The chain is then propagated when methane reacts with the hydroxyl radical to form water vapour and a methyl radical, which combines quickly with oxygen molecule to form a methyl peroxy radical.



The methyl peroxy radical then participates in a chain propagation sequence to convert nitric oxide to nitrogen dioxide and methoxy radical. The methoxy radical is then oxidized to formaldehyde and hydroperoxyl radicals.



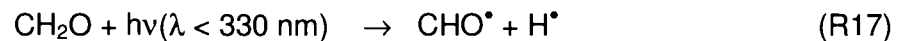
The hydroperoxyl radical combines with nitric oxide, if available, to produce hydroxyl radical and nitrogen dioxide, which is then photolyzed to ozone.



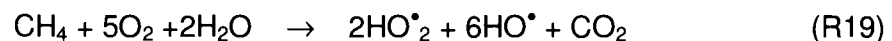
The net reaction is as follows: [Bahm *et al* 2004, Guicherit *et al* 2000, von Kuhlmann 2001]



Formaldehyde ( $\text{CH}_2\text{O}$ ) may also be photolyzed to produce additional  $\text{HO}_2$  radicals and branch the chain to carbon monoxide, which in subsequent reactions can be oxidized to carbon dioxide [Bahm *et al* 2004, Chan *et al* 1998, Jacob 2000].

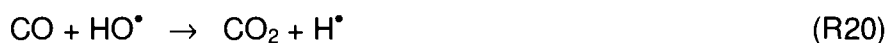


The atmospheric oxidation of methane thus ultimately produces carbon dioxide as a final stable carbon compound and the net reaction is given by R19 [vanLoon *et al* 2005].



### 2.5.2.3 Oxidation of carbon monoxide

Carbon monoxide follows the same oxidation mechanism as methane. It reacts with the hydroxyl radical to yield carbon dioxide and a hydrogen atom, which combines with an oxygen molecule to form the hydroperoxyl radical [Jacob 2000, Seinfeld 1986, Sloane *et al* 1991].



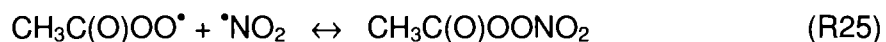
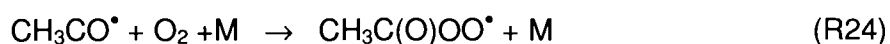
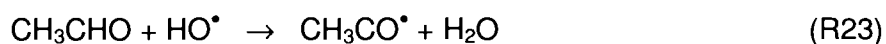
The hydroperoxyl radical then reacts with nitric oxide to form nitrogen dioxide, which is finally photolyzed to ozone.



The net reaction is as follows: [Bahm *et al* 2004, Crutzen 1998, von Kuhlmann 2000]



In these oxidation processes,  $\text{NO}_x$  act as catalysts and continues to do so until physical processes, e.g. surface deposition, permanently remove or transformed them to other  $\text{NO}_y$  compounds (e.g. PAN). Peroxyacetylnitrate, the major eye irritant in a photochemical smog, acts as a reservoir for nitrogen oxide species and is a relatively stable molecule especially at low temperatures [Monks 2000]. Long-range transport of PAN at high altitudes (low temperature) is a major source of  $\text{NO}_x$  in the remote troposphere [Jacob 2000]. PAN is produced from the oxidation of acetaldehyde by hydroxyl radicals [Jacob 2000].



Ozone productive cycles of CH<sub>4</sub> and NMHCs yield much higher ozone levels than those of CO [Lal *et al* 2000]. The major destruction of hydroxyl radical is the termination reaction with nitrogen dioxide to form nitric acid during daytime [Barker 1995, Jacob 2000, Seinfeld 1986]. HO<sup>•</sup> is also destroyed primarily by reactions with carbon monoxide and methane [Bahm *et al* 2004, Sloane *et al* 1991].



### 2.5.3 Chemistry of ozone destruction in the troposphere

The destruction of ozone takes place via a number of pathways including deposition at the surface, gaseous and aqueous chemical destruction. It appears that the surface deposition dominates the ultimate destruction process [Abdul-Wahab *et al* 2005, Ozone Science Assessment report 1999].

#### 2.5.3.1 Gaseous destruction of ozone

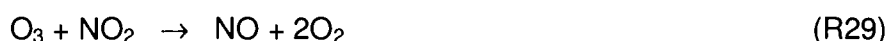
Ozone can be scavenged by reactions with various free radical species. In more polluted areas, the reaction of ozone with nitric oxide leads to a complete removal of ozone when sufficient NO is available. It is worth-mentioning that this reaction is two orders of magnitude faster than any other chemical loss reaction in the atmosphere [Lal *et al* 2000].



In less polluted or unpolluted areas (primarily rural areas with abundant emission of natural hydrocarbons) [Mauzerall *et al* 2005], NO concentrations

are too low to scavenge ozone and therefore nighttime ozone concentrations in rural areas are much higher than those in urban areas [Ozone Science Assessment report 1999].

Nighttime can lead to irreversible surface ozone destruction [Parrish *et al* 1999]. Ozone further oxidizes nitrogen dioxide to the nitrate radical or nitric oxide and oxygen molecule.



The nitrate radical then reacts further with nitrogen dioxide to attain a rapid equilibrium with dinitrogen pentoxide [Parrish *et al* 1999].



Ozone can be permanently lost, only if dinitrogen pentoxide and the nitrate radical are removed from the atmosphere by heterogeneous reactions with water in aerosols and on the surface. Nitric acid is formed heterogeneously through the hydrolysis of dinitrogen pentoxide in the atmosphere [Bahm *et al* 2004, Barker 1995, Brimblecombe 1996, Khoder 2002, Parrish *et al* 1999]. The destruction of nitrogen dioxide by HO radicals also leads to the formation of nitric acid [Bahm *et al* 2004, Brimblecombe 1996], which is soluble in water and can be removed effectively by rain [Brimblecombe] and is a sink for both the radicals and  $\text{NO}_x$  [Riga-Karandinos *et al* 2005].

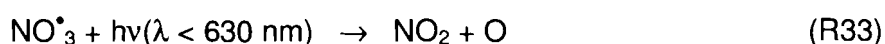


During the day, the reaction of  $\text{NO}_2$  with the OH radical is important whilst the hydrolysis of  $\text{N}_2\text{O}_5$  is believed to become an important source of nitric acid at night [Khoder 2002]. The lifetime of  $\text{HNO}_3$  is about two weeks in the tropics

and longer at mid-latitudes and wet deposition provides the dominant sink for HNO<sub>3</sub> in most of the troposphere [Jacob 2000].



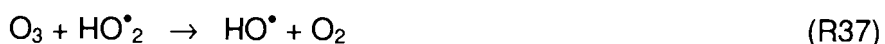
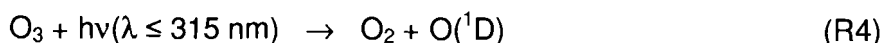
Concentrations of the nitrate radical are low during the daytime because it is quickly photolysed even at long wavelengths (< 630 nm) [Barker 1995, Brimblecombe 1996] and high daytime concentrations of NO (from NO<sub>2</sub> photolysis) may also reduce its concentrations [Brimblecombe 1996].



Although the hydroxyl radical is the main oxidizing agent during daylight hours [Barker 1995, Glavas *et al* 1999], the nitrate radical may be the main oxidizing species during the night hours [Barker 1995] since the hydroxyl radical concentrations are low at night. At night, the NO<sub>3</sub> radical can act as a hydrogen atom abstractor in much the same way as OH radical did during the day. For example, it can attack the alkane such as methane even though the reaction is not particularly fast, but reactions with alkenes, terpenes and aromatic compounds are more effective [Brimblecombe 1996].

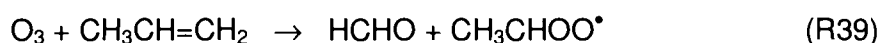
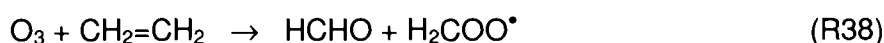


Ozone can be destroyed by wavelengths shorter than 315 nm and is also reactive towards hydroxyl and hydroperoxyl radicals [Möller 2004].



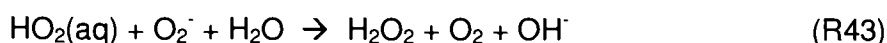
The amplitude of the diurnal ozone destruction rate of these reactions is mostly dependent on the availability of the solar radiation, which is a function of time of the year, latitude, altitude and cloud cover. This can imply that the destruction according to these three reactions is the major driving force for the ozone diurnal cycle and replaces photochemical formation in low hydrocarbon/NO environment [Helmig *et al* 2002], like in the rural areas.

In addition, reactions of unsaturated hydrocarbons such as ethylene (C<sub>2</sub>H<sub>4</sub>), propylene (C<sub>3</sub>H<sub>6</sub>) and butene (C<sub>4</sub>H<sub>8</sub>), with ozone also lead to surface ozone destruction [Seinfeld 1986].



### 2.5.3.2 Aqueous destruction of ozone

Ozone can also acts as an oxidant for some chemical species in the aqueous phase and these processes depend on the extent at which these species are soluble in water [Ozone Science Assessment 1999]. The influence of aqueous chemistry on ozone has been recently discussed and since ozone is produced and destroyed in the troposphere by the reactions involving HO<sub>x</sub> radicals, the cloud effects on HO<sub>x</sub> chemistry should be considered in this respect. Cloud droplets as a result of acid – base- dissociation of aqueous HO<sub>2</sub>, will efficiently scavenge HO<sub>2</sub> radicals, followed by electron transfer from O<sub>2</sub><sup>-</sup> to HO<sub>2</sub>(aq) to produce H<sub>2</sub>O<sub>2</sub>

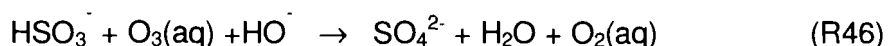
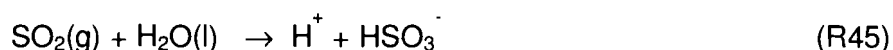


and reaction of O<sub>2</sub><sup>-</sup> with O<sub>3</sub>(aq)

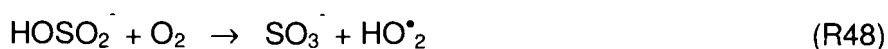


The decrease of HO<sub>2</sub>(g) suppresses the gas phase oxidation of NO (R8), which provides the major source of ozone in the troposphere by means of R10 [Guicherit *et al* 2000, Jacob 2000]. The decrease of O<sub>3</sub> production due to HO<sub>2</sub> scavenging is partially compensated by an increase in the NO/NO<sub>2</sub> ratio, which is important in converting NO to NO<sub>2</sub> in the gas phase [Jacob 2000].

In the aqueous phase, sulphur dioxide (SO<sub>2</sub>) is converted to bisulphite (HSO<sub>3</sub><sup>-</sup>), which is then oxidized by ozone to sulphate anion (SO<sub>4</sub><sup>2-</sup>) and molecular oxygen.



The rate of ozone formation can also be indirectly decreased by aqueous phase reactions involving free radicals, by scavenging hydroxyl radicals into bisulphite, which in turn reacts with molecular oxygen to form sulphur trioxide.

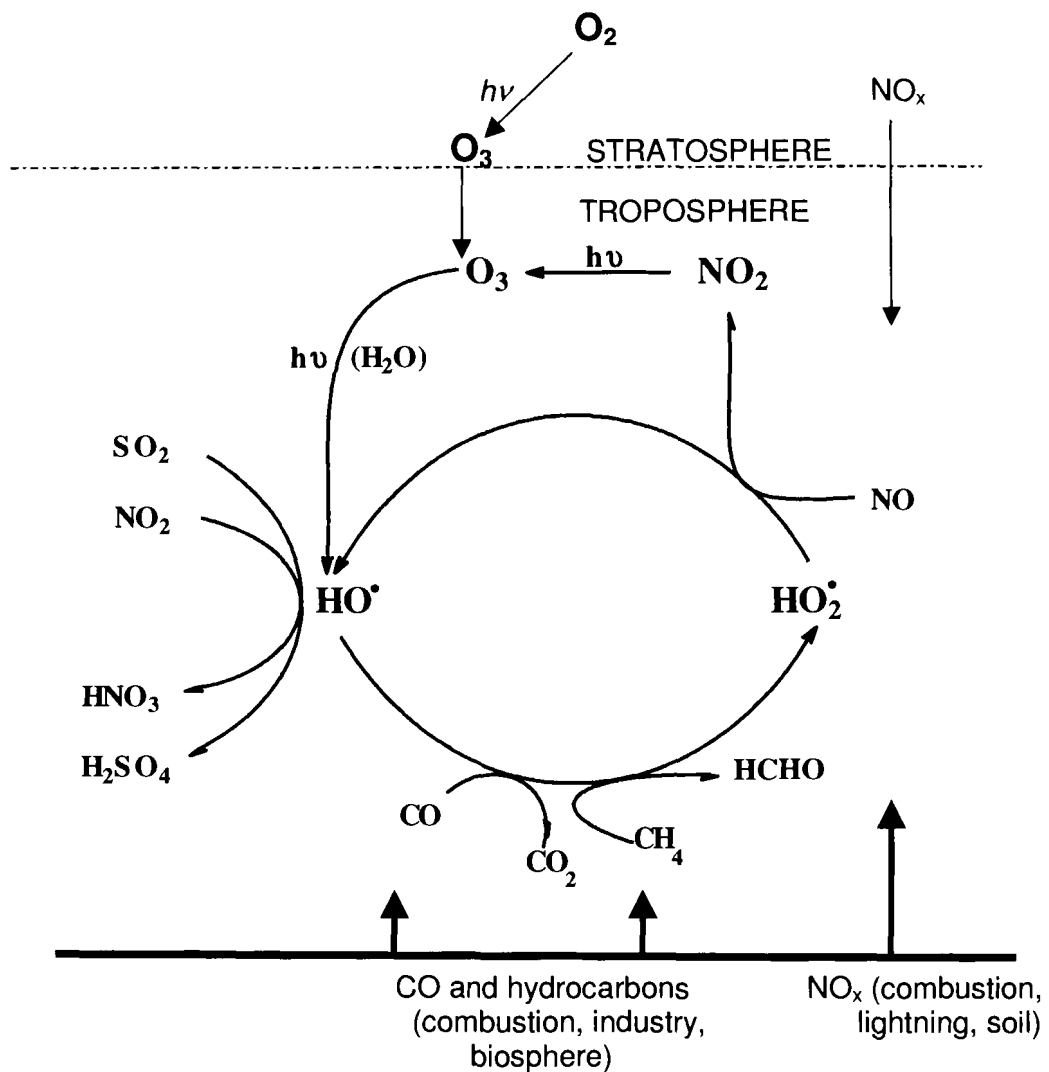


The sulphur trioxide then combines quickly with liquid water to produce sulphuric acid, which has a low vapour pressure and thus helps to form aerosol particles in the stratosphere as well as contributing to acid deposition in the troposphere [Barker 1995, Brimblecombe 1996].



The summary of reactions describing surface ozone formation and destruction is given in Figure 2.5.





**Figure 2.5:** Schematic of tropospheric O<sub>3</sub> chemistry illustrating the coupling between the chemical cycle of ozone, HO<sub>x</sub> and NO<sub>x</sub> [Adapted from Jacob 2000].

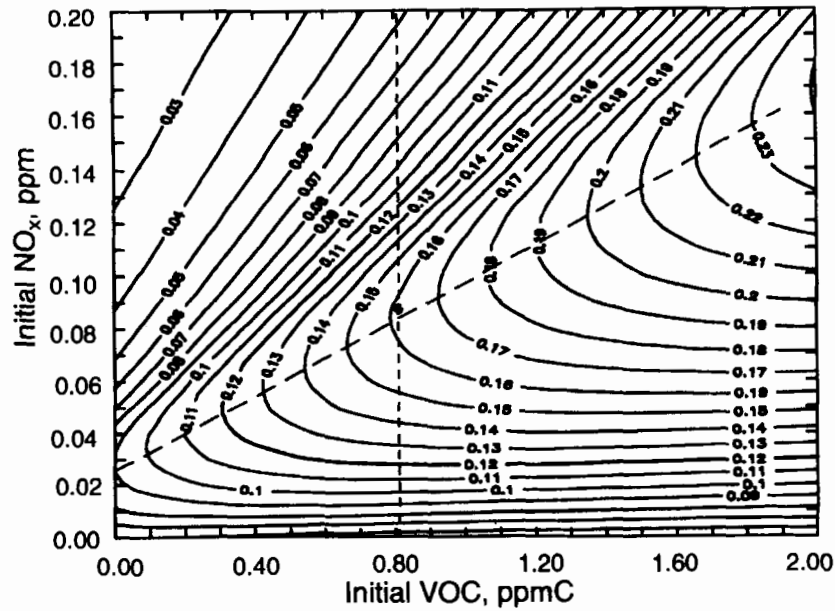
## 2.6 Relation between ozone, nitrogen oxides and volatile organic compounds

The relation between ozone and its main precursors, NO<sub>x</sub> (NO and NO<sub>2</sub>) and volatile organic compounds (VOC), can be understood in terms of a fundamental split into a NO<sub>x</sub>- and VOC-sensitive chemistry. It is generally

known that under certain conditions, increasing  $\text{NO}_x$  concentrations can increase ozone concentrations, while under other conditions more  $\text{NO}_x$  can actually decrease the ozone concentrations [Sillman 1999, Torres-Jardon 2004]. All this has to do with the fact that both these precursors react with hydroxyl radicals. So the ratio of  $\text{VOC}/\text{NO}_x$  is very important in determining which species will dominate the reaction with the OH radicals [Rickard *et al* 2002, Sillman 1999].

High  $\text{NO}_x$  concentrations near the source area can hinder ozone formation either by NO titration of  $\text{O}_3$  or by the reaction of  $\text{NO}_2$  and OH radicals to form nitric acid, which is a sink for both the radicals and  $\text{NO}_x$  [Riga *et al*]. This removes  $\text{NO}_x$  and also prevents VOC's from being activated to react with NO that leads to a slow formation of ozone. In  $\text{NO}_x$ -sensitive regions (i.e. more VOC's than  $\text{NO}_x$ ), ozone increases or decreases with increase/decrease in  $\text{NO}_x$  emissions ( $\text{NO}_x$ -limited), while in VOC-sensitive regions (i.e. abundant  $\text{NO}_x$  relative to VOC)  $\text{O}_3$  increase/decrease with a decrease/increase in  $\text{NO}_x$  emissions (VOC-limited or  $\text{NO}_x$ -saturated). [Riga-Karandinos *et al* 2005, Sillman 1999]. Ozone increases with increasing  $\text{NO}_x$  when  $\text{NO}_x$  concentrations are low and when  $\text{VOC}/\text{NO}_x$  ratios are high. As  $\text{NO}_x$  increases,  $\text{O}_3$  eventually reaches a maximum and then decreases in response to further increases in  $\text{NO}_x$  [Sillman 1999].

The ozone- $\text{NO}_x$ -VOC-sensitivity can also be explained in terms of the ozone isopleths diagram, which illustrates the dependency of ozone production on the initial amounts of VOC and  $\text{NO}_x$  [Fujita *et al* 2002]. A typical isopleths of  $\text{O}_3$  peak concentrations is shown in Figure 2.6.



**Figure 2.6:** Typical O<sub>3</sub> isopleths diagram showing [O<sub>3</sub>] in ppb as a function of initial VOC and NO<sub>x</sub> concentrations and the regions of the diagram that are characterised as VOC- or NO<sub>x</sub>-limited. [Torres-Jardon 2004]

The diagonal line (the ridgeline) that extends from the lower left to the upper right corner of the graph corresponds to the VOC/NO<sub>x</sub> ratio, at which ozone is most effectively formed [Fujita *et al* 2002, Torres-Jardon 2004]. At low VOC/NO<sub>x</sub> ratios to the left of the ridgeline, the ozone peak formed is VOC-sensitive (i.e. lowering VOC emissions reduces [O<sub>3</sub>]). For high VOC/NO<sub>x</sub> ratios to the right of the ridgeline, ozone formation is said to be NO<sub>x</sub>-sensitive (i.e. lowering NO<sub>x</sub> emissions reduces [O<sub>3</sub>]) [Fujita *et al* 2002, Torres-Jardon 2004].

NO<sub>x</sub>-VOC sensitive chemistry is affected by five major factors: VOC/NO<sub>x</sub> ratio, the reactivity of the VOC's involved, the role of biogenic hydrocarbons, the extent of photochemical aging and the severity of air pollution events [Sillman 1999].

- VOC/NO<sub>x</sub> ratio
 

At low VOC/NO<sub>x</sub> (VOC-sensitive conditions) ratios ozone increases with increasing VOC and decreases with increasing NO<sub>x</sub>, thus the ozone peak is VOC-sensitive. At high VOC/NO<sub>x</sub> (NO<sub>x</sub>-sensitive conditions) ratios ozone increases with increasing NO<sub>x</sub> and is relatively insensitive to increasing VOC and thus the ozone peak is NO<sub>x</sub>-sensitive.
- VOC reactivity
 

Locations with highly reactive VOC (xylenes or isoprene) are more likely to have NO<sub>x</sub>-sensitive chemistry than locations with similar total VOC concentrations but of lower reactivity. The impact of VOC reactivity is especially important with regard to biogenic hydrocarbons, which typically have relatively low ambient concentrations but high reactivity.
- Biogenic hydrocarbons
 

Total VOC concentrations are dominated by relatively less reactive alkanes, and biogenic VOC species are extremely reactive relative to most anthropogenic VOC. Consequently the impact of biogenic VOC is large relative to their ambient concentrations.
- Photochemical aging
 

A polluted air mass is most likely to have VOC-sensitive chemistry when it is close to its emission sources, but as the air mass ages, the chemistry tend to shift to the NO<sub>x</sub>-sensitive chemistry. The initial rate of ozone formation with a given VOC-NO<sub>x</sub> mixture is controlled by VOC, but NO<sub>x</sub> controls the total amount of ozone formed at the end of the aging process. The shift is often accelerated by the higher rate of biogenic emission in downwind locations. Rural areas appear to be predominantly NO<sub>x</sub>-sensitive.
- Severity of pollution events

Events with higher overall concentrations of ozone precursors are more likely to have ozone peak sensitive to VOC-sensitive chemistry, while those with lower precursors are more likely to have ozone peak sensitive to NO<sub>x</sub>-sensitive chemistry. Higher precursor concentrations are associated with either higher emission densities (i.e. larger cities) or events with more stagnant meteorology (i.e. light winds and lower vertical mixing)

## **2.7 Spatial and temporal patterns of ozone**

### **2.7.1 Seasonal variations**

The seasonal cycle of surface ozone is controlled by a contribution of processes acting on different spatial and temporal scales [Monks 2000]. As a result of the complex reactions of ozone precursors and sunlight, ozone exhibits important variations in space and time, i.e. hourly, daily, seasonally and annually. Chemical reactions of ozone formation and destruction occur within a time scale of a few hours over corresponding spatial scales of tens of kilometres. Ozone lifetime is a few weeks in summer and a few months in winter, during which ozone can be transported more than hundreds to thousands of kilometres [Ribas *et al* 2003, Vingarzan 2004]. The time-height cross section is usually used to show the change of vertical ozone distribution with time [Chan *et al* 1998].

The feature of the overall seasonal variation of the surface ozone is the high ozone mixing ratio in springtime and the low ozone mixing ratio in summertime, while autumn and winter seem to be the transitional periods [Chan *et al* 1998]. Heavily populated and industrialized regions show a broad summer maximum in surface ozone, which persists from spring into summer [Combrink *et al* 1995, Ribas *et al* 2003].

Annual variations in surface ozone concentrations depends on many factors such as proximity (closeness) to large source areas of ozone precursors, especially  $\text{NO}_x$  and VOC's, geographical locations and meteorological parameters [Monks 2000, Ribas *et al* 2003]. Due to specific meteorological conditions at the lower altitudes and the pollutant emission situated in the local area, the ozone-mixing ratio below 2 km may have a different seasonal behaviour from that above 2 km [Chan *et al* 1998]. The broad summer maximum is generally attributed to local photochemical productions of ozone associated with anthropogenic emission of  $\text{NO}_x$ , CO and hydrogen carbons from fossil-fuel combustion [Combrink *et al* 1995, Ribas *et al* 2003]. In this situation, the ozone is formed by the reactions involving VOC's and  $\text{NO}_x$  under the influence of the solar radiation [Monks 2000]. It can also reflect the greater availability of sunshine in the summer months [Combrink *et al* 1995].

There has been a long debate over whether the spring maximum is caused by photochemical production from anthropogenic emissions of precursors or intrusion of stratospheric air with a high ozone concentration [Chan *et al* 1998, Monks 2000]. The spring maximum appears mostly at the highest tropospheric altitudes, which suggests that the mixing downward of ozone from the stratosphere also contributes to this maximum [Chan *et al* 1998]. The spring maximum is most likely related to stratospheric-tropospheric injection, [Combrink *et al* 1995, Vingarzan 2004], or to a more controversially attribution of the enhanced photochemical activity resulting from solar radiation acting upon a pool of  $\text{NO}_x$  and VOC's that were accumulated during winter period [Ribas *et al* 2003, Vingarzan 2004].

An alternative explanation for spring ozone maximum was presented by Liu *et al.* 1987 who proposed that the long photochemical lifetime of ozone in winter, which is about 200 days, allows anthropogenically produced ozone to accumulate during this period and then contribute to the observed spring peak [Monks 2000, Vingarzan 2004]. Accumulation of other nitrogen containing ( $\text{NO}_y$ ) compounds such as peroxyacetylnitrate (PAN) in the troposphere during winter can also contribute to the observed ozone

maximum in spring, owing to its longer lifetime (in winter) compared to NO<sub>x</sub> [Monks 2000]. The summer minimum can be attributed to the increase in photochemical destruction of ozone or the weak transport of ozone from the stratosphere during this period.

The seasonal maximum over the southern African regions generally occurs in spring months from August to November and the minimum occurs in summer months from December to January. In the eastern Mpumalanga Highveld, the spring maximum is between 40 and 60 ppb, but reaches more than 90 ppb as an average in October [van Tienhoven *et al* 2004]. Typical average spring and summer surface ozone concentrations in the eastern United States are between 30 and 50 ppbv, whereby the summer enhancement is indicative of photochemical production of ozone in urban or industrialized areas [Combrink *et al* 1995]. In the tropics and savannah regions, spring ozone maximum is observed due to biomass burning where large amounts of dry grass are burned and wood is burned for cooking and heating [Curtzen 1998].

### **2.7.2 Daily variations**

In rural areas, photooxidant (NO<sub>2</sub> and O<sub>3</sub>) concentrations depend on NO<sub>x</sub> emissions [Ribas *et al* 2003, Silliman 1997] but the photochemistry in large cities mostly exhibit a negative response to NO<sub>x</sub> emissions, although there are also meteorological parameters, those on which the dispersion play a key role, under which the photochemistry becomes positively related to NO<sub>x</sub> emissions [Ribas *et al* 2003]. The diurnal cycle of chemical formation and destruction of surface ozone is driven by the pattern of the NO<sub>x</sub> and hydrocarbon emissions, as well as by solar radiation [Ribas *et al* 2003].

Boundary layer and meteorological parameters play an important role in the variabilities of ozone [Lal *et al* 2000]. The diurnal cycle of ozone is characterized by an increase from a minimum near sunrise and a maximum during noon hours, and decrease again to the early morning minimum [Combrink *et al* 1995, Debaje *et al* 2003, Lal *et al* 2000, Naja *et al* 1996,

Parrish *et al* 1999]. During the early hours of the morning, lower boundary layer heights reduce the mixing processes between the O<sub>3</sub>-poor surface layer and the O<sub>3</sub>-rich upper layer, thus contributing to the early low levels of ozone in the morning. After sunrise to noon hours, boundary layer height increases gradually (or breaks up) due to convective heating, allowing the downward transport of ozone by vertical mixing, and the layer becomes stratified. Air in the lower heights, which has low levels of ozone, mixes with the air of the higher heights, which is relatively O<sub>3</sub>-rich [Lal *et al* 2000, Möller 2004, Nair *et al* 2002].

The noontime higher ozone level is a characteristic of an urban area and occurs because of its photochemical production due to precursor gases like CO, CH<sub>4</sub> and other VOC's in the presence of sufficient NO<sub>2</sub>/NO ratios [Nair *et al* 2002, Naja *et al* 1996]. The rate of increase of ozone in the morning is faster, whereas the decrease in the evening is slower [Debaje *et al* 2003, Nair *et al*]. This reflects the relationship between the build-up of ozone precursor gases in the early hours of the morning and the subsequent photochemical formation of ozone. A steady decrease of surface ozone at night occurs through the physical adsorption at the ground (surface deposition) or chemical destruction, or both [Naja *et al* 1996, Combrink *et al* 1995, Parrish *et al* 1999]. During nighttime, there is no photooxidation of precursors causing ozone production and the titration of ozone by surface emission of NO in shallow boundary layer also continues [Lal *et al* 2000, Möller 2004].

The strong diurnal variation in the eastern Mpumalanga Highveld is typical of that generally found in populated and industrialized environments [Combrink *et al* 1995, van Tienhoven *et al* 2004]. Typical results were obtained by Lazutin *et al*. 1995 when studying surface ozone in Sao Paulo state, which is the most industrialized part of Brazil with many industrial plants and factories such as the largest petroleum refinery complex as a source of air pollution, and with heavy automobile traffic and a population of 1.2 million [Lazutin *et al* 1995].



The diurnal pattern is seasonally consistent, but higher nighttime ozone concentrations are observed in winter than in summer. This is most likely related to seasonal contrasts in the occurrence of nocturnal temperature inversions, which are prevalent in the interior of South Africa. Frequencies of nighttime surface inversions at meteorological stations near Pretoria range from over 80% in winter to about 40% in summer [Combrink *et al* 1995].

### **2.7.3 Temporal pattern of primary air pollutants**

The annual variation of the primary pollutant NO<sub>x</sub> shows the greatest values in winter since the concentration of NO<sub>x</sub> does not depend only on emission, but also on weather conditions. During winter the atmosphere is stable and the pollutants emitted from various anthropogenic and natural sources, are trapped in the boundary layer due to frequent temperature inversions, thus having higher concentrations compared to summer. Concentrations of NO<sub>x</sub>, CO and hydrocarbons are lower in summer due to the favourable polluted air mass exchange with free tropospheric air, causing the dilution of pollutants. In comparison with the NO, the NO<sub>2</sub> concentration shows only slight variations because this secondary pollutant is produced mainly by chemical reactions [Lal *et al* 2000, Mayer 1999].

The diurnal concentrations of NO<sub>x</sub> and hydrocarbons in urban areas are noticeably higher in the morning than in the evening because of the denser traffic flow during the shorter morning rush hours and the more stable atmosphere than in the evening [Mayer 1999]. The low NO levels in the early afternoon result mainly from the reactions with peroxy radicals that convert NO to NO<sub>2</sub>, while major NO<sub>2</sub> loss is due to photodissociation [Lal *et al* 2000, Mayer 1999]. The major chemical loss of CO and hydrocarbons is by the reaction with HO radical during the daytime, thus producing ozone [Lal *et al* 2000].

## 2.8 Meteorological parameters

Meteorology plays a significant role in ozone production and transport [Dueñas *et al*]. Certain meteorological parameters are required for the formation and destruction of high ozone concentrations. Light winds, high temperatures, relative humidity and high solar radiation are believed to be important factors influencing ozone production while rainfall and cloud cover decrease ozone concentrations [Debaje *et al* 2003, Dueñas *et al* 2001, Lazutin *et al* 1995]. The relationship between ozone concentration and temperature can be explained on a theoretical (hypothetical) basis, that temperature plays an enhancing role in the propagation rate of the radical chain and has an opposite outcome on the termination rate of these reactions [Abdul-Wahab *et al* 2002, Dueñas *et al* 2001].

Relative humidity may also play a role in the overall reactivity of the system, either by affecting chain termination reactions or in the production of wet aerosols, which in turn affect the ultraviolet actinic flux [Abdul *et al* 2002, Dueñas *et al* 2001]. It is also considered to be a restrictive factor in the disposition of NO<sub>2</sub> because elevated percentages of humidity favour the reaction of NO<sub>2</sub> with NaCl particles, especially in coastal places [Dueñas *et al* 2001].

Increased ozone concentrations can be observed when wind speed is decreased. Low wind speed hinders or slow-down transport and set up an air stagnation situation in which ozone and its precursors accumulate in the planetary boundary layer and near their source areas, which is a characteristic of many high ozone situations. Increased wind speed causes the dispersion of air pollutants and thus resulting in low levels of ozone. Higher levels of ozone can be observed in rural areas some hundred kilometres downwind from the source areas, compared to the upwind from the sources, The main meteorological requirements for high ozone

concentrations are the clear skies, and low speed surface wind that impedes transport [Nair *et al* 2002, Vukovich *et al* 2003].

During cloudy-rainy months, non-availability of enough solar radiation and the washout of pollutants by rain result in near absence of photochemical production of ozone [Lal *et al* 2000, Lazutin *et al* 1995, Nair *et al* 2002]. Sky cover inflects (returns back) the solar radiation reaching the surface layer and the inflection of radiation will affect the ozone chemistry. This contributes to the minimum ozone levels observed in summer months, especially during monsoon periods. Thus, rainfall and sky cover give a negative correlation with ozone concentration [Debaje *et al* 2003, Vukovich *et al* 2003].

Since solar energy is a very important ingredient in ozone chemistry, it is not surprising that, the highest values of ozone will be found when skies are clearer and the amount of solar radiation reaching the surface layer increases. The more solar radiation reaching the surface layer, the greater the potential to produce high ozone concentrations in that layer [Vukovich *et al* 2003].

## **2.9 Statistical models**

Statistical models that describe the complex relationships between ozone and various variables causing or hindering ozone formation are applied in air quality analysis to predict ozone concentrations [Abdul *et al* 2002, Elkamel *et al* 2001]. Since the relationship between ozone and its precursors is complicated by the interaction of meteorological parameters, different kinds of ozone forecasting models have been applied in many studies [Abdul *et al* 2005]

### 2.9.1 Chemometric or deterministic models

These are models that are based on the fundamental mathematical description of atmospheric processes in which effects are generated by cause [Abdul *et al* 2002]. They intend to solve the underlying chemical and physical equations that control pollutant concentrations and therefore require detailed emission data and meteorological conditions for the region of interest. These are the multiple linear regression (MLR) models known as principal component regression (PCR) and partial least squares (PLS) [Abdul *et al* 2005, Lengyel *et al* 2004].

Multiple regression analysis is used for expressing the dependence of the response variable (predictand) on several independent (predictor) variables [Abdul *et al* 2005]. When employing linear regression, one must assume all factors that influence both photochemical production and atmospheric accumulation of ozone to be independent [Abdul *et al* 2005, Diem *et al* 2002, Wang *et al* 2003, Gardner *et al* 2000]. The multicollinearity between the predictor variables in a regression equation can make it difficult to correctly identify the most important factors contributing to the high concentrations of the response variable [Abdul *et al* 2005, Pastor-Bárcenas *et al* 2005].

A stepwise multiple regression procedure automatically chooses variables that are of most importance and eliminates those are of least importance. The partial least square method is used to obtain a linear input-output relationship for a given data set, but if the functional relationship is non-linear, one or more inputs can be transformed first into a non-linear form by applying the logarithm function of the input [Elkamel *et al* 2001].

A linear regression analysis produces an equation that is derived from statistical relationships between a dependent variable and independent variables that are considered concurrently [Diem *et al* 2002, Wang *et al* 2003]. The equation yields the predicted values of the dependent variables and the general equation is as follows

$$Y = \alpha + b_1X_1 + \dots + b_nX_n \quad (\text{eq 2.1})$$

where Y is the predicted pollutant concentration (ozone),  $\alpha$  is the constant and  $b_1$  to  $b_n$  are the coefficients for the associated predictor variables  $X_1$  to  $X_n$  (ozone precursors and meteorological parameters). The major disadvantage of this linear regression equation is the assumption that the predictor variables are free of the measurement error [Diem *et al* 2002].

Yi *et al* 1996 employed a stepwise regression model whereby the independent variables have a measurement of error. The linear regression model for concentration of predicting daily maximum ozone levels was provided as follows:

$$Y = \beta_0 + \beta_1X_1 + \dots + \beta_nX_n + \varepsilon \quad (\text{eq 2.2})$$

where  $\beta_0$  is an intercept, the same term as  $\alpha$  used by Diem *et al* 2002,  $\varepsilon$  an error term and the other terms are the constants and coefficient of the independent variables. Chaloulakou *et al* 2003 has used a linear regression equation that was formulated as follows:

$$Y = \alpha + \sum_{i=1}^n b_i X_i + \varepsilon \quad (\text{eq 2.3})$$

### 2.9.2 Multivariate data analysis (MDA) techniques

These techniques are employed to solve the multicollinearity or high correlation between the independent variables [Abdul *et al* 2005]. One example of such techniques is the principal component analysis (PCA), which can be used for classification of data, finding similarities and detecting outliers. These techniques are also used to classify the spatial and temporal variations of ozone and to identify the most important factors influencing ozone concentrations [Lengyel *et al* 2004]. They are equally useful in

regression analysis for alleviating the problem of multicollinearity and in exploring the relations among the independent variables, especially if it is not clear which of the variables should be the predictors. The PCA maximizes the correlation between the original variables to form new variables that are equally orthogonal (unrelated), or uncorrelated [Abdul *et al* 2005].

### **2.9.3 Artificial neural network (ANN) techniques**

A neural network is a computing system made up of a number of interconnected processing elements. The two main components of a neural network are the processing elements (or neurons) and their interconnections [Abdul *et al* 2002, Elkamel *et al* 2001, Yi *et al* 1996]. These processing elements are placed in one of three types of the layers, that is, the input, hidden and output layers, connected together by a line of communication called connection [Abdul *et al* 2002].

Neural networks represent an alternative methodology to conventional statistical prediction techniques. They are extensively used in non-linear models, which have been widely applied to pattern recognition, system identification and time series prediction [Pastor-Bárcenas *et al* 2005, Yi *et al*, Gardner *et al* 2000]. The application of ANNs to ozone modelling is recently becoming available to capture those non-linear features of the relationship that a conventional statistical technique might overlook [Abdul *et al* 2002]. The most commonly used neural network technique for pollution prediction is the multilayer perceptron (MLP) [Abdul *et al* 2002, Gardner *et al* 2000, Yi *et al* 1996]

#### **Advantages of ANNs**

1. Neural networks models have proved to be a useful and cost-effective means of studying the relationship between ozone and other variables [Abdul *et al* 2002].

2. They give better predictions than the linear and non-linear regression models [Elkamel *et al* 2001].
3. They have the potential to describe highly non-linear relationships such as that controlling ozone production and also perform better when many extreme values exist, like in the ozone data [Abdul *et al* 2002, Gardner *et al* 2000, Yi *et al* 1996].
4. Their estimation can be automated, while the regression models must be re-estimated periodically when new data are available, and can also predict the concentrations of several pollutants at a time [Elkamel *et al* 2001, Yi *et al* 1996].
5. They have the ability to assess the importance of each of the input variables using the network weights [Elkamel *et al* 2001].

## **2.10 Conclusion**

Even though a lot is known about the dynamics of surface ozone, there still exist a large number of uncertainties, especially in understanding and describing ozone profiles at a specific location. In this regard no detailed study has been undertaken to explain the spatial and temporal variations of ozone on the Mpumalanga Highveld, and whether the areas in this region are VOC- or NO<sub>x</sub>- sensitive. The complex models for predicting ozone concentrations will not be used in this project due to lack of suitable software, only the information about that is given.



## CHAPTER 3

### EXPERIMENTAL METHODS

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*In this chapter...*

*The description of the monitoring sites is given in section 3.1, followed by the procedure that Eskom uses to collect data of gaseous pollutants at different monitoring sites, in section 3.2. Section 3.3 describes the field campaign for VOC sampling that took place on 30 and 31 August 2005 at Elandsfontein. Section 3.4 gives the description of preparation of the sampling tubes and the sampling procedure, and finally the sample analysis.*

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#### **3.1 Site description**

The geographical locations of the two Eskom ambient air quality monitoring sites, Elandsfontein and Verkykkop are shown in Figure 3.1. Elandsfontein is located centrally on the Mpumalanga Highveld, at latitude 26°15'S and longitude 29°25'E and an altitude of 1742 m above sea level. It is located near most of Eskom active power stations, Sasol Secunda synthetic fuel plants and is about 45 km SSE of Witbank town. This site is also influenced by numerous coal-mining activities in this area, domestic coal burning and other industrial emissions.

Verkykkop is located 130 km to the south east of the Mpumalanga industrial region at latitude 27°18'S and longitude 29°53'E and an altitude of 2047 m above sea-level. It is a mountain top location, which is ±5 km north of Volksrust [Combrink *et al* 1995].



**Figure 3.1:** Geographical locations of the monitoring stations

## 3.2 Data collection

### 3.2.1 Instrumentation

Gas analysers used by Eskom have been purchased from four major manufacturers, namely Monitor Labs (ML), Thermo Electron Co (TECO), Dasibi and Advanced Pollution Instruments (API). All instruments use the same measurement principles. All are continuous sampling analysers, designated by the United States Environmental Protection Agency (USEPA) as equivalent methods for determining the various gases in ambient air when operated in the ranges 0 – 500ppb or 0 - 1000ppb, and were installed for the duration of the monitoring period.



**Table 3.1:** Types of sampling analysers used for different pollutants at each site

Site	Verkykkop	Elandsfontein	Comment
NO <sub>x</sub>	ML 8840	API 200A	Measures NO <sub>x</sub> and NO, and NO <sub>2</sub> is calculated by difference
O <sub>3</sub>	Dasibi 1008RS	Dasibi 1008RS	Measures O <sub>3</sub> in the range 0 – 1000 ppb
BTA	Dasibi 7001	Eberline FH62IR	Measurement of particulate matter less than 10 µm in diameter

### 3.2.2 Data acquisition

Data at the monitoring sites are logged directly by means of a dedicated CR-10 Campbell Scientific data logger. Permanent data records of all calculated hourly mean values of all parameters monitored, together with minimum and maximum values, are stored on the logging device. These are derived from 10-second scans. Software automatically calculates vector winds.

### 3.2.3 Data recovery

Eskom's air quality monitoring stations are set up and operated in accordance with the South African National Accreditation System (SANAS), Laboratory number T0199. Eskom's strategic ambient air quality monitoring network was accredited by SANAS in 2003 in accordance with ISO/IEC 17025:1999(E) *General Requirements For The Compliance Of Testing And Calibration Laboratories*, SANAS RO7-01 *Supplementary Requirements For The Accreditation Of Continuous Ambient Air Pollution Stations* and ISO 9000 TSI procedure 60P2084 *Ambient Air Quality Monitoring Procedure*. Each air quality monitoring station consists of a shelter, security fence, sensors and

support equipment. Shelters are insulated, re-locatable buildings, equipped with 2.5Kw cooling capacity air conditioners, which are set to control the internal temperature at  $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

Instrumentation is set out in a 2.0 m tall standard instrument rack, in exactly the same configuration at all sites. A 9.0 m tall collapsible mast, which supports the wind speed and direction sensors, is erected as close to the shelter as practically possible. The ambient temperature sensor, which is fitted with a radiation shield, is accommodated on the mast at the 1.2 m level.

Each monitoring site is visited every fortnight by trained technicians for routine servicing. Zero and span checks are carried out on each analyser during routine services and any discrepancies are logged and used during data verification at Eskom Research and Innovation Department (ERID). Recorded data are downloaded onto a laptop computer during routine site visits and returned to ERID, where it is transferred onto a central computer for verification and editing. After verification, the data is stored in a master file for report generation. Back-up copies of both raw data and verified data are stored for future reference.

### **3.3 Elandsfontein field campaign**

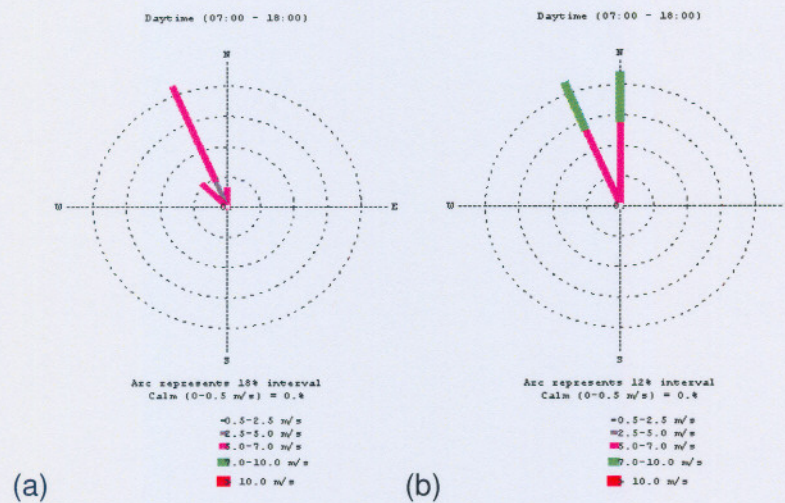
The vertical profile monitoring took place on 30<sup>th</sup> – 31<sup>st</sup> August 2005 at Elandsfontein. This period was selected on the basis that at this time of the year, the highest ozone concentrations were normally recorded. This period normally signals the end of highly polluted cold winter months, and the air pollutants that were accumulated during winter were not washed-out by the rain. Five flights were made in a clockwise movement starting from the North direction, in the mornings and afternoons, during this campaign. The flights were made that the measurements should be done in the atmospheric boundary layer at different altitudes.



On the first day (30 August 2005), measurements were made in the morning from 07:18 to 09:19 (Flight no. 1), in the noontime from 12:37 to 13:26 (Flight 2) and in the afternoon from 15:34 to 16:22 (Flight 3). In the morning it was a little bit misty and there was a light breeze. From the noon until afternoon, the atmosphere was unstable and strong winds were blowing at speed between 5 and 7 m/s, dominant from the NNW direction (Fig 3.2 (a)) and dense smoke from veld fires were all over the place.

On the second day (31 August 2005), measurements were done in the morning from 06:56 to 08:56 (Flight 4) and in the afternoon from 12:25 to 13:13 (Flight 5). In the morning it was clear with very gentle breeze and in the afternoon there were strong winds dominant from the North and NNW directions and intense smoke from veld fires all over the monitoring site. The wind speed was between 7 and 10 m/s (Fig 3.2 (b)).

During the period of the experiment, there was biomass burning over Elandsfontein, with strong winds from North and NNW. Figure 3.2 illustrates the wind roses for the study period.



**Figure 3.2:** Wind roses for the study period on the (a) 30<sup>th</sup> and (b) 31<sup>st</sup> August 2005



The strong wind conditions ranging from 5.0 – 7.0 m/s occur about 85 % with no calm wind conditions on the 30<sup>th</sup> August. On the 31<sup>st</sup> August, the stronger wind conditions ranging from 7.0 – 10.0 m/s occur about 38 % and strong winds ranging from 5.0 – 7.0 m/s occur about 62 %. There were no calm wind conditions on this day.

### 3.4 Volatile organic compounds data

#### 3.4.1 Sample collection

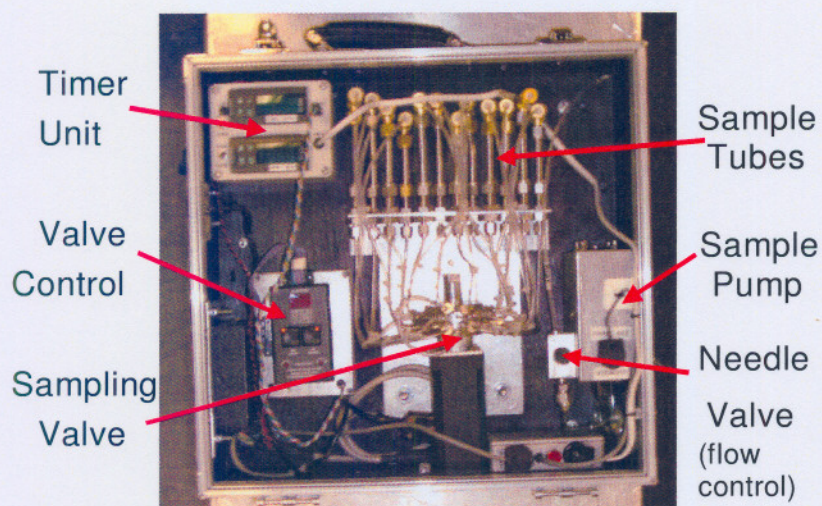
To collect the VOC samples, passive sampling method using Perkin-Elmer Carbotrap<sup>TM</sup> 300 stainless-steel adsorbent tubes (see Figure 3.3), purchased from Supelco were used for this survey. The tubes were preconditioned by purging with 50 ml/min helium at 300°C, to remove any impurities. The desorption time was 30 minutes. The tubes were then capped with Swagelock storage end caps, wrapped individually in an aluminium foil and stored in a refrigerator until they were used.



**Figure 3.3:** Carbotrap<sup>TM</sup> 300 tubes used in this survey



Vertical profile samples from the aircraft were collected using a non-methane hydrocarbon (NMH) tube sampler (see Figure 3.5) that maintains a constant flow rate. Air samples were collected through Teflon tubing positioned on the left wing of the aircraft. The tube sampler accommodates a total of 12 sampling tubes and was operated manually. Samples were collected at sampling rate of 180 ml/min for 20 minutes on each altitude. Field blanks were also taken on sampling excursions.



**Figure 3.5:** NMH tube sampler

### 3.4.2 Sample analysis

A calibration standard obtained from Supelco (Cat no: 41900-U), containing 39 compounds of approximately 53.2 ml each was performed and used as an external standard (Table 3.2).

**Table 3.2:** Supelco calibration standard used to quantify identified VOC's

<b>Nr.</b>	<b>COMPONENT</b>	<b>Conc. (ppm)</b>
35	Freon-12	1.01
	Chloromethane	1.00
34	Freon-114	1.02
	Vinyl Chloride	1.02
33	Bromomethane	1.03
32	Chloroethane	1.03
31	Freon-11	0.99
30	1,1-Dichloroethene	1.03
29	Methylene chloride	1.03
28	Freon-113	1.03
27	1,1-Dichloroethane	1.03
26	Cis-1,2-Dichloroethylene	1.03
25	Chloroform	1.02
24	1,2-Dichloroethane	1.03
23	1,1,1-Trichloroethane	1.03
22	Benzene	1.03
21	Carbon Tetrachloride	1.00
20	1,2-Dichloropropane	1.02
19	Trichloroethylene	1.03
18	Cis-1,3-Dichloropropene	0.99
17	Trans-1,3-Dichloropropene	1.03
16	1,1,2-Trichloroethane	1.05
15	Toluene	1.02
14	1,2-Dibromoethane	1.04
13	Tetrachloroethylene	1.01
12	Chlorobenzene	1.02
11	Ethylbenzene	1.01
10	p-Xylene	1.01
10	m-Xylene	1.01
9	Styrene	1.00
8	o-Xylene	1.02
8	1,1,2,2-Tetrachloroethane	1.02
7	1,3,5-Trimethylbenzene	1.02



**Table 3.2:** Continued

Nr.	COMPONENT	Conc. (ppm)
6	1,2,4-Trimethyl Benzene	1.01
5	1,3-Dichlorobenzene	1.00
4	1,4-Dichlorobenzene	1.01
3	1,2-Dichlorobenzene	0.99
2	1,2,4-Trichlorobenzene	0.96
1	Hexachloro-1,3-Butadiene	0.98

All the samples were thermally desorbed on a thermal desorber. Thermally desorbed compounds were then chromatographed on a Hewlett Packard Agilent 6890 GC–EI fitted with data handling (retrieving) facilities. Mass spectral analysis using a high-resolution Micromass Autospec-TOF mass spectrometer was carried out, utilising spectrometer in full magnetic scan mode (1.00 , 878.00). The separation was achieved by a capillary column Perkin - Elmer PE-1 (60 m long, 320 µm ID, 1.0 µm film thickness). The basic operating conditions on the mass spectrometer were as follows:

Mass range: 40 – 300 atomic mass unit

Scan time: ±0.9 min scan<sup>-1</sup>

Temperature: 250°C

GC – MS transfer line: Open – split mode

The calibration curve was used to quantify sample VOCs that were present in the external standard. Firstly, the response factor ( $R_f$ ) or analysis constant for each compound in the calibration standard was calculated using the following formula:

$$R_f = \frac{A}{C * V} \quad (\text{eq 3.1})$$

where A is peak area of each compound in the standard

C is the standard concentration ranging from 0.96 – 1.05 ppm

V is sample volume (ml) = sample time x flow rate

$$= 2 \text{ min} \times 26.6 \text{ ml/min}$$

$$= 53.2 \text{ ml}$$

then concentration (ppb) of each VOC in the sample was calculated using the following formula:

$$C = \frac{A * DF}{V * R_f} * 1000 \quad (\text{eq 3.2})$$

where A is the peak area of each VOC in the sample

DF is a dilution factor, which is 1

V is sampling volume = sampling time x flow rate

= 20 min x 180 ml/min

= 3600 ml

VOC's that were not present in the calibration standard were identified using the MS data system library called NIST and since they could not be quantified, arbitrary units were used to determine their abundance in the atmosphere and were calculated as follows:

$$\text{Abundance in arbitrary units} = \frac{A}{V} \quad (\text{eq 3.3})$$

where A is the peak area of each VOC in the sample

V is sampling volume

## CHAPTER 4

### RESULTS AND DISCUSSIONS OF ACTIVE DATA

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*In this chapter...*

*Data from the monitoring sites were presented and attempts were made to draw as many conclusions as possible concerning surface ozone and the ambient air quality. Surface ozone data from selected years were correlated with some of ozone precursors and meteorological conditions to try to identify the most important factors in determining ozone levels. These results were used to explain the diurnal and seasonal variations of O<sub>3</sub>, NO and NO<sub>2</sub>, and the trends enclosed in the data, based on the current knowledge of sources and sinks. The data were also used to evaluate the exceedances of air quality SA DEAT guideline values and to predict the importance of each variable on O<sub>3</sub> concentrations by means of scatter plots and regression techniques.*

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#### 4.1 Data analysis

Eskom supplied the five-year data set used in this study from the monitoring sites Elandsfontein and Verkykkop. The available data contain the averages of continuous measurements of concentrations of air pollutants, ozone (ppb), NO (ppb), NO<sub>2</sub> (ppb) and BTA (µg/m<sup>3</sup>), and of meteorological parameters, temperature (°C), wind speed (m/s), wind direction (degree) and solar radiation (W/m<sup>2</sup>), which were monitored hourly for a maximum of 24 hrs. Although the data were incomplete for some pollutants and weather conditions, the monitoring covered the period from 2000 to 2004. NO and NO<sub>2</sub> data were missing in 2003 at Verkykkop and O<sub>3</sub> data at Elandsfontein in 2004. Data missing for the variables might be due to power failure or

problems experienced with the analysers. Tables 4.1 and 4.2 shows the percentage data captured at both monitoring sites during the period.

**Table 4.1:** Percentage data captured at Elandsfontein (2000 – 2004)

NO	NO <sub>2</sub>	Ozone	UV RAD	TEMP	WDR	WSP	Reliability
83	81.9	84.9	44.5	95.3	95	95	80.6

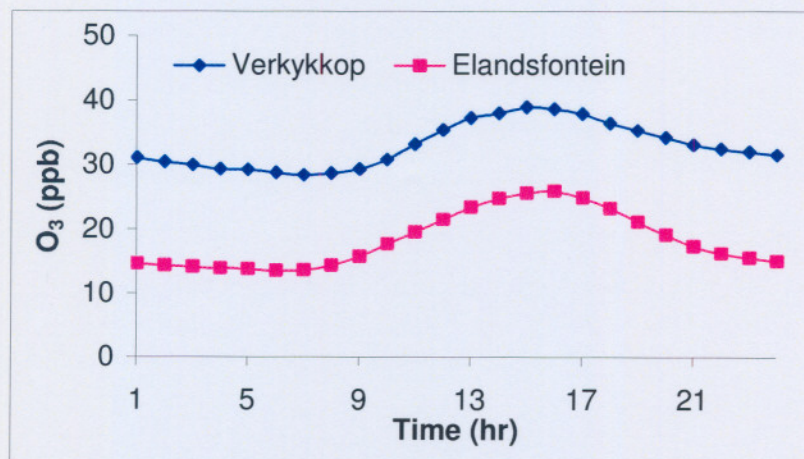
**Table 4.2:** Percentage data captured at Verkykkop (2000 – 2004)

NO	NO <sub>2</sub>	Ozone	UV RAD	TEMP	WDR	WSP	Reliability
86.22	86.22	91.82	0.00	96.94	78.16	79.64	86.48

## 4.2 Diurnal variations of air pollutants

### 4.2.1 Diurnal variations of ozone

The diurnal variations of average ozone concentrations for the period 2000 – 2004 period observed at Verkykkop and Elandsfontein are shown in Figure 4.1.



**Figure 4.1:** The diurnal variation of surface ozone concentrations

The diurnal cycle of ozone is characterized by the maximum ozone concentration in the afternoon and minimum concentration in the early hours of the morning and in the evening. The cycle shows the relationship between the build up of ozone precursor gases in the early morning and the photochemical formation of ozone in the afternoon.

In the morning, the  $\text{NO}_x$  concentrations are high, thus inhibiting ozone formation. Therefore at high  $\text{NO}_x$  concentrations near the sources,  $\text{NO}_x$  is a major scavenger of both the radicals and ozone, resulting in low radical and ozone concentrations (Figure 4.2).

The increase of ozone concentrations during daylight hours is attributed to the photolysis reactions of  $\text{NO}_2$  and photooxidation of VOC's, CO, hydrocarbons and other  $\text{O}_3$  precursors. It is also attributed to the downward transport of ozone by the vertical mixing, due to convective heating, which takes place during daytime hours [Lal *et al* 2000, Tyson *et al* 1988].

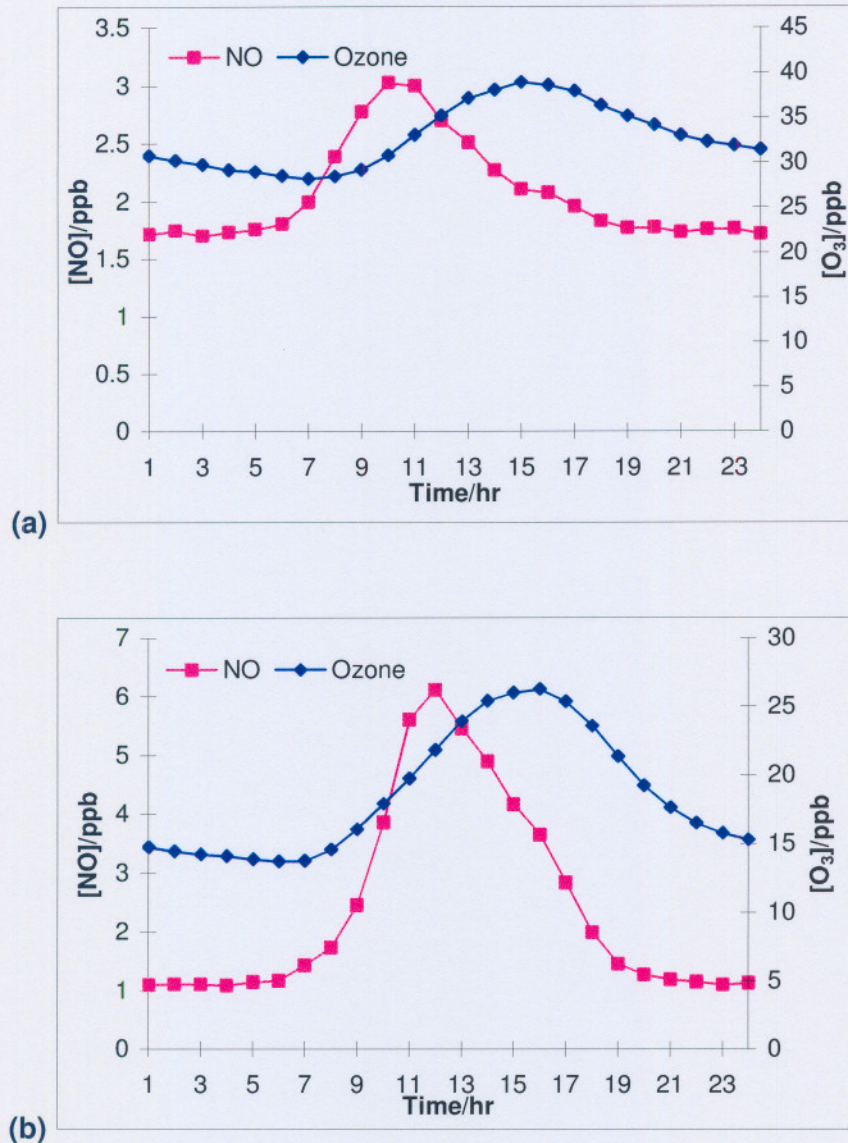
In the evening, ozone concentration decreases steadily because the night inversion layer is formed and once it is formed, no great changes occur [Tyson *et al* 1988]. The low values are attributed to the destruction of ozone by a rapid reaction between ozone and nitric oxide (sometimes referred to as NO titration) in the absence of sunlight and at this time there is no photolysis of  $\text{O}_3$  precursors taking place since there is no solar radiation. The rate of increase in the morning is faster whereas the rate of decrease in the evening is quite slower. This means that, in situations with significant ozone formation (including most urban and polluted rural areas during weather conditions favourable to ozone formation), the removal of  $\text{O}_3$  is small compared to the rate of  $\text{O}_3$  production. The process of  $\text{NO}_x$  titration can only remove at most one  $\text{O}_3$  per emitted NO, whereas that of ozone formation typically produces four or more  $\text{O}_3$  per NO emitted [Silliman 1999]. The slow ozone formation in the evening is attributed to the reduction of hydroxyl radical concentrations [Borrel *et al* 2000].

Ozone concentrations are consistently higher at Verkykkop than at Elandsfontein. With dominant northwesterly winds, Verkykkop is downwind of the precursor source areas and this causes the transport of O<sub>3</sub> precursors which leads to high ozone levels observed. The other reason for high O<sub>3</sub> levels might be elevation since Verkykkop is located at higher altitudes than Elandsfontein. Low O<sub>3</sub> concentrations at Elandsfontein can be attributed to NO titration of O<sub>3</sub> (R27) or the reaction of NO<sub>2</sub> with HO<sup>•</sup> to form HNO<sub>3</sub> (R28) because power plant plumes frequently emit high concentrations of NO<sub>x</sub> and Elandsfontein is located near many Eskom power stations. Power plants are often associated with decreased ozone concentrations within 80 km of the plume source [Silliman 1999].

The background ozone at Verkykkop is ±28 ppb and the maximum peak is ±39 ppb. At Elandsfontein, the background O<sub>3</sub> is ±13 ppb and the maximum peak is ±26 ppb. Ozone concentration peaks an hour (15:00) earlier at Verkykkop than at Elandsfontein (16:00).

The relation between NO and O<sub>3</sub> is shown in Figure 4.2 below. Nitric oxide concentrations are high in the early morning because the free (hydroxyl and peroxy) radicals needed to convert NO to NO<sub>2</sub> are not yet present in sufficient quantities. After sunrise, the radical concentrations increase, causing oxidation cycle of VOC's and CO (R12 and R20). Subsequent conversion of NO to NO<sub>2</sub> by peroxy radicals (R8) results in NO<sub>2</sub> becoming the dominant NO<sub>x</sub> species. When the ratios of NO<sub>2</sub> to NO increase, ozone concentrations increase and NO<sub>2</sub> concentrations decrease via the sink reaction (R26). The NO<sub>x</sub> are also diluted by the diurnal rising of the inversion layer, allowing for more mixing during the day. In the evening the reactions, R27 and R28, are the most dominant.





**Figure 4.2:** Average hourly diurnal variations of NO and O<sub>3</sub> at Verkykkop (a) and Elandsfontein (b) (2000 – 2004)

The morning NO peak at Elandsfontein (~6 ppb) exceeded by far the respective NO peak at Verkykkop (~3 ppb), resembling a clear effect of the extent of fresh morning precursor emissions and stagnant morning conditions at Elandsfontein. Since the length of ozone inhibition is essentially determined by the concentration of NO, it is expected that this period be shorter at areas of high amounts of fresh NO<sub>x</sub> emissions. Seemingly, the average period of

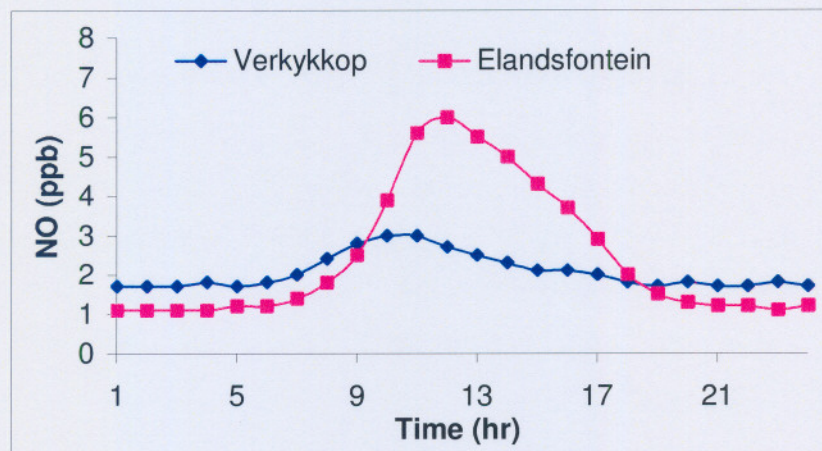


ozone inhibition at Elandsfontein (~1.9 ppb) is shorter than that at Verkykkop (~3 ppb).

The average NO-O<sub>3</sub> crossover concentration at Verkykkop (~35.2 ppb) was almost 1,5 times higher than at Elandsfontein (~23.7 ppb). Apparently, the average rate of ozone build-up at Verkykkop (~1.27 ppb/hr) was also 1,5 times greater than at Elandsfontein (~0.84 ppb/hr). This might suggest the high emissions of fresh NO<sub>x</sub> at Elandsfontein and that the production of NO<sub>2</sub> available for ozone formation at Verkykkop was strongly enhanced by the availability of VOC's.

#### 4.2.2 Diurnal variations of nitrogen oxide

The diurnal concentrations of NO are high in the morning (from 06:00 to 10:00) than in the evening due to NO emitted by tall stack sources being mixed to the surface (Figure 4.3). The low NO concentrations in the afternoon hours is due to oxidation of nitric oxide to nitrogen dioxide, initiated by the rising sun on a series of secondary photochemical reactions and the low values in the evening result mainly from the reaction of ozone and NO (R27).



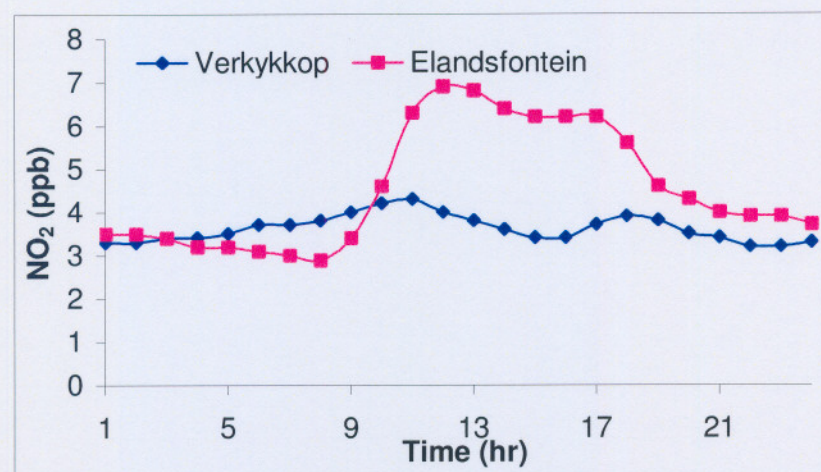
**Figure 4.3:** Daily cycle of NO concentrations (2000 – 2004)



At Verkykkop, NO concentrations are high from 06:00 and reach the maximum of approximately 3.0 ppb at 10:00. At Elandsfontein, NO level peaks at 12:00 with the value of 6 ppb. NO concentrations are emitted from power stations that are situated near Elandsfontein, thus resulting in higher levels of NO at Elandsfontein than at Verkykkop.

#### 4.2.3 Diurnal variations of nitrogen dioxide

The diurnal variations of NO<sub>2</sub> concentrations observed at both the monitoring stations are shown in Figure 4.4.



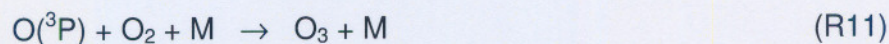
**Figure 4.4:** Diurnal variation of NO<sub>2</sub> concentration (2000 – 2004)

The cycle shows the increase of NO<sub>2</sub> concentrations in the morning and in the late afternoon. The increase in the morning can be attributed to the oxidation of NO that is initiated by the solar radiation as the sun goes up:



The major loss of NO<sub>2</sub> in the early afternoon is due to photodissociation of NO<sub>2</sub>, which requires UV radiation to form ozone.





Thus, ozone formation is dependent on the amount of sunlight that reaches the  $\text{NO}_2$  molecules. Consequently, high ozone concentrations are observed in the afternoon.

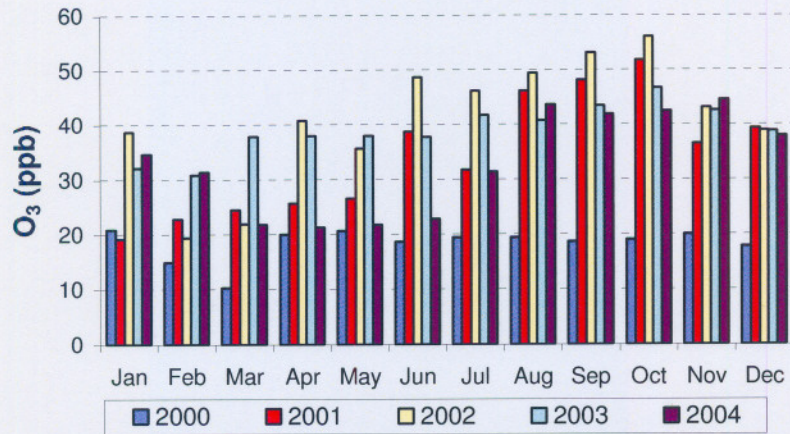
The increase of  $\text{NO}_2$  levels in the late afternoon just before sunset can be due to motor vehicle emissions because of the afternoon traffic density and also due to domestic activities (such as heating and cooking), which take place in the afternoons. Motor vehicles emit  $\text{NO}$ , which is oxidized to  $\text{NO}_2$ , and since at this time, the intensity of the solar radiation has decreased, it means that not all of  $\text{NO}_2$  molecules will be photolysed. Some of the  $\text{NO}_2$  molecules will be trapped in the inversion layer and contribute to high levels observed before sunset.

$\text{NO}_2$  concentration at Elandsfontein peaks at 12:00 with a maximum peak of  $\pm 7$  ppb and decreases steadily until 17:00.

### 4.3 Annual variations of ozone

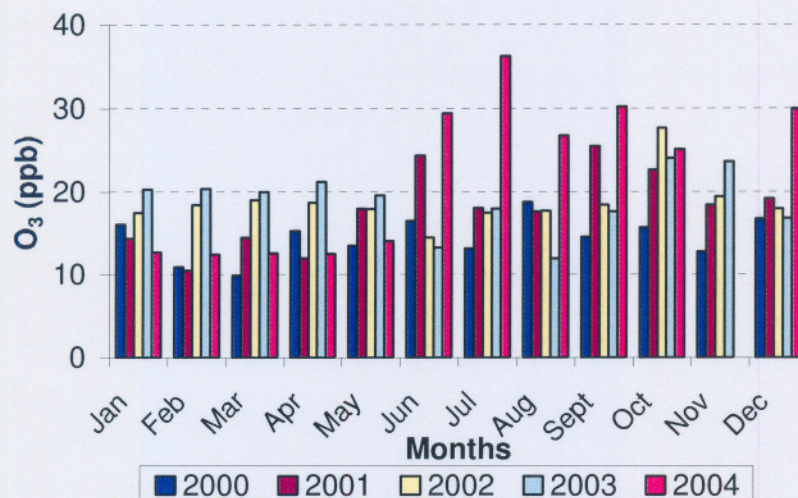
Figure 4.5 shows that the annual trends of ozone concentrations in Verkykkop for all years differ significantly from each other.





**Figure 4.5:** Monthly variation of O<sub>3</sub> levels at Verkykkop

The spring maximum seems to be reached almost at the same time of the year (Sept/Nov), for all years, with the exception in 2000. The highest average ozone concentration (~56.1 ppb) was reached in October 2002, while the lowest value was reached in March 2000. In the year 2000, the average ozone levels lie below 21 ppb for all the months and no explanation could be detected from the data at hand. In the years 2001, 2002 and 2003, the highest monthly average of ozone was observed during October while the highest monthly average in the year 2004 occurred in November.



**Figure 4.6:** Monthly variation of O<sub>3</sub> levels at Elandsfontein



The highest monthly ozone average of approximately 36.3 ppb was observed in July 2004. This might be due to biomass burning emissions since biomass burning take place during winter and into spring from July to September [Zunkel *et al* 2004]. The monthly minimum was between 10 and 15 ppb. In 2000, the monthly averages were below 20 ppb but according to the results obtained by Zunkel *et al* 2004, the monthly ozone averages were above 20 ppb with the highest of about 35 ppb reached in October.

## **4.4 Seasonal variation of air pollutants**

### **4.4.1 Seasonal variation of O<sub>3</sub>**

Seasonal grouping of data into four groups were made: summer months (Dec, Jan, Feb), autumn months (Mar, Apr, May), winter months (Jun, Jul, Aug) and spring months (Sept, Oct, Nov) [Combrink *et al* 1995]. Results of diurnal variation of ozone concentrations for each season are represented in Figures 4.7 and 4.8 below. This figure displays the diurnal pattern of surface ozone with three main stages previously observed in the daily cycle of ozone concentrations (Figure 4.1) in all seasons, becoming intense during spring.

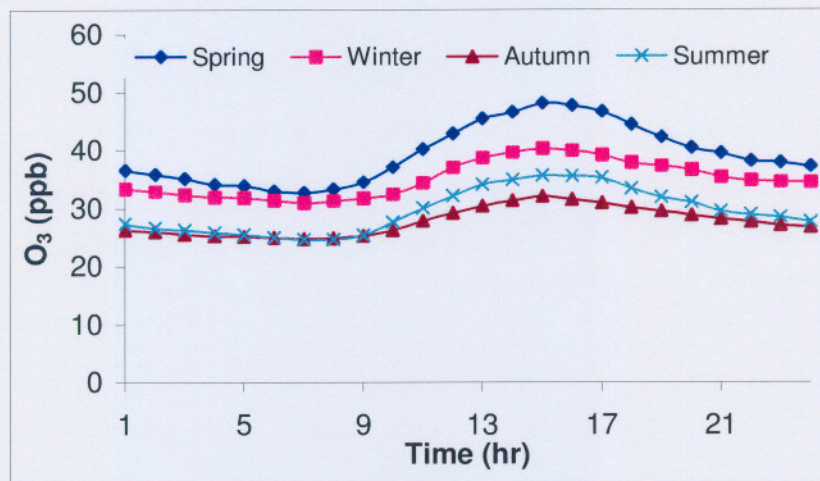
High levels of average O<sub>3</sub> concentrations were reached in spring followed by winter and low values in summer and autumn at both sites. The spring maximum can be attributed to biomass burning which take place during winter and into spring from July to September [Zunkel *et al* 2004]. Savannah fires emit large quantities of air pollutants in the form of smoke, which lead to the formation of ozone, such as unburned hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen and ash [Boubel *et al* 1994].

The solar radiation becomes intense in spring, causing photochemical reactions of ozone precursors that were accumulated during winter and this contribute to high O<sub>3</sub> observed in spring. The long lifetime of ozone in winter, which is about 200 days [Monks 2000], also allows the anthropogenically formed O<sub>3</sub> to accumulate in the inversion layer and then contributes to the



high spring O<sub>3</sub> levels. The high ozone levels in spring also correspond to the beginning of summer rains, and the associated spring growth in vegetation and nitrogen from soil wetting [Zunkel *et al* 2004].

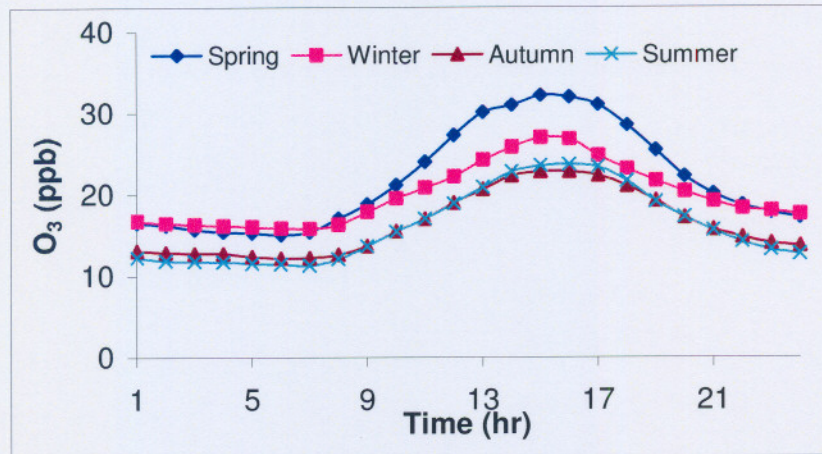
Low ozone concentrations were observed in summer than in winter, even though summer is the hottest season of the year. This can be attributed to the non-availability of enough solar radiation due to the cloudy skies that reflects back the solar radiation from reaching the surface, and also the washouts of air pollutants from the atmosphere by rain, which takes place during this season.



**Figure 4.7:** Seasonal variation of O<sub>3</sub> at Verkykkop (2000 – 2004)

As shown in Figure 4.7, the ozone concentration starts to decrease from 01:00, reaching its minimum at 07:00. The concentration starts to increase from 08:00, reaching its peak at 15:00. Maximum peaks were observed at the same time of the day (15:00) for all the seasons. The maximum ozone concentration observed in spring is 48 ppb. At approximately 20:00, a continuous steady decrease of concentration begins, reaching its minimum at 24:00.



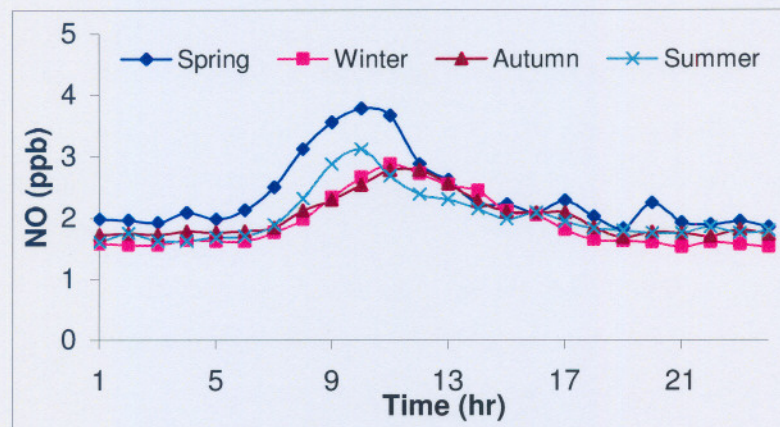


**Figure 4.8:** Seasonal variation of O<sub>3</sub> at Elandsfontein (2000 – 2004)

Ozone concentration starts to increase from 07:00 reaching its peak at 15:00 in spring, winter and autumn, and peaking at 16:00 in summer. The maximum ozone peak observed in spring is 32.2 ppb.

#### 4.4.2 Seasonal variation of nitrogen oxide

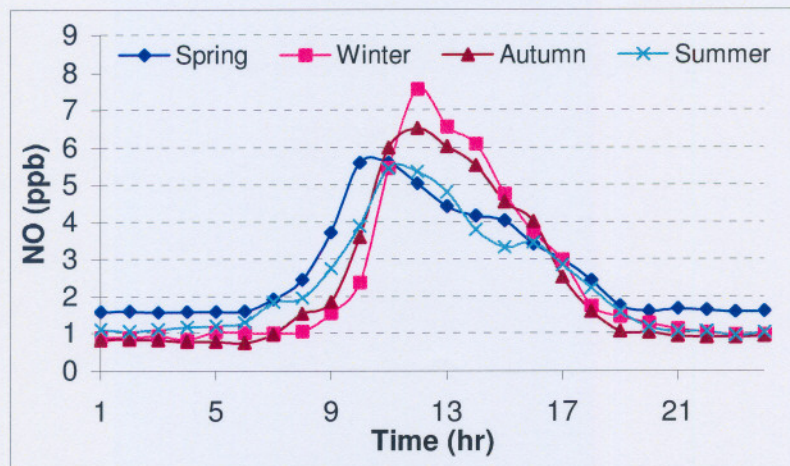
Nitric oxide concentrations peak earlier in spring and summer than in winter and autumn as shown in Figures 4.9 and 4.10.



**Figure 4.9:** Seasonal variation of NO at Verkykkop (2000 – 2004)



High NO concentrations are observed in spring and summer, and peak at 10:00, an hour earlier than in winter and autumn at Verkykkop. The high levels might be due to motor vehicle emissions and domestic fuel burning. The average background NO is  $\pm 1.75$  ppb and the average maximum is  $\pm 3.1$  ppb.



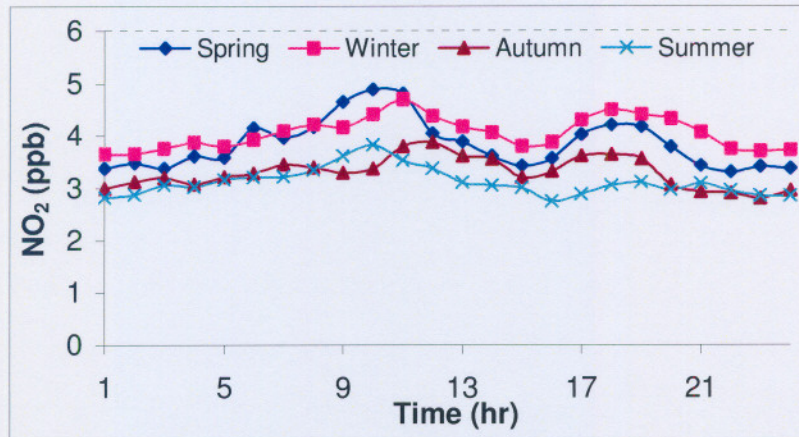
**Figure 4.10:** Seasonal variation of NO at Elandsfontein (2000 – 2004)

Nitric oxide concentrations are high in winter and autumn, and this is due to low temperatures in winter. During these seasons, the lower solar radiation intensity does not cause intense photochemical reactions, which would lead to NO destruction [Riga-Karandinos *et al* 2005]. When temperature decreases, more electricity is demanded for heating and this contributes to the increased levels of NO emitted from the power plant plumes. Maximum peaks are observed at 10:00 in spring and at 12:00 in winter. The average background NO is  $\pm 1.1$  ppb and the average maximum is  $\pm 6.2$  ppb.

#### 4.4.3 Seasonal variation of nitrogen dioxide

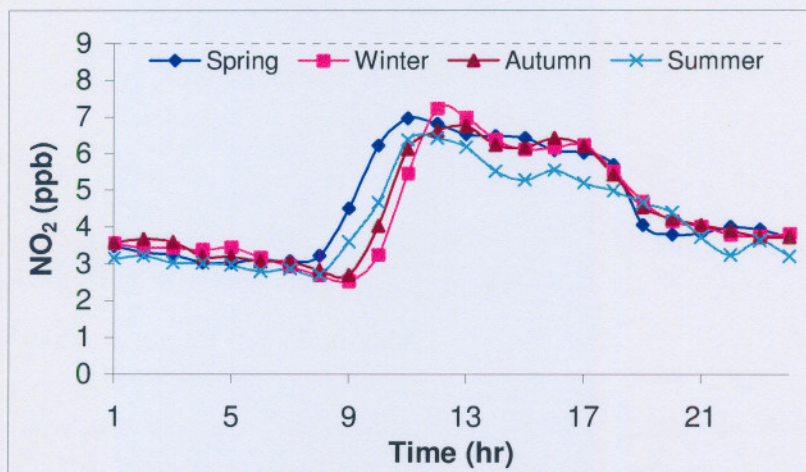
The average seasonal concentrations of NO<sub>2</sub> are given in Figure 4.11. High values are observed in winter and spring at both monitoring sites





**Figure 4.11:** Seasonal variation of NO<sub>2</sub> at Verkykkop (2000 – 2004)

Spring and summer NO<sub>2</sub> peaks are observed at 09:00, while in winter and autumn peaks are observed at 10:00 and 11:00, respectively. Maximum peaks are reached in the morning and in the afternoon and there is no conclusive explanation for this observation.



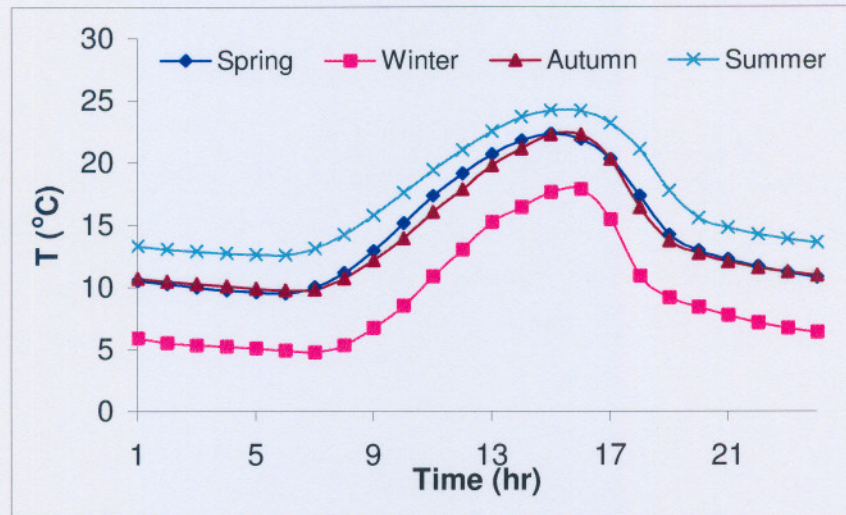
**Figure 4.12:** Seasonal variation of NO<sub>2</sub> at Elandsfontein (2000 – 2004)

Nitrogen dioxide peaks at 11:00 in spring, at 13:00 in autumn and at 12:00 in both winter and summer



#### 4.4.4 Seasonal variation of temperature

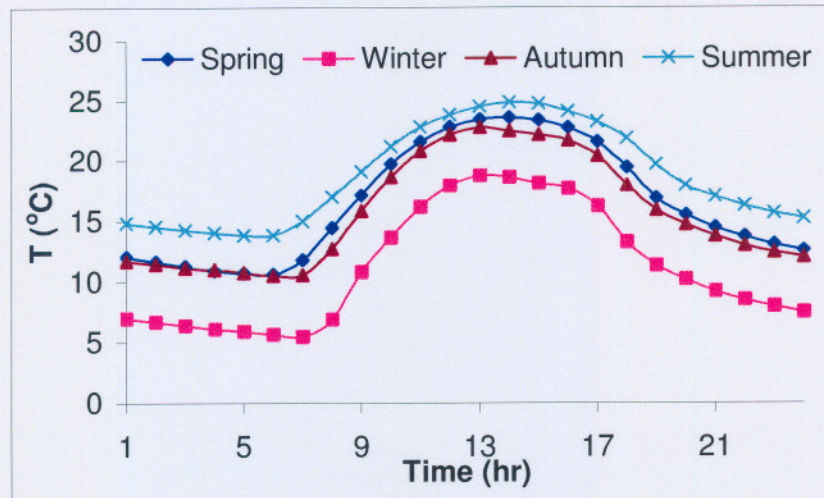
Ambient air temperatures differ with seasons of the year and time of the day. Maximum temperatures are observed in summer and spring. Low temperatures of about 20°C are observed in winter. Temperature tends to reach its maximum value during daytime at about 15:00 (see Figures 4.13 and 4.14)



**Figure 4.13:** Diurnal variation of temperature at Verkykkop (2000 – 2004)

In all the seasons, the highest temperature was reached at 15:00, except in winter where it was reached an hour later at 16:00.





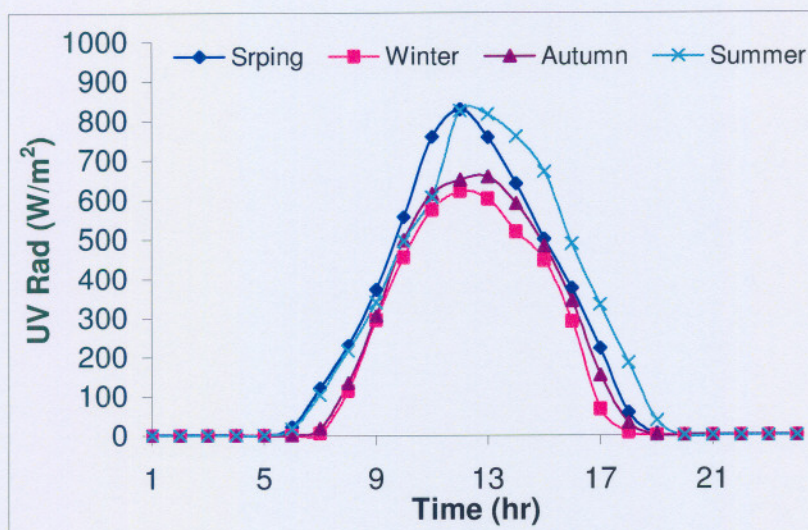
**Figure 4.14:** Diurnal variation of temperature at Elandsfontein (2000 – 2004)

At Elandsfontein, maximum temperatures were reached earlier in all seasons. Highest temperatures were reached earlier in winter and autumn (13:00) and an hour later in spring and summer (14:00). This might indicate the varying degrees of meteorological conditions at these sites.

#### 4.4.5 Seasonal variation of solar radiation

The solar radiation begins at sunrise, reaching its maximum peak at noon and shut off at sunset.





**Figure 4.15:** Seasonal averaged diurnal variation of solar radiation at Elandsfontein (2004)

In summer and spring, the radiation becomes intense at 06:00 and in winter and autumn at 07:00. This could explain the shift observed in the diurnal patterns of NO and NO<sub>2</sub> at both sites and why their concentrations peak an hour later in winter and autumn than in summer and spring. The solar radiation peaks at 12:00 in all the seasons, except in autumn where it peaks at 13:00.

#### 4.5 Variations of ozone with meteorological parameters

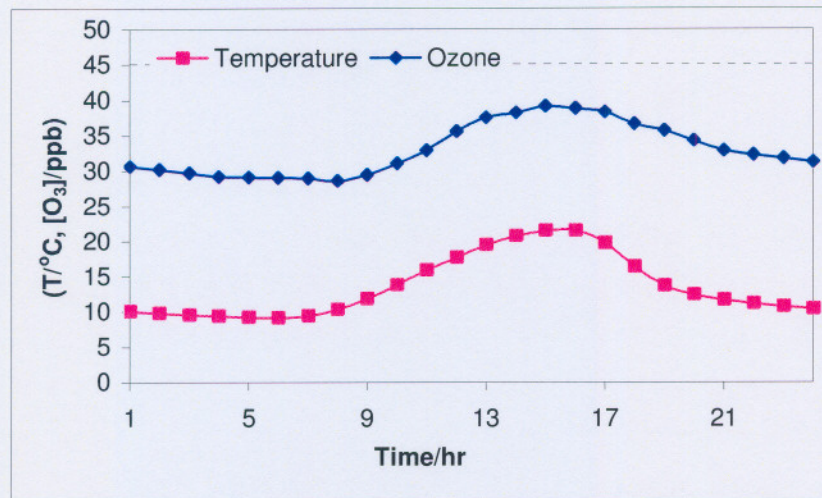
A survey, to assess the behaviour of surface ozone concentrations with several meteorological conditions available, was carried out in this study.

##### 4.5.1 Influence of temperature

Ozone concentration is directly related to temperature because the concentration peaks at the hour in which temperature is the highest and temperature is the measure of solar insolation. Nighttime ozone concentrations are higher in winter than in summer and this is most likely



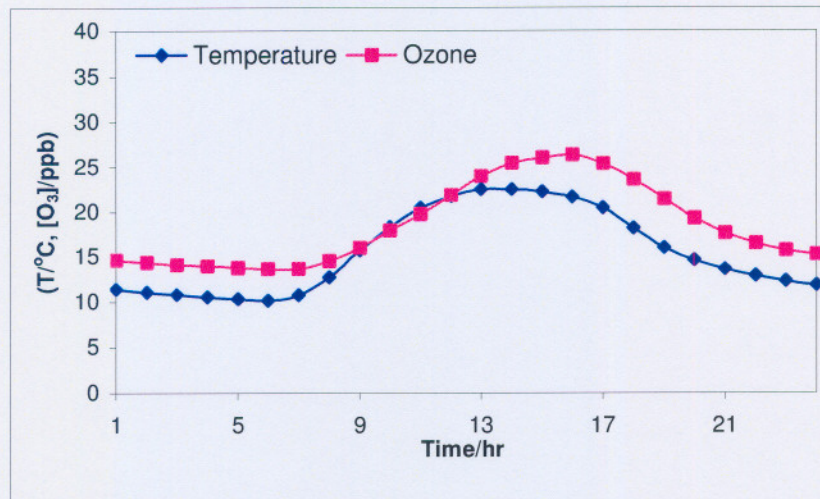
related to seasonal contrasts in the occurrence of nocturnal temperature inversions, which are common in the interior of South Africa [Combrink *et al* 1995]. The relation between ozone concentrations and temperature is shown in Figures 4.16 and 4.17 at Verkykkop and Elandsfontein, respectively.



**Figure 4.16:** Averaged diurnal variations of ozone and temperature at Verkykkop (2000 – 2004)

At Verkykkop, the maximum ozone peak was observed at 15:00 where the highest temperature was reached, in spring, summer and autumn and the only exception was in winter whereby the highest value of ozone was observed at 15:00 and the highest temperature was reached at 16:00.





**Figure 4.17:** Averaged diurnal variations of ozone and temperature at Elandsfontein (2000 – 2004)

At Elandsfontein, ozone concentrations peak 16:00, but the highest temperature was reached around 14:00.

#### 4.5.2 Influence of wind direction and speed

It is known that there is a clear relationship between ambient air quality and wind speed and direction. These two parameters are important for the dispersion and transport of ozone and its precursors from their emission sources [Dueñas *et al* 2002].

Wind roses in all sectors of the monitoring sites during daytime hours (07:00 – 18:00) were created for all the seasons by means of the software, web-Mathematica developed by Eskom Air Quality Management, analysing the influence of both wind speed and direction on surface ozone. The number in the centre of the circle shows the percentage of calm winds [Dueñas *et al* 2002]. For the wind speed, the following intervals were considered: calm winds (speed lower than 0.5 m/s); very soft winds (speed between 0.5 and 2.5 m/s); soft wind (speed between 2.5 and 5.0 m/s); moderate winds (speed



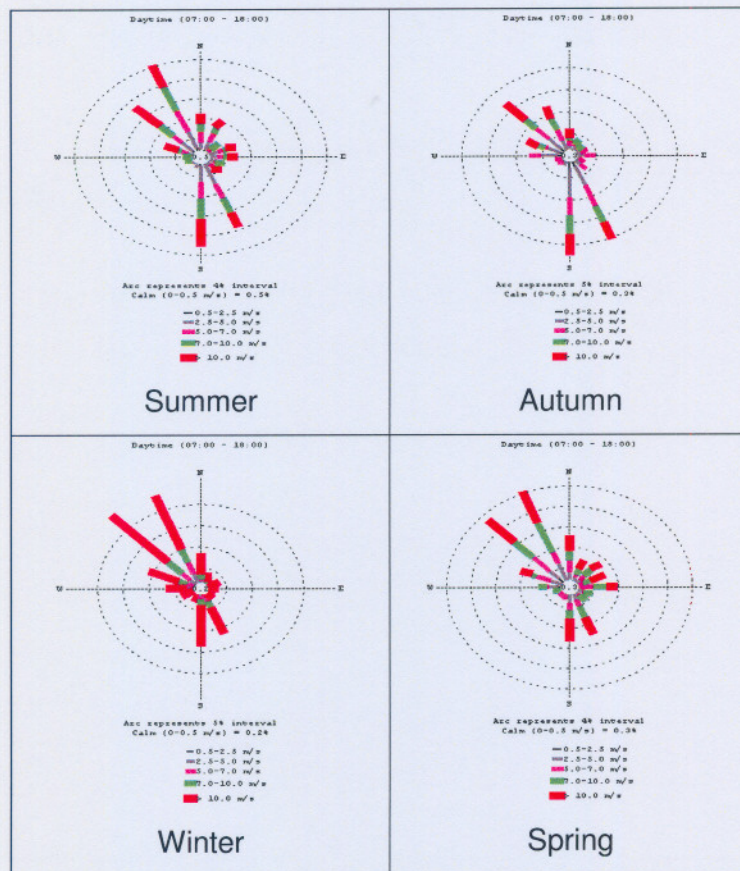
between 5.0 and 7.0 m/s); strong winds (speed between 7.0 and 10.0 m/s); and very strong winds (speed higher than 10.0 m/s).

Table 4.3.shows the percentage data captured at Verkykkop in 2004, where most of the data was captured as compared to other years.

**Table 4.3:** Percentage data captured at Verkykkop (2004)

NO	NO <sub>2</sub>	Ozone	UV RAD	TEMP	WDR	WSP	Reliability
85.8	85.8	96.6	0.0	99.8	100	91.8	93.3

Figure 4.18 shows the seasonal frequency of wind directions and speed for every sector in all the seasons at Verkykkop



**Figure 4.18:** Frequency of wind directions at Verkykkop in 2004



- In summer, the NNW winds prevail (20.0%), as well as the South winds ( $\pm 17.2\%$ ) and the NW winds ( $\pm 14.0\%$ )
- In autumn, wind prevails from the South ( $\pm 23.0\%$ ) and the SSE (20.0%) directions. The NW winds range third with a contribution of  $\pm 16.5\%$ .
- A balance is nearly achieved in winter, between the two main components representing the NW wind ( $\pm 25.0\%$ ) and the NNW winds ( $\pm 24.5\%$ ). Winds from the South and SSE should also be considered. The winds during winter are very strong from all sectors (with speed above 10.0 m/s) because August is a winter month and a very windy month of the year.
- The behaviour in spring is similar to that in winter but it is reversed, with prevailing winds from the NNW direction (20.0%) and the NW direction ( $\pm 18.5\%$ ).

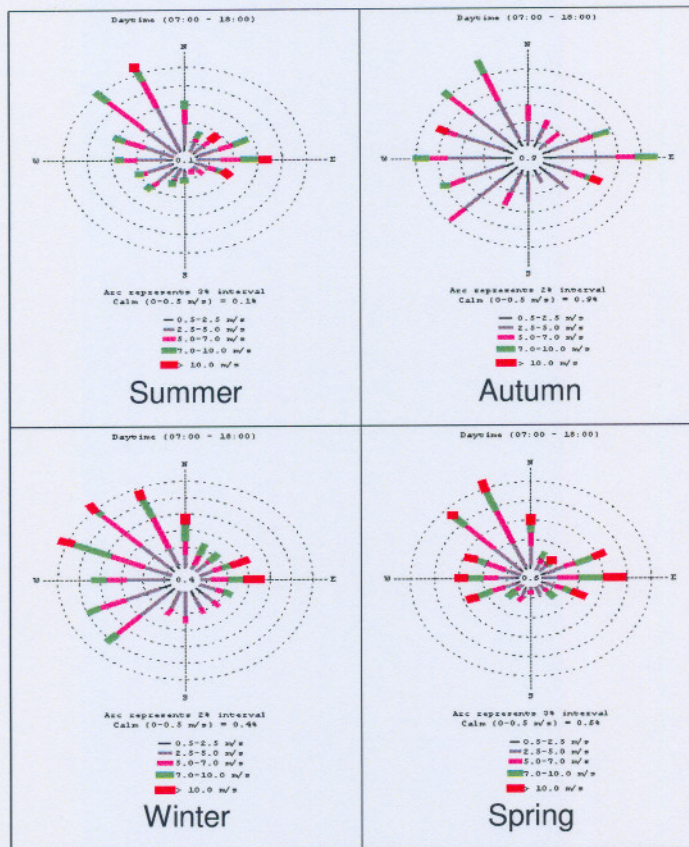
Table 4.4 shows the percentage data captured at Elandsfontein in 2002, where most of the data was captured as compared to other years.

**Table 4.4:** Percentage data captured at Elandsfontein (2002)

NO	NO <sub>2</sub>	Ozone	UV RAD	TEMP	WDR	WSP	Reliability
96.8	96.8	96.4	0.0	99.8	99.9	99.9	96.7

Figure 4.19 shows the seasonal frequency of wind directions and speed for every sector in all the seasons at Elandsfontein.





**Figure 4.19:** Frequency of wind directions at Elandsfontein in 2002

- In summer, winds prevail most dominantly from the fourth quadrant, NNW winds ( $\pm 17.5\%$ ) and NW winds ( $\pm 16.0\%$ ). The East winds ( $\pm 10.5\%$ ) also prevail.
- In autumn and winter, winds prevail from the fourth and third quadrants, with the fourth quadrant dominating. The East winds ( $\pm 11.5\%$ ) are also outstanding during autumn.
- The situation in spring is almost similar to that in summer, with an exception that the winds during spring are at higher speed.

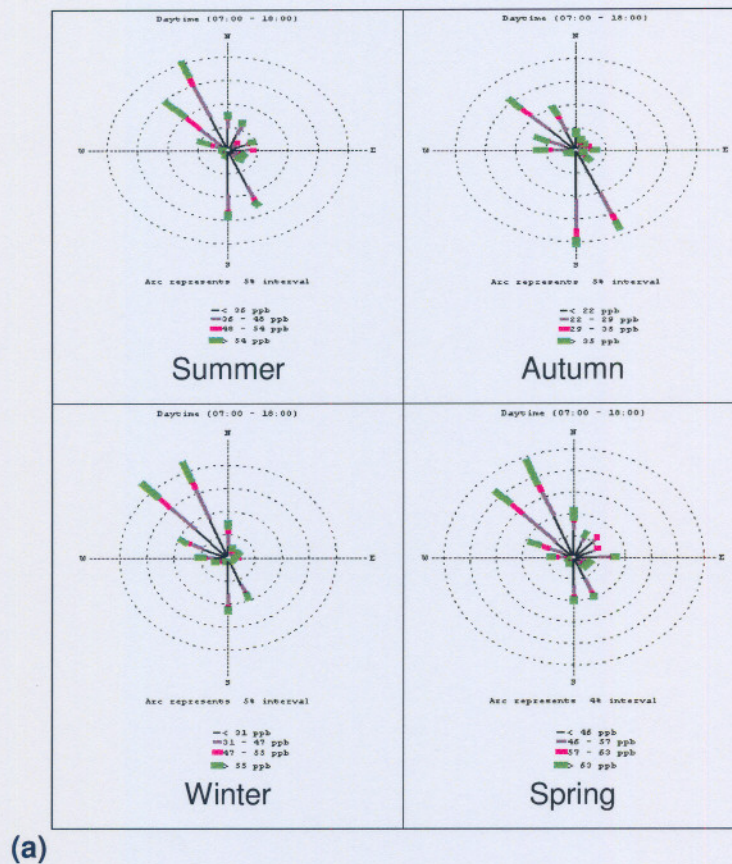


## 4.6 Ozone roses

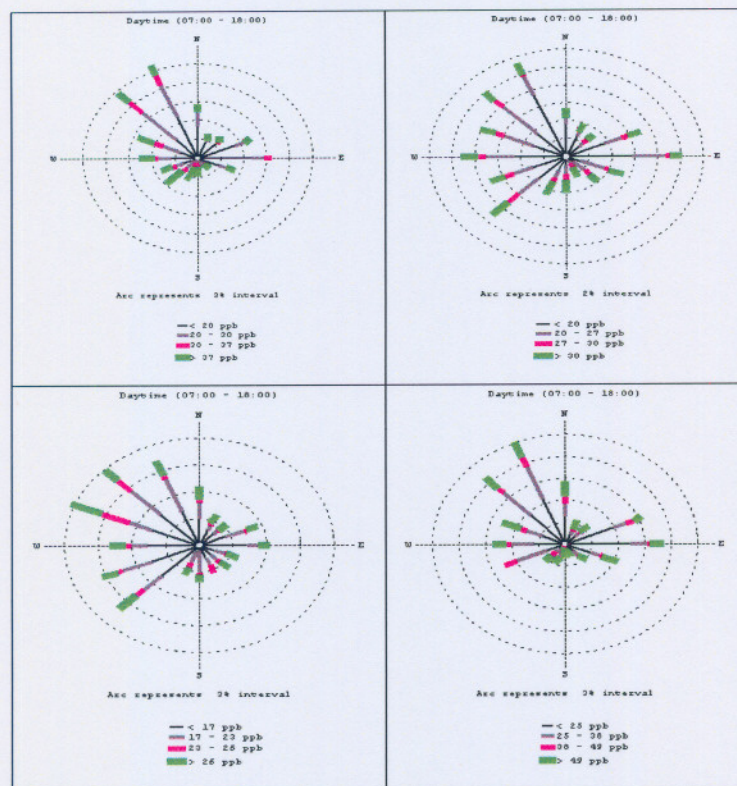
Ozone pollution and 98 percentile exceedance roses were created to indicate the relation between ozone and wind direction on surface ozone.

### 4.6.1 Ozone pollution roses

Ozone pollution roses in all sectors of the monitoring sites during daytime hours (07:00 – 18:00) have been created for all the seasons, showing the influence of both wind speed and direction (see Figure 4.20).







(b)

**Figure 4.20:** Seasonal averaged O<sub>3</sub> concentration at Verkykkop in 2004 (a) and Elandsfontein in 2002 (b)

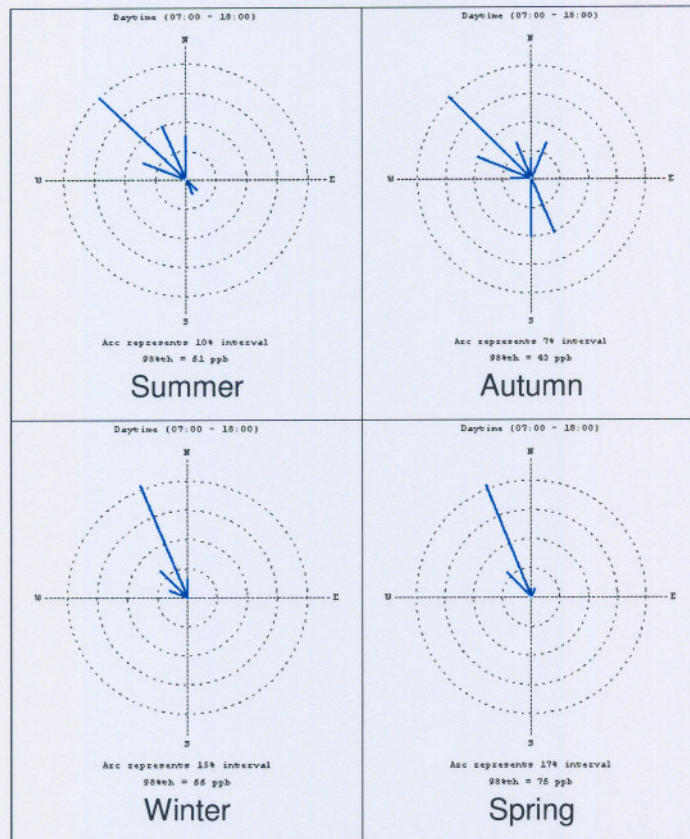
The ozone pollution roses follow the same pattern as the wind roses at both sites and this indicates that there is indeed a relationship between ozone and wind. The maximum ozone concentrations coincide with the most frequent wind sectors and the minimum concentrations have a close relationship with the less frequent wind sectors [Dueñas *et al* 2002]. The exception is only in summer where ozone concentrations were the highest in the East and ESE directions, while wind prevails in the NW and NNW directions.

#### 4. 6.2 Ozone 98 percentile exceedance roses

In order to see the sectors where ozone concentrations exceeded the DEAT guideline value with 98%, the ozone 98-percentile exceedance roses were created. The 98 percentile roses also indicate the position of the emission



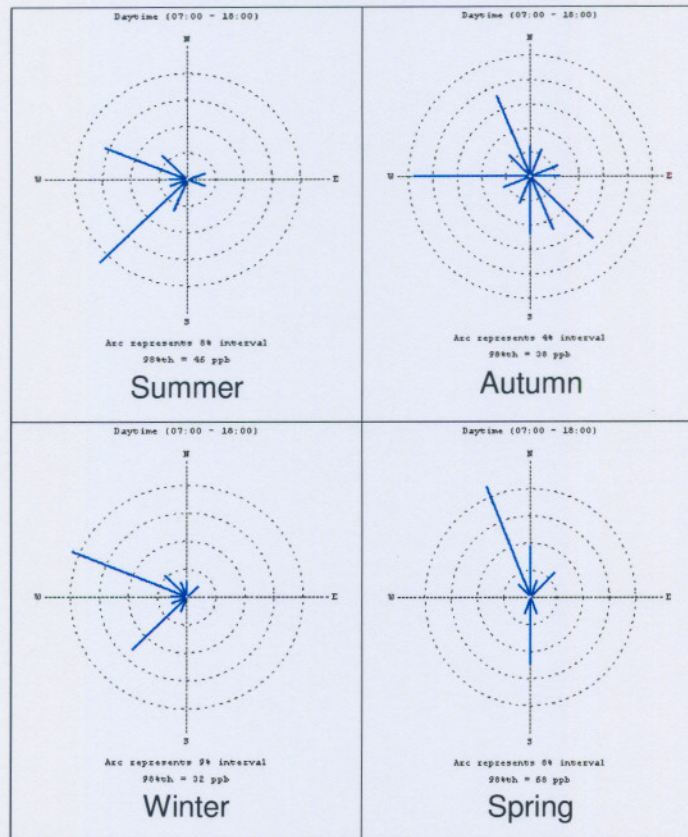
source areas that have contributed to the high ozone concentrations observed in the specific sector.



**Figure 4.21:** Seasonal averaged O<sub>3</sub> 98 percentile exceedance roses at Verkykkop in 2004

- Ozone concentrations in summer and autumn correspond to the NW sector where Majuba power station is situated. In autumn, the South and SSE sectors should also be mentioned because the Iscor industry in Newcastle and Volksrust, which  $\pm 5$  km from Verkykkop, are situated in these sectors.
- Winter and spring periods are similar with the highest levels recorded in the NNW sectors where most of the industries are situated, Eskom power stations, Witbank coal-processing and Sasol Secunda fuel synthetic plant.





**Figure 4.22:** Seasonal averaged O<sub>3</sub> 98 percentile exceedance roses at Elandsfontein in 2002

- In summer, highest ozone levels were recorded in the SW and WNW sectors. Secunda plant is situated in the SW of Elandsfontein and contributes to high levels observed in this direction. High concentrations recorded in the WNW are attributed to motor vehicle emissions in Gauteng highways and Kendal power station.
- High concentrations in autumn correspond to all the sectors with the highest levels appearing in the West, where emissions are emitted from motor vehicles in Johannesburg freeways and Kriel and Matla power stations, NNW (Witbank) and SE sectors, respectively.
- Winter exhibits the same pattern as summer, with the exception that in winter, there were no levels recorded in the second quadrant.

- The increase in ozone concentrations in spring was observed in the direction of Witbank coal processing, NNW sector and South sector where Secunda plant is located.

#### 4.7 Exceedances of air quality guideline values

In order to assess the air quality, the measured concentration values of ozone have been analysed and compared with the limit and guideline values specified by the most recent DEAT documents. The Department of Environmental Affairs and Tourism (DEAT) ambient air quality standards Document 39 of 2004 stipulates a one hour average of 120 ppb as current guideline values for the protection of human health. During the period 2000 – 2004, a number of high exceedances of ozone were recorded at both Verkykkop and Elandsfontein.

##### 4.7.1 Diurnal variation roses of ozone

At Verkykkop, the highest ozone exceedance incidents occurred in 2001, 2002 and 2003 for all hours, and the highest records occurred in August 2001 and September/October 2002.

**Table 4.5:** Ozone exceedances at Verkykkop (2000 – 2004)

Year	Month	Day	Hour	Conc.	Conc. Diff.
2002	9	9	16	174	54
2001	8	19	16	169	49
2001	8	29	20	168	48
2001	8	29	14	165	45
2001	8	19	17	164	44
2001	8	19	15	164	44
2002	9	9	17	160	40
2001	8	29	12	159	39
2001	8	19	18	158	38
2002	9	25	23	158	38
2001	8	19	19	155	35



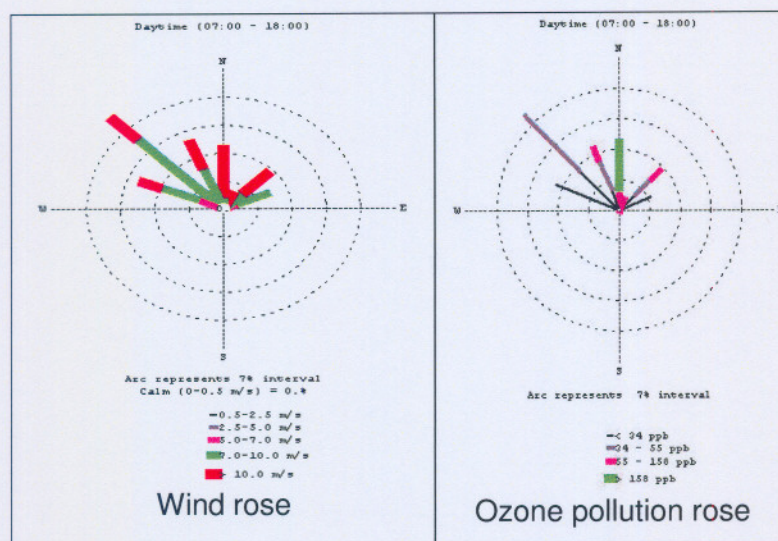
**Table 4.5:** Continued

2001	4	9	1	152	32
2002	9	9	15	152	32
2001	8	29	13	151	31
2002	9	25	22	150	30
2002	10	2	23	149	29
2001	8	29	8	146	26
2001	8	23	20	143	23
2002	10	2	23	143	23
2001	8	19	20	142	22
2001	8	24	6	141	21
2001	8	19	14	141	21
2001	8	31	11	139	19
2001	8	31	12	139	19
2001	8	29	21	137	17
2001	8	24	11	137	17
2001	8	29	7	137	17
2002	10	29	3	136	16
2001	4	9	2	135	15
2002	10	29	4	135	15
2002	10	29	5	135	15
2002	10	29	6	135	15
2002	10	29	2	133	13
2001	8	24	10	131	11
2002	10	3	1	131	11
2001	8	29	22	130	10
2001	8	19	21	130	10
2002	9	9	13	130	10
2002	1	17	22	129	9
2002	10	28	21	128	8
2002	10	29	1	128	8
2002	10	29	7	128	8
2001	8	19	22	127	7
2001	8	24	8	127	7
2002	10	4	19	127	7
2002	9	9	14	127	7
2002	10	28	20	126	6
2002	10	28	23	125	5
2001	8	20	1	124	4
2002	6	13	23	124	4
2002	7	15	23	124	4

**Table 4.5:** Continued

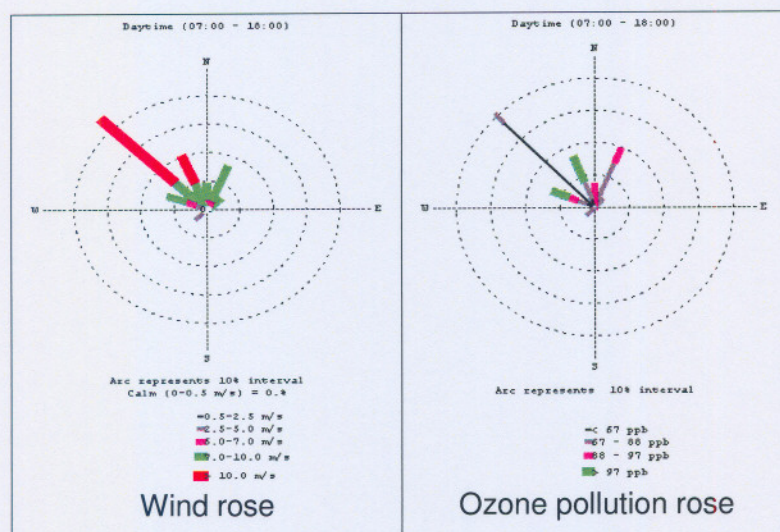
2001	8	19	23	123	3
2002	7	15	23	123	3
2002	10	28	22	123	3
2003	8	19	2	122	2

The highest exceedance of 169 ppb was observed at 16:00 in August 2001 and 174 and 149 ppb at 16:00 and 02:00 in September and October 2002, respectively.



**Figure 4.23:** The exceedance roses on 18 – 20 August 2001





**Figure 4.24:** The exceedance roses on 27 – 31 October 2002

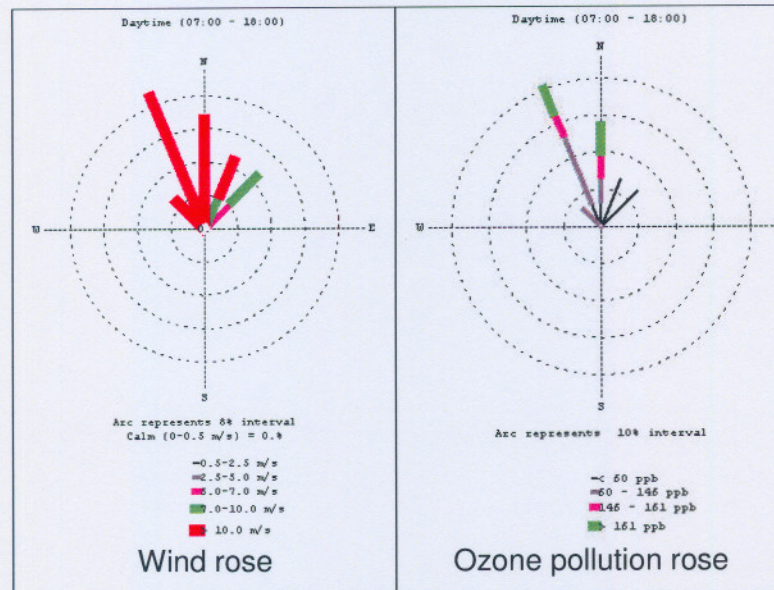
At Elandsfontein the exceedances were recorded in 2002 and 2004 for all hours, but the highest records occur in September 2004 during daytime.

**Table 4.6:** Ozone exceedances at Elandsfontein (2000 – 2004)

Year	Month	Day	Hour	Conc.	Conc. Diff.
2002	7	1	16	154	34
2004	9	25	14	187	67
2004	9	25	13	161	41
2004	7	13	16	150	30
2004	9	25	16	146	26
2004	9	25	17	141	21

The highest values were recorded on 25 September 2004 during daytime hours. The highest concentrations of 187 and 161 ppb were recorded at 14:00 and 13:00, respectively.



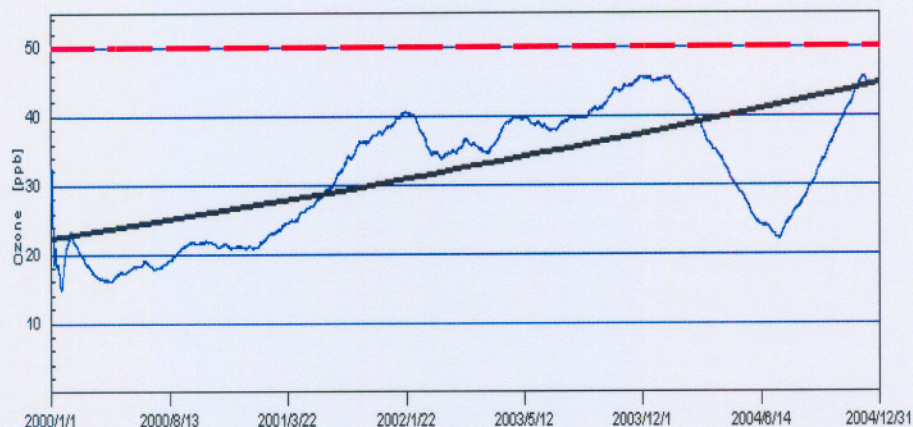


**Figure 4.25:** The exceedance roses on 25 September 2004

#### 4.7.2 Sectoral and temporal trends in ozone concentrations

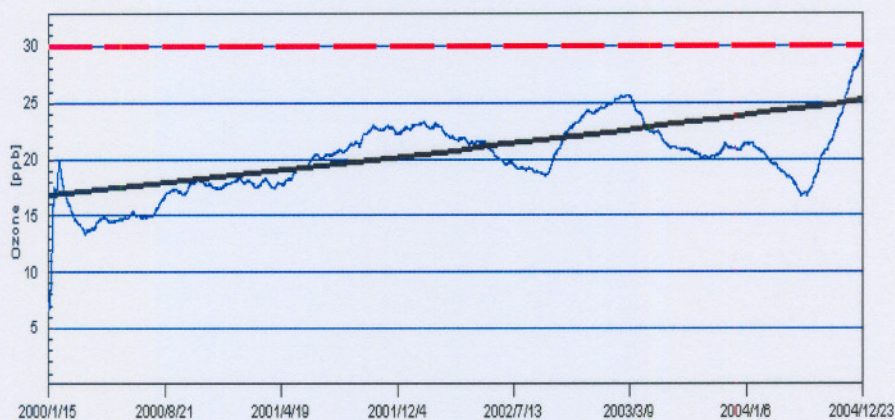
Ambient concentrations are likely to vary temporally in time with human activity patterns, increasing the resulting health effects. The concentrations increase during the day and decline at night. In addition to diurnal variations, ozone concentrations tend to exceed the guideline values mostly during the day than at night. Ozone concentrations also vary seasonally, with highest concentrations recorded in spring. Thus, the maximum peak of ozone corresponds with the season of the year when people tend to be most active outdoors. Also, ozone concentrations can vary from year to year in response to meteorological parameters that promote more or less dispersion of emissions.





**Figure 4.26:** Hourly Verkykkop ozone sectoral and temporal trends

At Verkykkop, the number of exceedances above the guideline value were 2234 out of 15954 hourly values during daytime and the percentage exceedances was 14.0%. The guideline concentration is 50 ppb (dashed line) and the mean and median concentrations are 32.9 and 31.2 ppb, respectively. The period ozone concentration difference was 22.5 ppb and the difference per year was 0.52 ppb



**Figure 4.27:** Hourly Elandsfontein ozone sectoral and temporal trends

At Elandsfontein, the guideline concentration was 30 ppb (dashed line) and the average and median concentrations were 20.9 and 18.9 ppb, respectively. The period ozone concentration difference was 8.39406 ppb and the

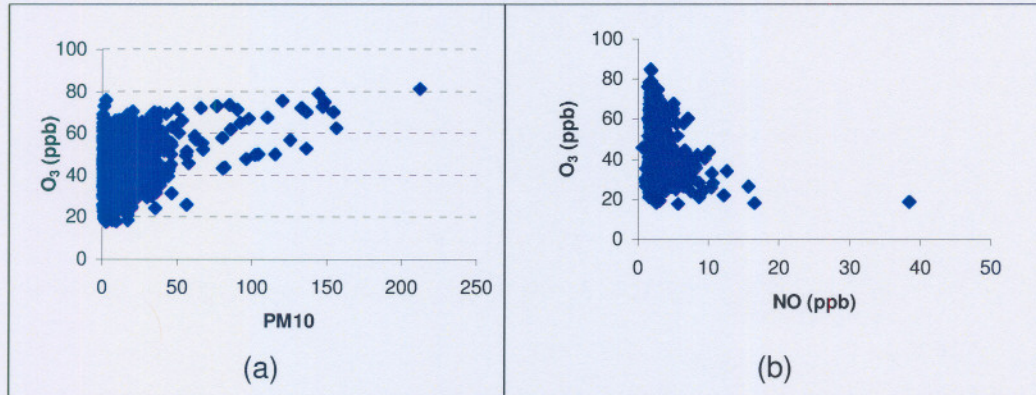


difference per year was 0.17 ppb. The numbers of exceedances recorded above the guideline value were 2988 out of 17942 hourly values and the percentage exceedances above the guideline was 17.0%.

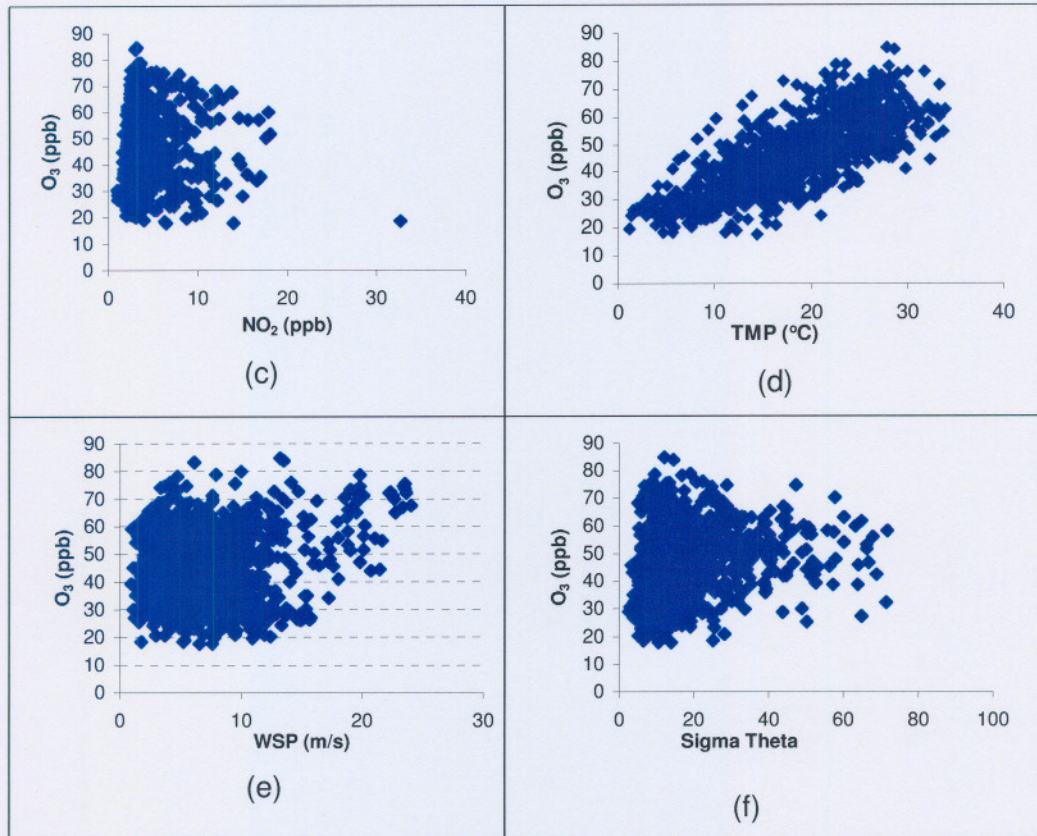
## 4.8 Predictor variables

### 4.8.1 Scatter plots

Scatter plots were created to determine the effect of various variables (meteorological conditions and precursor concentrations) on the response variable (ozone concentrations) [Elkamel *et al* 2001]. Only data collected in spring season were selected for regression evaluation and to create scatter plots since high ozone events had occurred during this season. These plots indicate which variable might have a direct influence on the secondary air pollutant ozone and they also show the nature and strength of the relationship between the response variable and the predictor variables [Elkamel *et al* 2001].



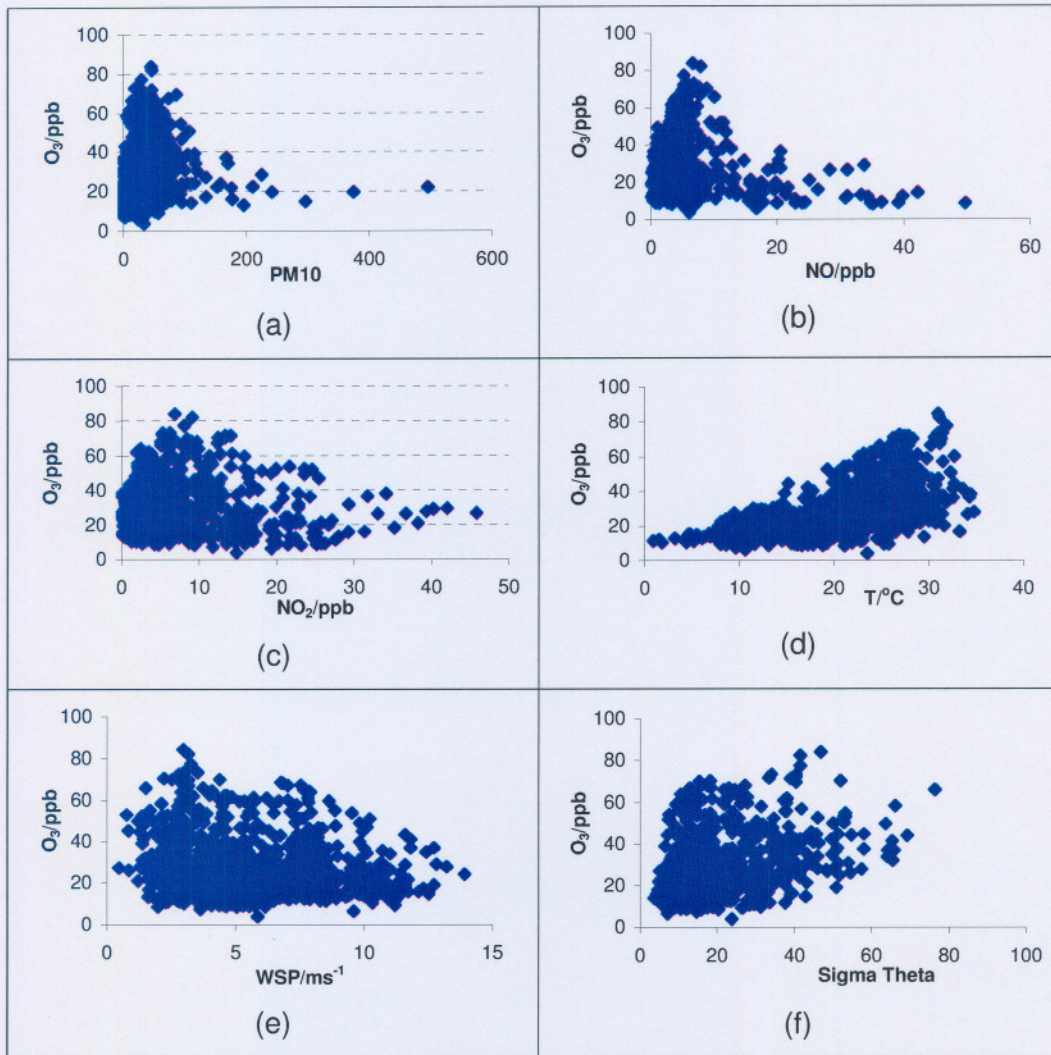




**Figure 4.28:** Scatter plots of O<sub>3</sub> concentrations as a function of various variables at Verkykkop in 2004

Temperature shows a direct relationship with ozone (d). Ozone concentrations increase with increasing temperature and the highest ozone levels were recorded between 27 and 30 °C. NO is inversely proportional to O<sub>3</sub>, which means that when NO concentrations increase, the concentration of ozone decreases. High ozone concentrations were observed at NO concentrations less than 10 ppb (b). Increase in concentration of fine particulate matter (a) and increase in sigma  $\sigma$  (f), increases ozone concentrations. The plots of NO<sub>2</sub> (c) and wind speed (e) do not show a clear relationship with ozone levels.





**Figure 4.29:** Scatter plots of  $O_3$  concentrations as a function of various variables at Elandsfontein in 2002

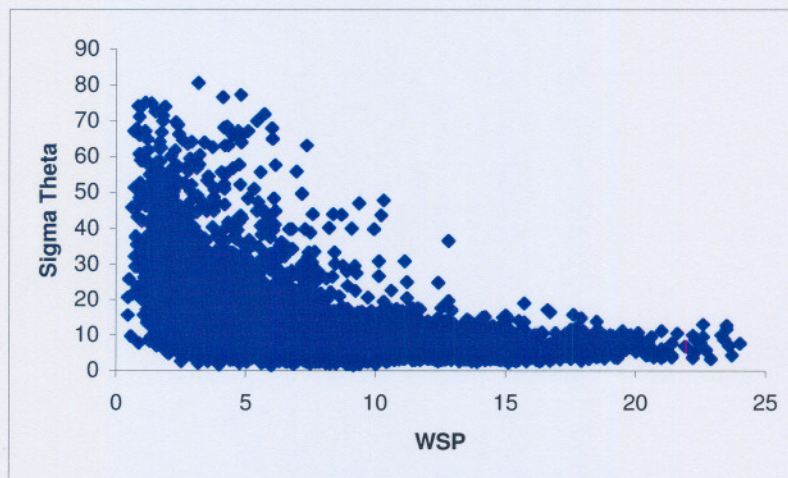
At Elandsfontein, the plot of PM10, NO and  $NO_2$  show an inverse relationship between the precursors and ozone (a, b, c). Ozone concentrations decrease with increasing concentrations of the precursors. High ozone concentrations were observed at low wind speed because low wind speeds allow the accumulation and recirculation of precursors near the source area, while high speed winds impede ozone formation by dispersing the precursors (e), therefore ozone decrease with increasing wind speed. The plots of



temperature (d) and sigma  $\sigma$  (f) show a direct relationship between ozone and the conditions. Ozone increases with increasing temperature and SGT.

#### 4.8.2 Relation between ozone, wind speed and sigma theta

Sigma  $\sigma$  (sigma theta sometimes called variability of wind direction fluctuations) is related to horizontal turbulence and was used to estimate the potential for the atmosphere to spread the plume. The atmospheric stability is dependent on the speed of the wind. At low wind speeds, the turbulence of the plume is strong, which means that the plumes will go up and down frequently, therefore increasing pollution near the surface (e.g. looping plume). At high wind speed, the vibration of the plume is less and the plume will rise above the surface, then there will be less contact of pollution at the surface. Therefore, ozone concentrations increase with decreasing wind speed and increasing sigma  $\sigma$ , and decrease with increasing wind speed and decreasing sigma  $\sigma$  (e, f).



**Figure 4.30:** Plot of sigma theta versus wind speed



### 4.8.3 Linear regression analysis

A simple linear regression analysis on diurnal concentrations of ozone in spring, and available meteorological conditions and O<sub>3</sub> precursors was carried out, to indicate the most important contributors to ozone formation. The R<sup>2</sup> values were used to indicate the order of importance of the variables and the slopes of the equations were used to show whether the variable influences formation or destruction of ozone. The importance of the variables in relation to ozone concentrations was, in order of importance, given in tables 4.7 and 4.8.

**Table 4.7:** Linear regression results for daytime ozone concentrations at Verkykkop

Variable	R <sup>2</sup> -value	Slope
Temperature	0.5568	1.3860
Particulate matter	0.1039	0.1667
Sigma theta	0.0407	0.2240
Nitric oxide	0.0274	-1.1492
Wind speed	0.0150	0.3841
Nitrogen dioxide	0.0028	0.2491

At Verkykkop, temperature and PM10 played significant role in enhancing the formation of ozone. The positive slope of wind speed gives an indication of ozone precursor dispersion from source areas. Nitric oxide contributed to the formation of ozone but the negative slope indicates that ozone concentrations decrease with further increase in NO concentrations. This might suggest that NO was not emitted by nearby sources, but carried by wind from distant sources.

**Table 4.8:** Linear regression results for daytime ozone concentrations at Elandsfontein

Variable	R <sup>2</sup> -value	Slope
Temperature	0.3588	1.2735
Sigma theta	0.1522	0.4681
Wind speed	0.0442	-1.1622
Particulate matter	0.0325	0.0730
Nitrogen dioxide	0.0034	0.1217
Nitric oxide	0.0004	-0.0507

Temperature also played important role at Elandsfontein. The R<sup>2</sup> value of wind speed might suggest the recirculation of the formed ozone but the negative slope indicates that ozone concentrations decreased with increase in wind speed. Nitrogen dioxide and nitric oxide contributed least to the formation of ozone. Their concentrations near the monitoring site were so high that they hinder ozone formation either by NO titration of O<sub>3</sub> or by the reaction of NO<sub>2</sub> and OH radicals to form nitric acid, which is a sink for the radicals. This indicates that Elandsfontein is located near emission source areas, which contribute to high concentrations of these precursors. The negative slope of NO shows that, high levels of NO decrease the formation of ozone near the sources.



## CHAPTER 5

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*In this chapter...*

*The results and discussions of VOC's sampled during Elandsfontein field campaign are given. The principal sub-classes of VOCs that were detected in the samples at different altitudes are given in section 5.1. Section 5.2 gives the discussions of vertical profiles of VOC's and the quantification of sample VOC's that were present in the calibration standard. The diurnal variations of some of the VOC's are discussed in section 5.3 and the identification of sample VOC's not found in the standard, using NIST library, are given in section 5.4.*

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### RESULTS OF ELANDSFONTEIN FIELD CAMPAIGN

#### 5.1 Sub-classes of volatile organic compounds

A total of 14 samples were collected during the study period and about seventy species were identified. Volatile organic compounds were detected on each level and the principal VOC subclasses identified were aromatics, alkanes and alkenes, organohalogens and oxygenates. Some of the VOC detected are listed in Table 5.1.

**Table 5.1:** VOC subclasses that were detected at Elandsfontein at different altitudes

VOC subclasses	Compound
Volatile aromatics	Benzene, toluene, ethylbenzene, propylbenzene, 1,4-dimethylbenzene. Naphthalene, <i>m,o,p</i> -xylene, 1-ethyl-3,5-dimethylbenzene, 4-ethyl-1,2-dimethylbenzene, 1,2,4- 1,3,5-trimethylbenzene,

	1,2,3,4- diethylbenzene, 1,2,3,5-tetramethylbenzene, 1,4-
Volatile alkanes and alkenes	Butane, heptane, 1-pentene, diisopropyl, 3-ethyloctane, cyclohexane, hexane, 4-methyloctane, hexane, decane, octane, 2,3,4-trimethylpentane, hexamethylethane, 2,4-dimethylheptane, 2,2-dimethylhexane, 2,4-dimethyl-1-heptene, 2-methyl-1-heptene, 2-methyl-1,3-butadiene, 2,2-trimethylpentane
Volatile organohalogens	Chloroform, trichloroethylene, 1-chloro-3-methylbutane, 1,2-dichlorobenzene, 1-chloro-3-methylbutane, 1-chloropentane, 1-chloro-2-fluoroethene, methylene chloride
Miscellaneous VOC	4-methyl-5-hexen-2-ol, benzaldehyde, acetic acid, 2-methylpentanal, acetone, benzoic acid, butanoic acid, formic acid, dibenzofuran, methanamine, indene, azulene, pentanal

## 5.2 Vertical profiles of volatile organic compounds

The knowledge about vertical distribution of air pollutants is very important for the assessment of an air quality situation, which is not only influenced by the amount of emissions but also by the atmospheric conditions for transport and dilution. VOC sampling was done at different altitudes (5825, 6650, 8300 and 12300 ft) at different times of the day on the 30<sup>th</sup> and 31<sup>st</sup> August 2005. The VOC's that were detected at different altitudes were given in tables 5.2 and 5.3. The VOC's were identified using the Supelco as well as the MS NIST library database.

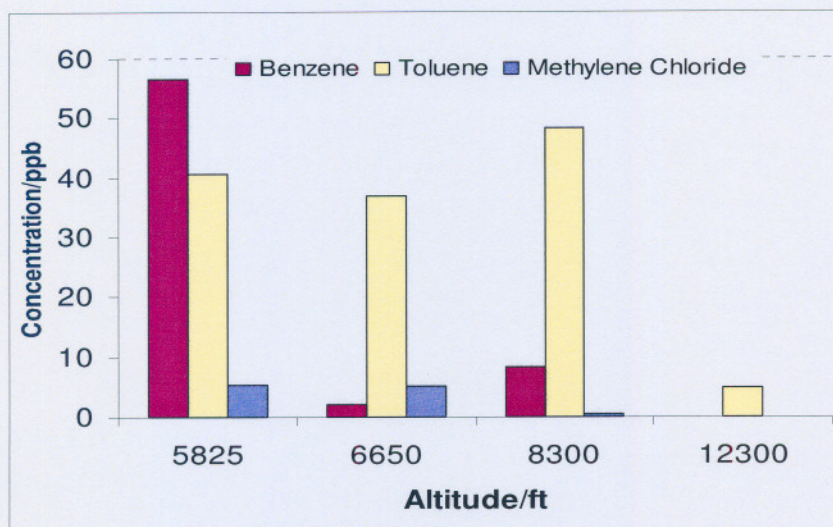


**Table 5.2:** Concentrations of VOC's sampled at different altitudes above the ground on the 30<sup>th</sup> August 2004

Altitude ASL (ft)	5825	6650			8300		12 300
Time	AM	AM	NOON	PM	AM	NOON	AM
Compound							
Methylene chloride	–	5.3	14.1	15.7	5.1	16.5	0.5
Chloroform	–	–	–	–	0.7	–	0.8
Benzene	56.5	2.0	7.1	30.2	8.2	6.0	–
Carbon Tetrachloride	26.6	–	–	–	–	–	–
Cis-1,3-Dichloropropene	1.4	–	–	–	–	–	–
Toluene	40.6	37.6	47.9	74.4	48.3	61.5	4.9
Tetrachloroethylene	0.7	–	–	–	–	–	–
<i>p</i> -Xylene	0.1	–	–	14.2	–	–	–
<i>m</i> -Xylene	0.1	–	–	1.6	–	–	–
Styrene	0.22	–	–	–	–	–	–
<i>o</i> -Xylene	–	–	–	3.4	–	–	–
1,3,5-Trimethylbenzene	0.45	–	–	8.7	–	–	–
1,2,4-Trimethyl Benzene	0.84	–	–	6.2	–	–	–
1,3-Dichlorobenzene	–	–	–	0.2	–	–	–
1,4-Dichlorobenzene	–	–	–	0.2	–	–	–
1,2-Dichlorobenzene	0.13	–	–	0.2	–	–	–

(\*– detected, Concentrations of VOC's that were detected are given in ppb)

In all the measurements, toluene and benzene were the most dominant species that were detected. Toluene was in the range of 4.7 – 74.4 ppb with average concentration of 45.3 ppb and benzene in the range of 2.0 – 56.5 ppb. Most VOC's were detected at 5825 and 6650 ft and the only VOC's that were detected at 12 300 ft were methylene chloride, chloroform and toluene. Benzene, carbon tetrachloride and toluene had the highest concentrations at the lowest altitude of 5825 ft.



**Figure 5.1:** Vertical profiles of benzene, toluene and methylene chloride

Concentration of methylene chloride decreases with increasing level, while those of benzene and toluene fluctuate with increasing levels. Concentrations of benzene and toluene are high at 5825 ft, decrease at 6650 ft, increase at 8300 ft and decrease again to the lowest concentrations at 12300 ft. The following VOC's were only detected at 5825 ft in the morning and at 6650 ft in the late afternoon: tetrachloroethylene, *o*-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3-dichlorobenzene, 1,2-dichlorobenzene and 1,4 dichlorobenzene.

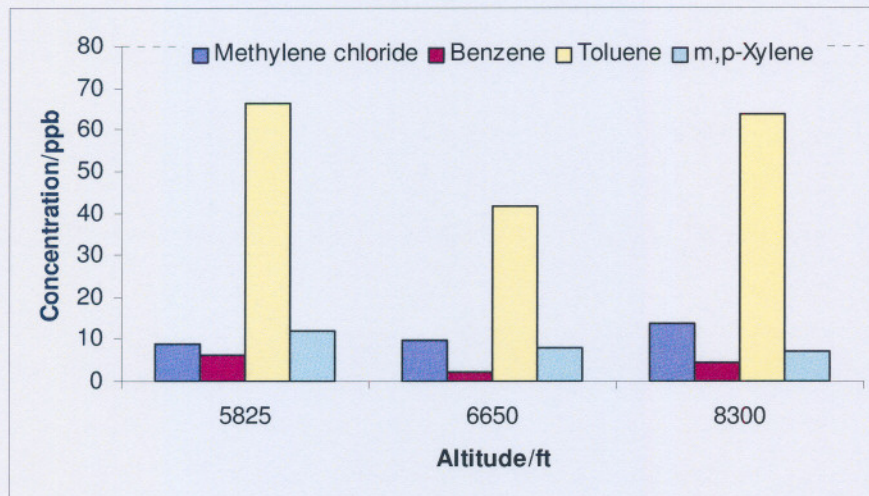
**Table 5.3:** Concentrations in ppb of VOC's sampled at different altitudes above the ground on the 31 August 2004

Altitude ASL (ft)	5825	6650			8300	
	AM	AM	NOON	PM	AM	NOON
Compound						
Methylene chloride	8.7	9.8	2.5	10.7	13.6	13.4
Chloroform	–	–	35.9	–	–	–
Benzene	6.4	2.4	9.4	19.9	4.4	2.1
Trichloroethylene	–	–	20.3	–	–	–
Toluene	66.5	41.4	22.2	38.3	63.6	47.1
Ethylbenzene	5.6	–	8.3	3.2	–	–



<i>p</i> -Xylene	12.0	8.1	13.8	7.9	7.1	10.8
<i>m</i> -Xylene	12.0	8.1	13.8	7.9	7.1	10.8
Styrene	–	–	0.0	–	–	–
<i>o</i> -Xylene	–	1.8	0.0	–	–	1.5
1,3,5-Trimethylbenzene	–	–	4.9	–	3.64	2.4
1,2,4-Trimethyl Benzene	–	3.2	1.7	–	3.73	2.4

Most of the VOC's that were detected on the second day were found on level 6650 ft. The most abundant VOC's were benzene, toluene, methylene chloride and *p,m*-xylenes. Toluene was found to be the most abundant VOC pollutant compared to the other four species. The average toluene concentration was 46.5 ppb and the maximum was 66.5 ppb.



**Figure 5. 2:** Vertical profiles of VOC's that were detected at all levels in the morning

Concentration of methylene chloride increases with increasing altitude while *m*- and *p*- xylenes decrease with increasing altitude. Concentrations of benzene and toluene fluctuate with increasing altitude. Concentration of toluene was found to be the highest in the lowest level, ranging from 66.5 ppb at 5825 ft to 34.3 ppb at 8300 ft above sea level. The highest concentration of benzene of 6.4 ppb was recorded at 5825 ft above sea level.



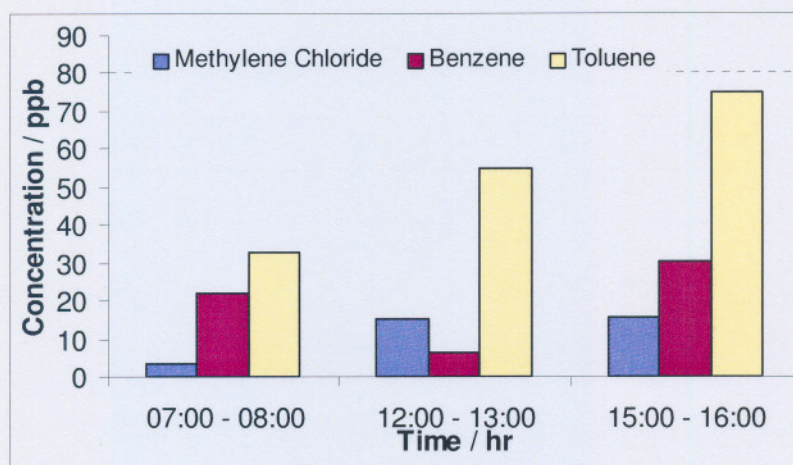
### 5.3 Diurnal variations of volatile organic compounds

To observe the diurnal variations of VOC concentrations, without considering the altitude, the three 1-hr averaged concentrations were measured in the morning (07H00 – 08H00), afternoon (12H00 – 13H00) and late afternoon (15H00 – 16H00).

**Table 5.4:** The average concentrations (ppb) of the most abundant VOC measured during the campaign

Date	30 <sup>th</sup> Aug			31 <sup>st</sup> Aug		
Compound	AM	NOON	PM	AM	NOON	PM
Methylene Chloride	3.63	15.3	15.7	10.7	12.05	10.7
Benzene	22.23	6.55	30.2	4.4	7.95	10.7
Toluene	32.85	54.7	74.4	57.17	32.65	38.3
m, p - Xylene	0.1		14.1	10.3	10.45	7.9

The diurnal variations of abundant VOC concentrations detected during the field study are shown in Figures 5.3 and 5.5.

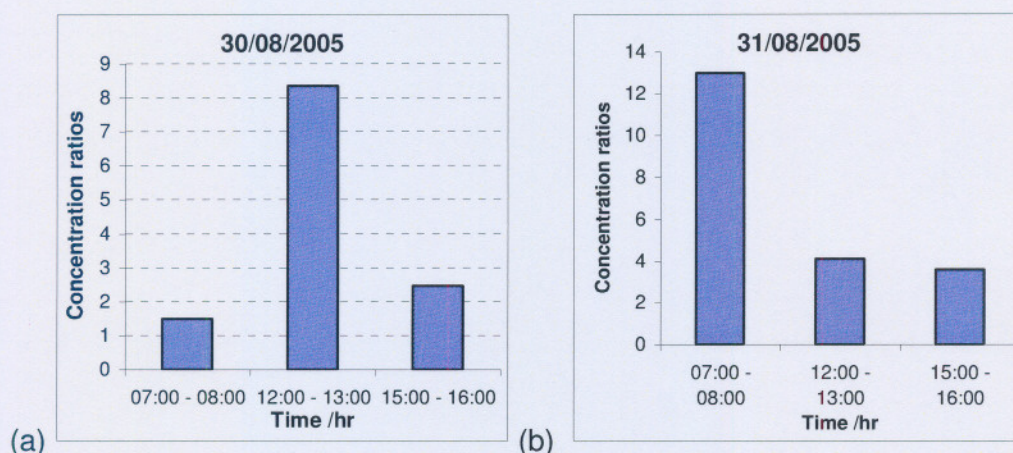


**Figure 5.3:** Diurnal variations of abundant VOCs detected on the 30<sup>th</sup> August 2004.



The benzene concentrations show diurnal variations with high concentrations in the morning and late afternoon, and low concentrations at noon. High concentrations might be explained by higher emissions from the traffic during the morning and the late afternoon rush hours. Low concentrations at noon can be attributed to the dilution effects by an increase of mixing depth during noontime and photochemical destruction due to increased solar radiation.

The concentrations of toluene increased with increasing time of the day, with higher concentrations in the afternoon than in the morning. The reason for this might be that toluene is emitted not only from vehicle exhaust and gasoline, like benzene, but is also emitted from solvent usage in many industries [Na *et al* 2003], waste dumping sites and emissions from incinerators burning hazardous wastes [Leach *et al* 1999]. Diurnal variations of the concentration ratios of toluene to benzene (Figure 5.4) were used to explain the effect of solvent evaporation on ambient VOC concentrations, since toluene is the most dominant species in solvent usage [Na *et al* 2004].

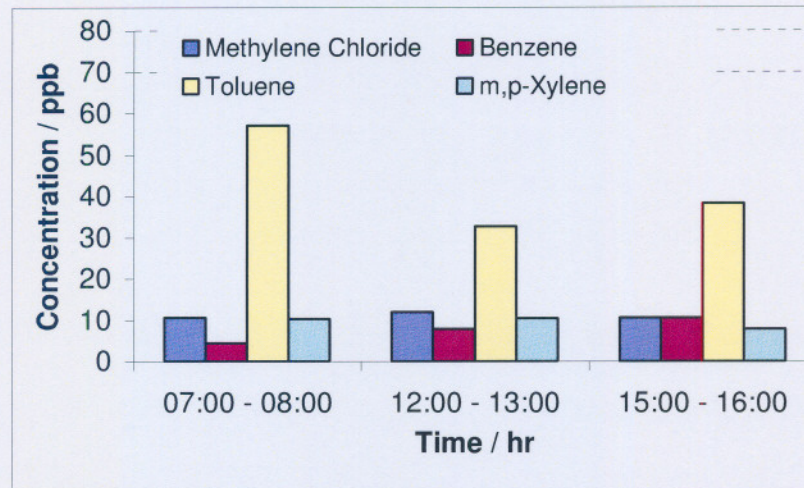


**Figure 5.4:** Diurnal variations of toluene/benzene concentration ratios

An increase in the ratios from morning to afternoon suggests that the contribution of evaporative emissions, by solvent usage and burning waste, to the ambient VOC concentrations increases with the day [Na *et al* 2003]. This might be explained that the increase in the evaporation emissions is



dependent on elevated temperature, and that activities related to solvent usage, waste dumping and incineration occur mostly during normal daily working hours, leading to higher concentrations observed in the afternoons. A decrease in the concentration ratios from the morning to the afternoon might reflect photochemical destruction of toluene due to photo-oxidation by hydroxyl radicals, which lead to the formation of photochemical ozone.



**Figure 5.5:** Diurnal variations of abundant VOCs detected on the 31<sup>st</sup> August 2004.

The average concentrations of the VOC's measured on the second day of the campaign were lower than those measured on the first day and concentrations of toluene decrease with the time of the day. The reason might be that the average wind speed was higher at 7 – 10 m/s (see Figure 3.2), thus causing stronger dilution and ventilation of the VOC's emitted.

Burger 2006 has also reported that toluene had higher concentrations and the most abundant VOC in the samples from higher altitudes than the ground samples sampled in Vaal Triangle during August 2004. She also reported that lower concentrations of VOC's were observed on other days and might be due to the wind diluting pollutants at the time of sampling.

## 5.4 Identification of volatile organic compounds not quantified

A large number of volatile organic compounds not included in the calibration standard were observed in the samples and since no standards were available, these compounds could not be quantified, therefore, the abundance in arbitrary units of the VOC's were used and shown in the table below.

**Table 5. 6:** Compounds sampled at different altitudes during the campaign that could not be quantified (Abundance in arbitrary units)

Time	VOC	5825 ft	6500 ft	8300 ft	12 300 ft
3:03	Nitrous oxide	–	41300	49660	36363
3:34	Propane	33323	30327	24485	–
4:08	1-Chloro-1-fluoroethene	–	4860		8311
4:18	1-Chloro-2-fluoroethene	–	–	8588	3035
4:29	Butanone	–	–	–	3524
4:39	Formic acid	19847	7234	8669	11812
5:05	Cyclobutane	–	–	–	8075
5:41	Butane	–	9211	8564	–
7:02	Methanamine	49958	60107	–	–
8:01	2-Butanone	–	–	–	4254
8:15	2-Methylpentanal	–	–	88764	–
8:21	Acetaldehyde	9581	3848	–	–
8:25	Acetone	–	29917	22510	12042
8:40	1-Pentene	–	69463	48332	34768
9:05	4-Methyl-5-hexen-2-ol	–	51289	–	–
9:10	Pentane	–	9028	8310	7833
9:14	Isopentane	–	19233	8433	–
9:22	1,2-Diethylethane	–	–	19984	–
9:44	Ether	–	28533	21467	16929
10:06	2-Methylbutane	33613	14170	–	–
10:49	Isopentyl alcohol	–	35056	–	–
10:31	1-Chloropentane	72487	40653	–	–
10:39	2,2-Dimethylbutane	–	–	–	8497



**Table 5.6: (Continued)**

10:54	2-Methyl-1-propanol	41043	–	–	–
12:01	Diisopropyl	–	28631	–	–
12:19	2,3-Dimethylbutane	28408	19408	17611	–
12:20	2-Methylpentane	–	14170	11084	10199
12:53	3-Methylpentane	–	10659	58459	8205
12:55	2,3-Dimethylpentane	68902	81488	126409	–
12:59	2-Bromopentane	–	–	–	31436
13:07	Heptanal	134642	80443	70494	40470
13:33	Hexane	221554	210503	145527	68123
13:41	3-Methylhexane	136202	104133	–	–
14:32	1-Hexene	107746	106383	84776	31929
14:40	2,4-dimethylpentane	–	–	20291	10199
15:07	2-Methyl-1-pentene	–	45230	10648	–
15:47	Cyclohexane	69648	59196	26891	9037
16:27	Pentanal	–	3596	–	–
16:50	Hexamethylethane	–	–	8270	–
16:53	2,2-Dimethylhexane	–	19835	27371	18332
16:55	2,2,3-Trimethylpentane	–	14433	–	5762
17:18	Heptane	38831	16951	15072	14037
18:44	2,4-Dimethylhexane	26545	–	–	–
18:48	Acetic acid	–	91283	–	–
19:05	2,3,4-Trimethylpentane	26789	9324	–	–
20:47	2,4-Dimethylheptane	46636	36637	28491	–
20:48	Octane	–	23999	11073	3007
20:51	4-Methyloctane	–	–	24834	–
21:31	Hexamethylcyclsiloxane	19202	–	–	–
22:06	2,4-Dimethyl-1-heptene	–	5481	–	–
22:07	1-Chloro-3-methylbutane	–	4305	–	–
23:20	Benzene ethanamine	–	5017	–	–
23:51	n-Nonane	–	7381	–	–
25:05	Benzaldehyde	11882	9181	–	–
25:22	Propylbenzene	–	120	–	–
26:46	Decane	30891	21688	17176	14783
27:43	Indene	–	2130	–	–
28:03	m-Propyltoluene	–	6186	–	–

**Table 5.6: (Continued)**

28:08	1,2,3,4-Tetramethylbenzene	–	11371	–	–
28:08	1,2,3,5-Tetramethylbenzene	–	11371	–	–
28:12	1,4-Diethylbenzene	–	8251	–	–
28:31	<i>p</i> -Propyltoluene	–	3485	–	–
28:45	2-Ethyl-1,4-dimethylbenzene	–	7358	–	–
28:46	4-Ethyl-1,2-dimethylbenzene	–	8543	–	–
29:00	1-Ethyl-3,5-dimethylbenzene	–	7298	–	–
29:07	Nonanal	19162	18809	13390	12830
30:27	Benzoic acid	–	11214	–	–
31:37	Azulene	78562	59214	28645	16685
31:41	Naphthalene	78562	146144	78069	114544
34:22	Butanoic acid	32755	42964	34718	–
34:48	Isobenzofuranone	–	9345	–	–
36:01	Tetradecane	–	8513	12935	–
37:11	Acenaphthalene	–	899	–	–
37:46	3-Ethyldecane	31707	32992	24324	–
38:17	Dibenzofuran	–	12066	–	–
38:48	4-Methyldecane	–	8013	–	–
39:16	2-Acetylbenzoic acid	–	17929	–	–
41:04	Benzoate	–	11718	–	–

(\*Samples were taken on the 30<sup>th</sup> and 31<sup>st</sup> August 2004 for a period of 20 min between 07:30 – 17:00 at a constant flow rate of 180 ml/min)

(\*\* – Not detected)

Most of the VOC's were detected at an altitude of 6650 ft above sea level. Alkanes were the abundant species detected in the samples and they show a decrease with increasing altitude. They are abundant VOC's in the atmosphere but not important contributors in the production of ozone, since their reactivity towards hydroxyl radicals is so slow (see Table 2.3). Na et al 2003 has also shown that alkanes rank low on the OH-reactivity-based scale but high in the rankings of concentrations based on carbon. Alkenes and benzene-substituted compounds are not so abundant in the atmosphere and the reason might be that they are highly reactive towards hydroxyl radicals. This can indicate that they are capable of high ozone production.



## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

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*In this chapter...*

*The summary of the research findings is presented, as well as the critical evaluations of the project and further recommendations for future research based on experience acquired during the study.*

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#### 6.1 Final remarks

It was observed that during the day, the concentrations of ozone were much higher than at night time. The concentrations would build up rapidly from the early hours (10:00) of the day, peak in the afternoon around 15:00 and then drop just steadily to lower values in the evening. Higher ozone concentrations were observed at Verkykkop, which is downwind the industrial area, than at Elandsfontein. The differences in ozone concentrations at these sites are due to differences in the concentrations of precursor gases, chemical processes and meteorological parameters. The observed ozone concentrations at Verkykkop may be due to elevation and the transport of photochemically formed ozone and its precursors. These precursors are mainly the emissions from north western and north of northwestern directions.

Higher NO<sub>x</sub> concentrations were observed at Elandsfontein, which is located near the industrial area. The concentrations are influenced by emissions from power stations, light industries, synthetic fuel plant, refineries, motor traffic and domestic activities. Low ozone concentrations at Elandsfontein are mainly due to high concentrations of NO<sub>x</sub> emissions, since high NO and NO<sub>2</sub> concentrations near the site hinder ozone formation either by NO titration of O<sub>3</sub> or reaction of NO<sub>2</sub> and OH radicals.

Nitrogen dioxide concentrations peak in the morning and in the late afternoon at Verkykkop and there is no conclusive explanation for these peaks. This could have been explained by traffic emissions during morning and late afternoon traffic rush hours, but the traffic density close to this site is rather low. Even though  $\text{NO}_x$  concentrations are generally lower at Verkykkop than at Elandsfontein, they are capable to generate higher ozone concentrations. This indicates varying degree of interactions among emissions, deposition, chemical transformation and transport at these sites.

Verkykkop is  $\text{NO}_x$  – sensitive because ozone concentrations were high while  $\text{NO}_x$  concentrations were low and Elandsfontein is VOC – sensitive because low ozone concentrations were observed with high  $\text{NO}_x$  concentrations.

The monthly ozone concentrations were at their maximum values in spring, while those recorded in summer and autumn showed their lowest levels at both sites. The appearance of a spring maximum in surface ozone remains a fascinating dilemma but from the results presented and the review of available literature, the following conclusions can be reached:

- The ozone spring maximum in the southern Africa is mainly attributed to biomass burning, which takes place during the dry season of the year.
- Intense solar radiation in spring causes photochemical reactions of ozone precursors that were accumulated during winter and thus contributing to the spring maximum observed.
- The long lifetime of ozone in winter allows anthropogenically formed ozone to accumulate in the inversion layer and then contributes to high  $\text{O}_3$  concentrations in spring by vertical mixing due to convective heating.
- High ozone levels might also correspond to nitrogen from soil wetting due to the beginning of summer rains and associated spring growth in vegetation, which emits lot of BVOC's.
- Most ozone exceedance incidents were recorded mainly in spring season.



Low ozone concentrations observed in summer than in winter can be attributed to by the following factors:

- Reduced availability of sunshine because of cloudy skies that reflects back the solar radiation from reaching the surface.
- Washouts of air pollutants from the atmosphere by rainfalls that take place during this season.

The seasonal trends of data indicated that levels of air pollutants are generally higher during winter months since the climate conditions in winter do not favour the removal and dispersion of pollutants. The lower temperatures create a need for burning of biomass or coal, especially in rural areas, and the combustion of such organic materials emits large quantities of air pollutants, which lead to ozone formation.

Correlation of ozone concentrations with meteorological parameters showed that there is a direct relationship between ozone and ambient temperature because ozone concentration peaks at an hour where temperature has reached its maximum. The effect of solar intensity was not well observed because the UV radiation data were not captured in full, with nothing captured at Verkykkop. Wind and ozone pollution roses at both sites showed a direct relation between ozone concentrations and wind direction and speed. At Verkykkop, wind was dominant in the 2<sup>nd</sup> and 4<sup>th</sup> quadrants, mostly NW and NNW sectors and South and SE sectors throughout the period (2000 – 2004). The 98 percentile exceedance roses indicated that air pollution at Verkykkop is mainly due to the transport of pollutants mostly from source areas in the NW and NNW directions. Air pollution at Elandsfontein is influenced by all the source areas in almost all the sectors as indicated by the wind, ozone pollution and 98 percentile exceedance roses.

The DEAT guideline value of a 1-hr average of 120 ppb was used in this research. Ozone concentrations tend to exceed the guideline values mostly during the day compared to the night but at Verkykkop, high – ozone incidents occurred many times (33) in the early morning hours and evening than during the day (21), out of the total of 54 recorded in 2001, 2002 and

2003, and a conclusive explanation for this could not be found. Kuttler *et al* 1999 has observed a second ozone peak during the night at 2 a.m. and concluded that it cannot be caused by chemical reactions since the photochemically formed atomic oxygen is not available due to lack of solar radiation at that time. He said this might be due to meteorological reasons like the vertical transport of ozone from residual layer at higher altitudes to the surface due to interruption of temperature inversion (breakdown of stability). At Elandsfontein, ozone exceedances occurred only during the day, between 13:00 and 17:00.

Linear regression analysis indicated that meteorological conditions contributed significantly to high ozone concentrations than ozone precursors at Verkykkop. I think this analysis method was not the best method to use since the relationship between ozone and its precursors is complicated by the fact that meteorological and chemical processes can also interact. This multicollinearity between the independent variables can make it difficult to correctly identify the most important contributor.

A broad range of anthropogenical VOCs were identified in samples taken at Elandsfontein (n = 14 samples) and more than 70 individual VOCs were identified in the samples. In terms of relative abundance, volatile compounds sub-classes were identified in succession of alkanes/alkenes, aromatics, organohalogens and miscellaneous. Alkanes identified might have resulted from the use of natural gas and vehicle exhaust gas.

The diurnal variation of the VOC's showed high concentrations in the morning than in the afternoon. The highest VOC concentrations during the morning hours reflected high emission into a still stable surface layer. On average, toluene was found to be the most abundant VOC species in the ambient air. Measurements of toluene increasing from morning to the afternoon are confirmed by the results obtained in earlier studies [Na *et al* 2003, Wohrnschimmel *et al* 2006]. High amounts of toluene were found throughout the day, for which solvent usage and waste disposal might be the principal



cause. Higher concentration ratios of toluene to benzene observed in the afternoon than in the morning might suggest that the contribution of solvent, waste disposal and incineration emission of toluene is higher than that of loss by photochemical activity during daytime, even though toluene is destroyed faster (1.2 days) by oxidation (reaction with OH radicals) than benzene (5.7 days) [Fowler *et al* 1997].

## 6.2 Recommendations

Data should be continually collected at background stations and a number of monitoring stations should be increased, which would greatly assist in filling in some of the current gaps between air quality standards and background levels. It is very vital to have a good understanding of the anthropogenic emission enhancement to the background levels, which can then be used as a target for future emission controls. In estimating health effects, both ozone and all its precursor concentrations including hydrocarbon species, should be investigated in future studies as this could help in assessing the co-impacts of emission reductions on health risks to population caused by high concentrations above guidelines, to facilitate effective further control strategy development.

Long-term monitoring of VOC's should also be considered as this will help in identifying whether the region is VOC- or NO<sub>x</sub>-sensitive and helps in reducing emissions of precursors that enhance ozone formation in a specific region.

This research should also be directed towards elaborating on the effect of other meteorological data such as rainfall, humidity and perhaps the inversion layer, since it is indicated that the inversion layer played a role in the increase of ozone and its precursor concentrations. Transport is also one of the most difficult aspects of the ozone phenomena to evaluate. It will eventually be necessary to distinguish among the specific sources of ozone formed from local precursor emissions, ozone formed from precursors transported from

upwind sources and ozone formed during transport from upwind sources.

Thus, some of the outstanding issues such as:

- the role of long-range transport of ozone versus photochemical production in determining the seasonal variation of the observed ozone, and
- the role of photochemistry in the production of high ozone concentrations in winter than in summer, even though the solar radiation is more intense in summer than in winter,

should be investigated.

Advanced analysis methods should be used in this research to determine the order of importance of each variable towards the enhancement of ozone formation, as this would help in emission control. The use of multivariate data analysis (MDA) techniques such as principle component analysis (PCA) and artificial neural network (ANN) is highly recommended in previous studies.

VOC models such as OH-reactivity-based and carbon-based should be used to show the ranking of each VOC in terms of its reactivity and abundance in the atmosphere. This will help us to know which VOC's are photochemical ozone creation potentials so that their emissions should be reduced.

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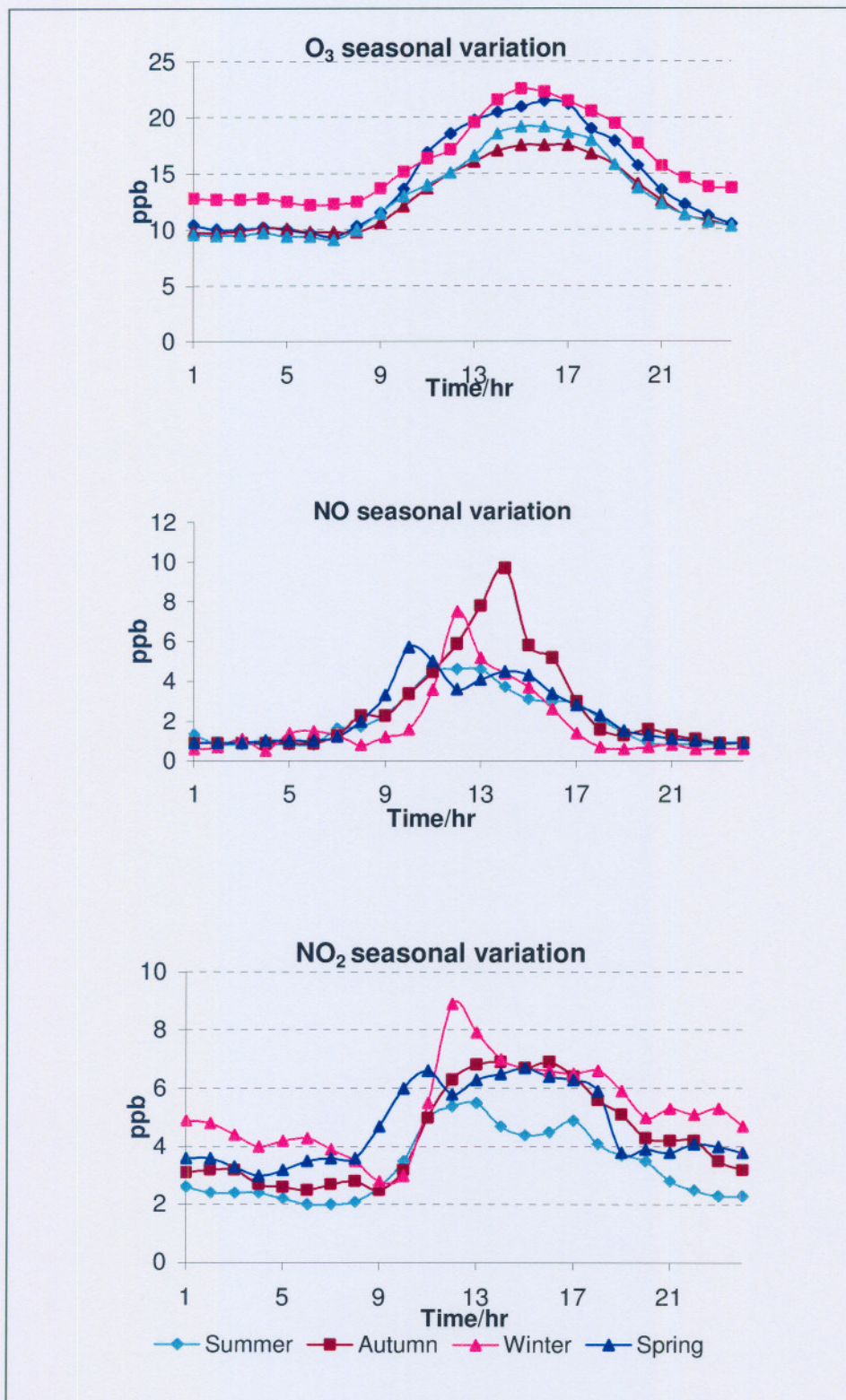
# APPENDIX

## Supplementary data

### Section I: Elandsfontein

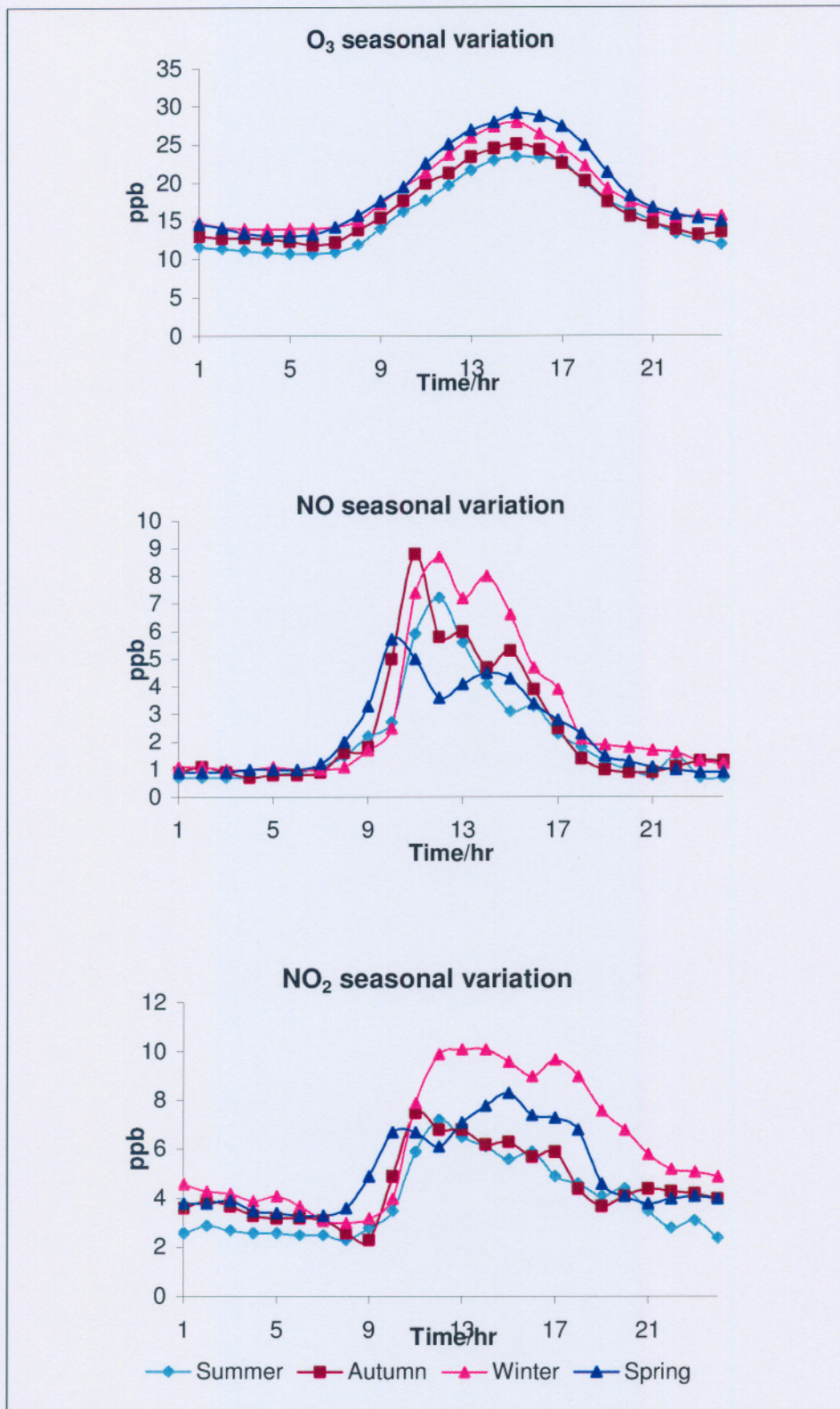
**Table A1:** Percentage data captured at Elandsfontein

Year	PM <sub>10</sub>	NO	NO <sub>2</sub>	O <sub>3</sub>	UV	TMP	WDR	WSP	Reliability
2000	40.7	94.3	94.3	94.6	97.3	97.3	97.3	97.3	89.1
2001	43.9	97	97	91.6	37.6	100	100	100	83.4
2002	87.1	96.8	96.8	96.4	0	99.8	99.9	99.9	96.7
2003	67.9	42.6	42.6	79.7	0	80.6	79.1	79.1	67.4
2004	87.1	84.5	78.8	62.3	87.4	98.6	98.6	98.6	87



**Figure A1:** Seasonal variation of air pollutants (1999-2000)





**Figure A2:** Seasonal variation of air pollutants (2000-2001)



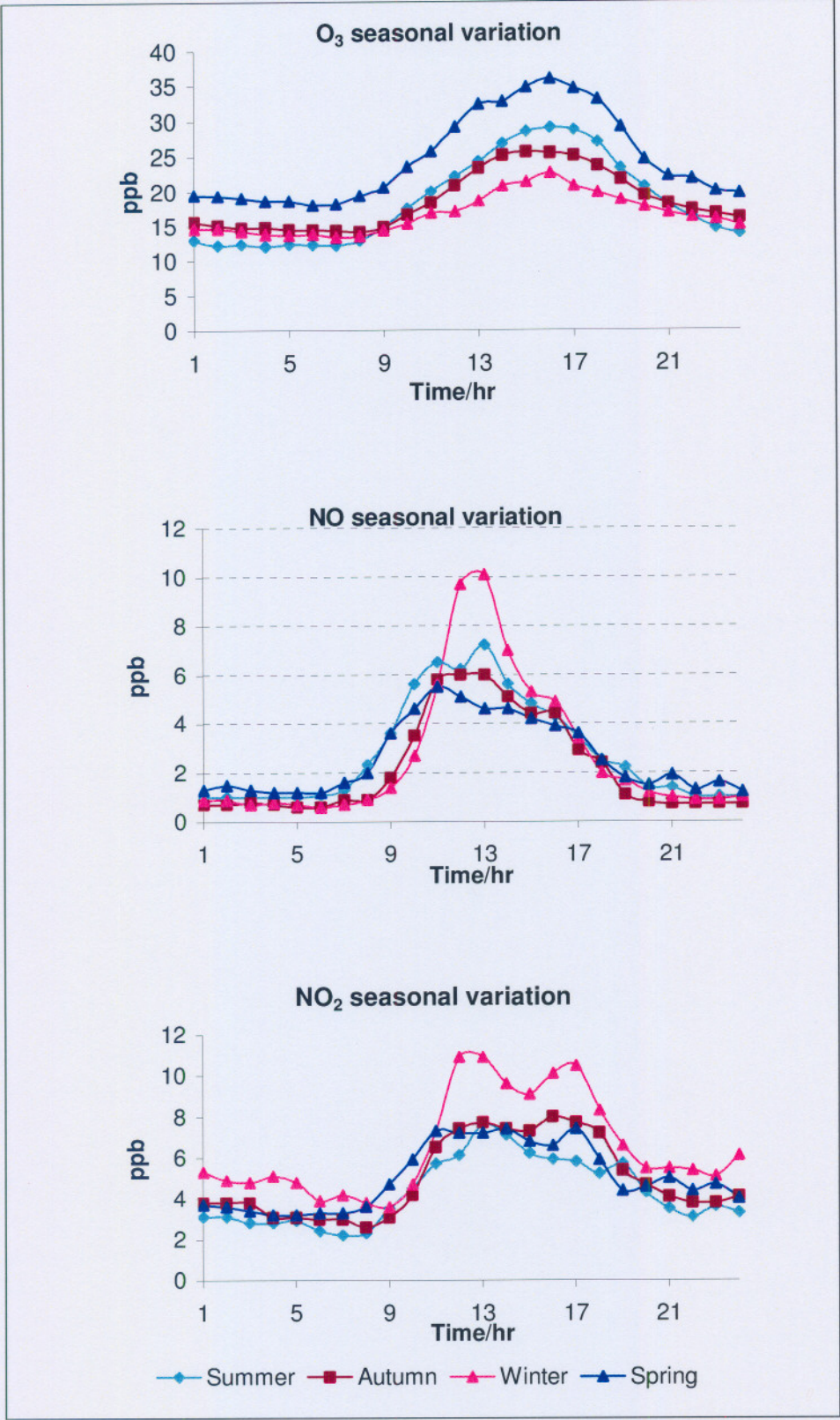
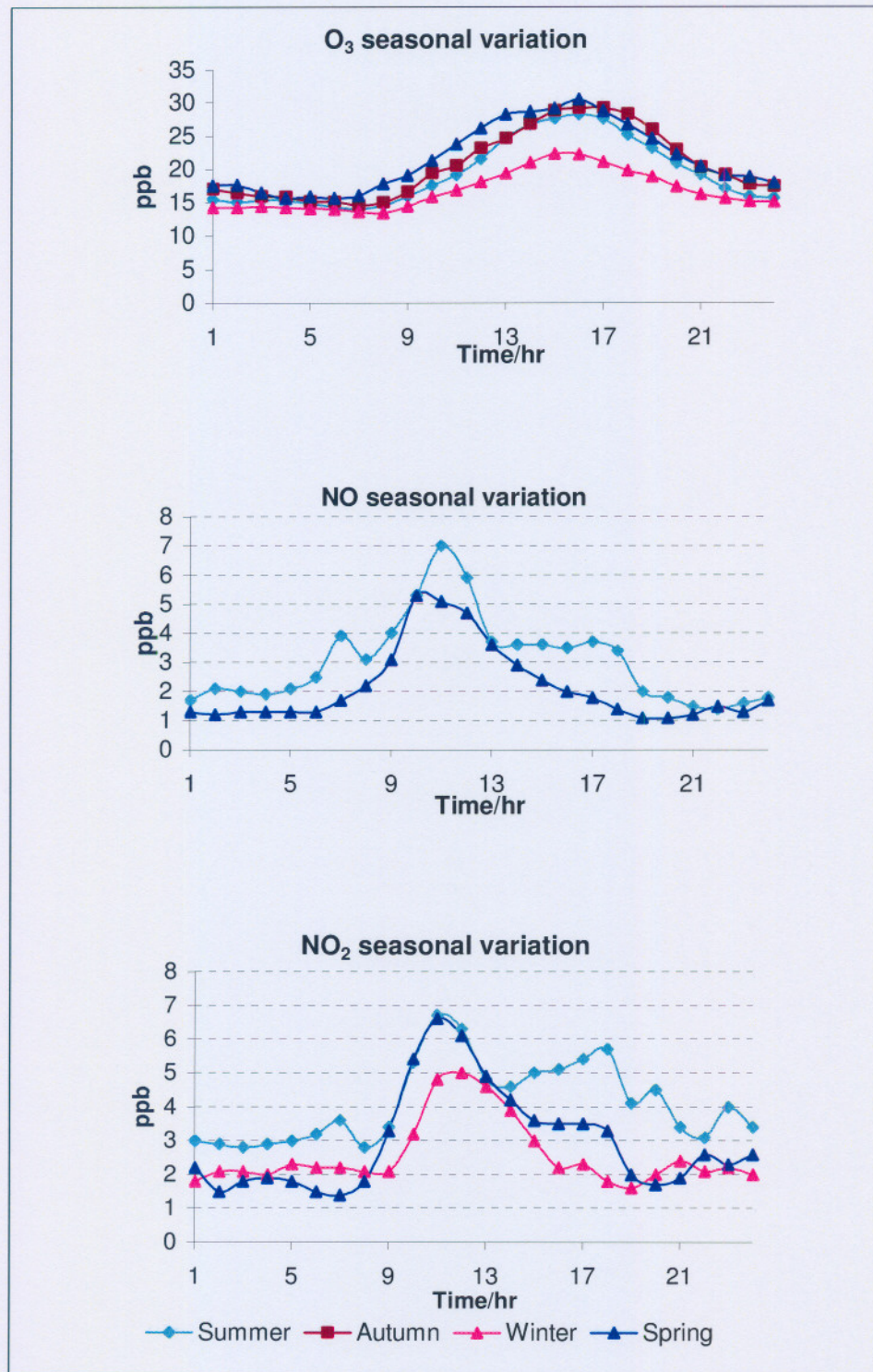


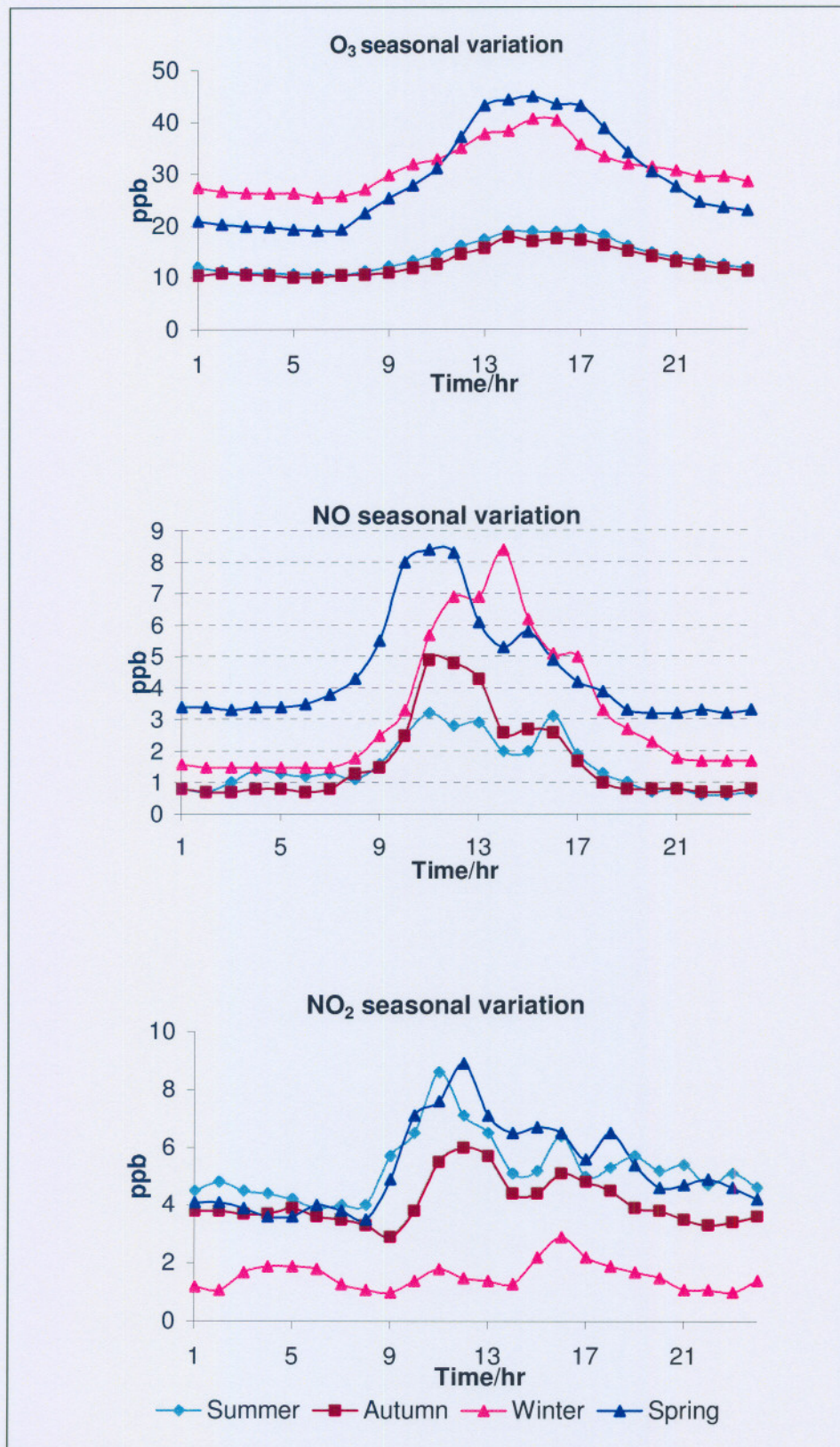
Figure A3: Seasonal variation of air pollutants (2001-2002)





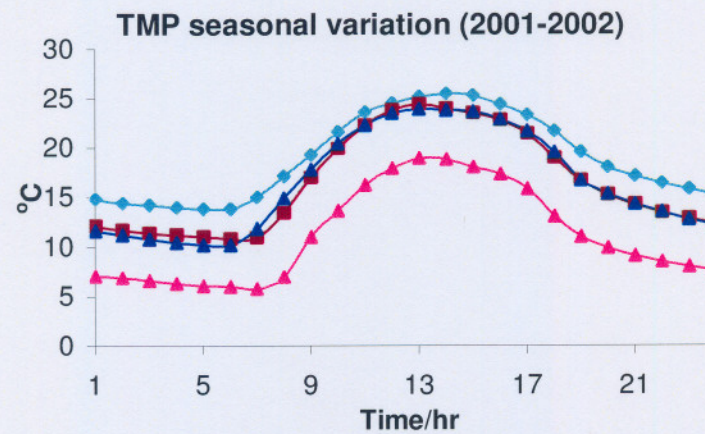
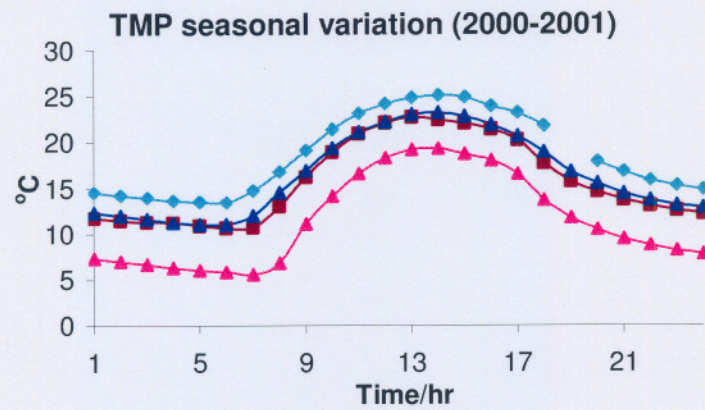
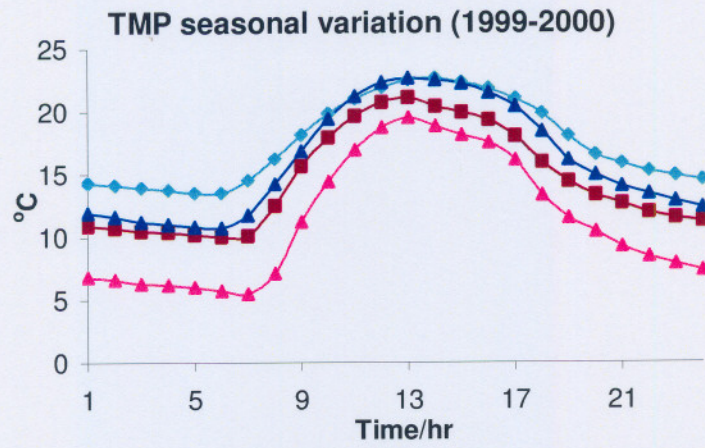
**Figure A4:** Seasonal variation of air pollutants (2002-2003)



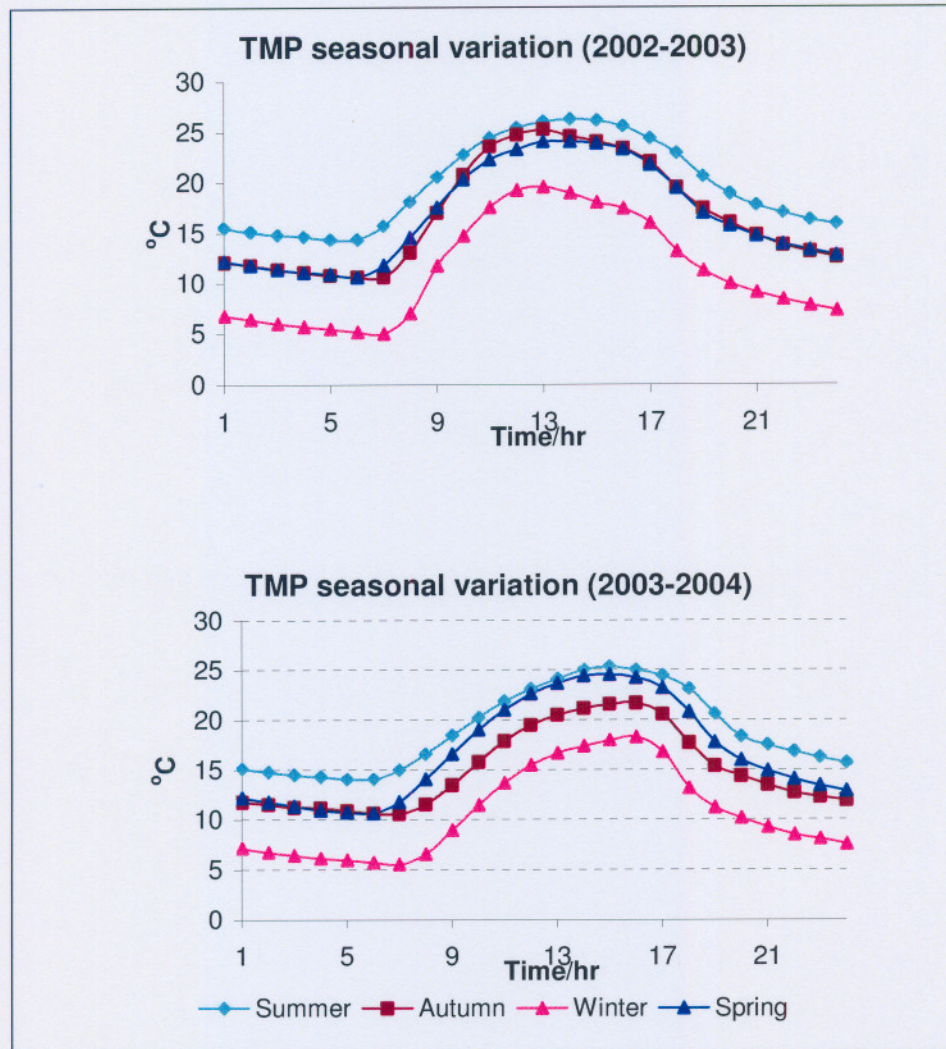


**Figure A5:** Seasonal variation of air pollutants (2003-2004)









**Figure A6:** Seasonal variation of ambient temperature









Figure A8: Seasonal ozone pollution roses (2000-2004)



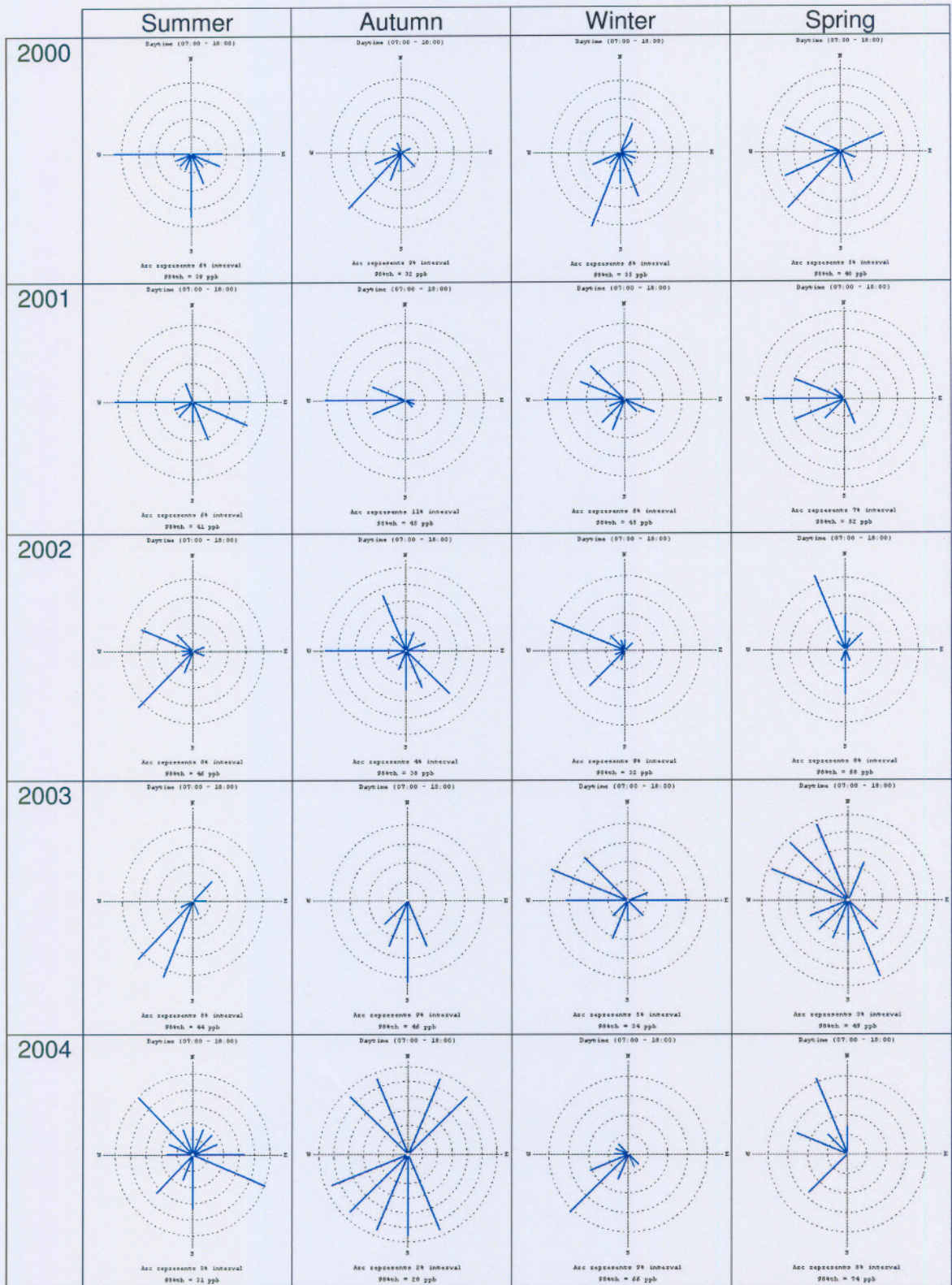


Figure A9: Seasonal 98 percentile ozone exceedance roses (2000 – 2004)

## Section II: Verkykkop

**Table A2:** Percentage data captured at Verkykkop

Year	NO	NO <sub>2</sub>	O <sub>3</sub>	TMP	WDR	WSP	Reliability
2000	90.9	90.9	97.2	92.3	92.3	92.3	92.6
2001	88.9	88.9	79.4	100	74.4	90	86.9
2002	89.5	89.5	89.6	93.1	33.6	33.6	71.5
2003	76	76	96.3	99.5	90.5	90.5	88.1
2004	85.8	85.8	96.6	99.8	100	91.8	93.3



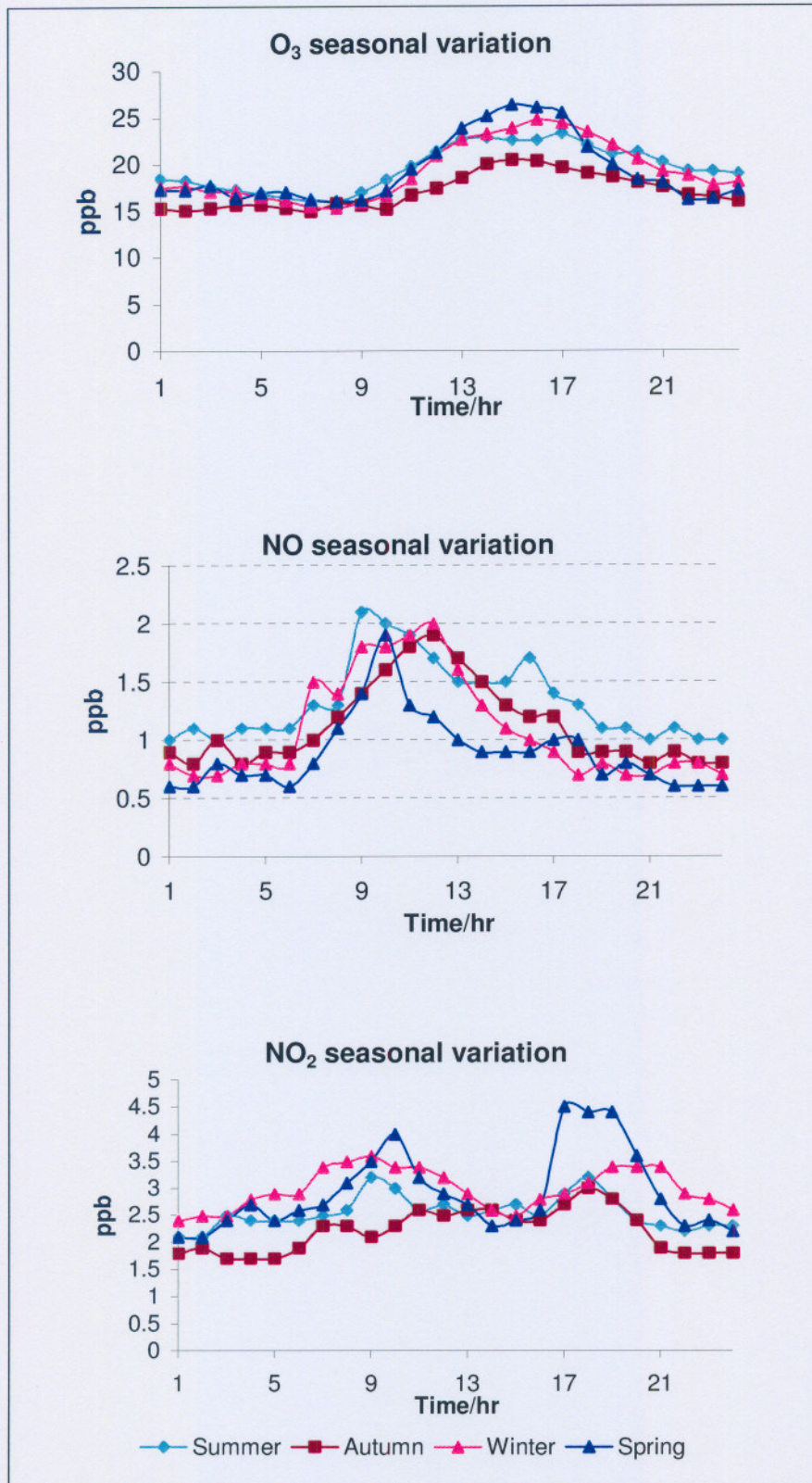


Figure A10: Seasonal variation of air pollutants (1999-2000)



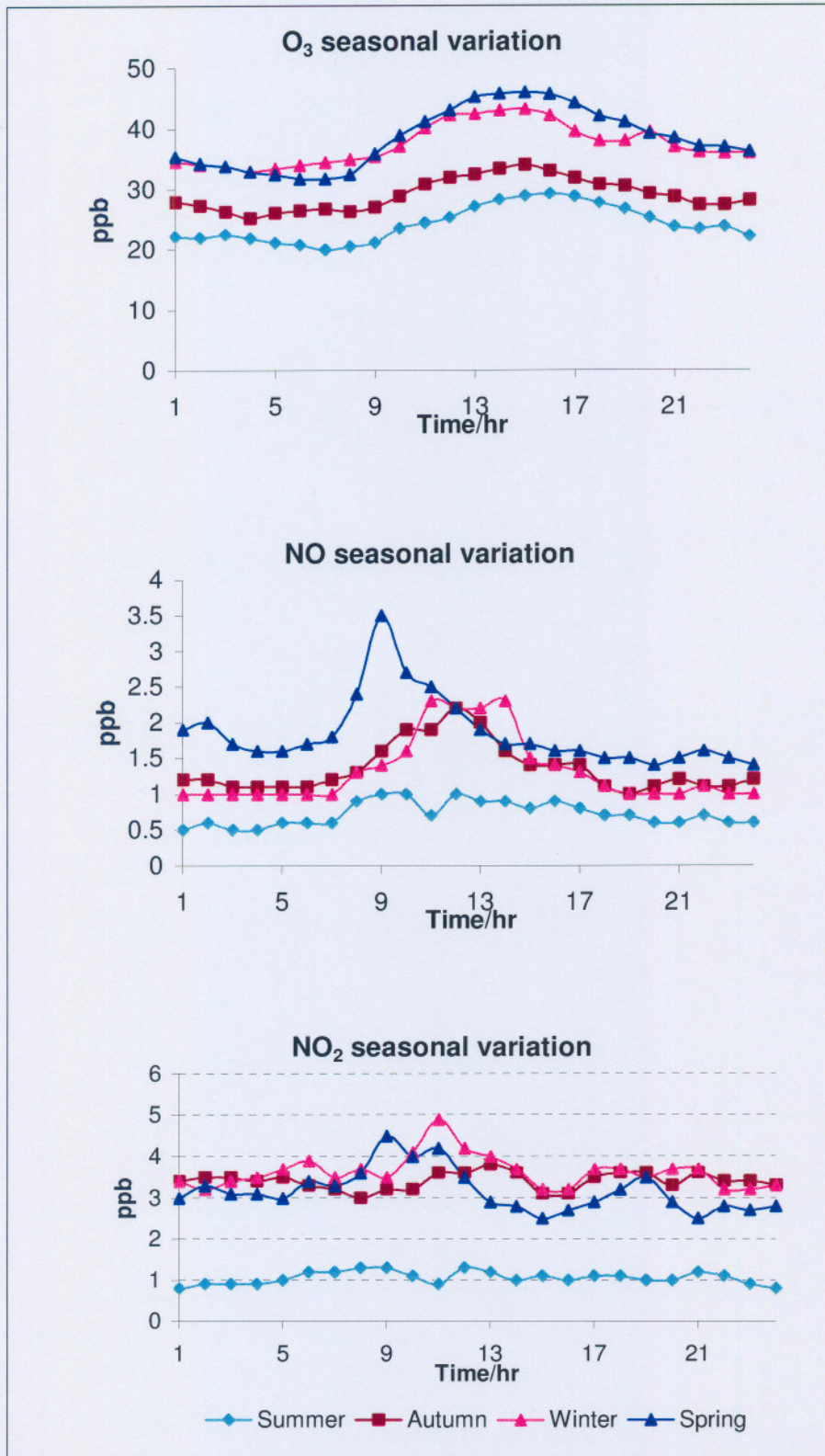
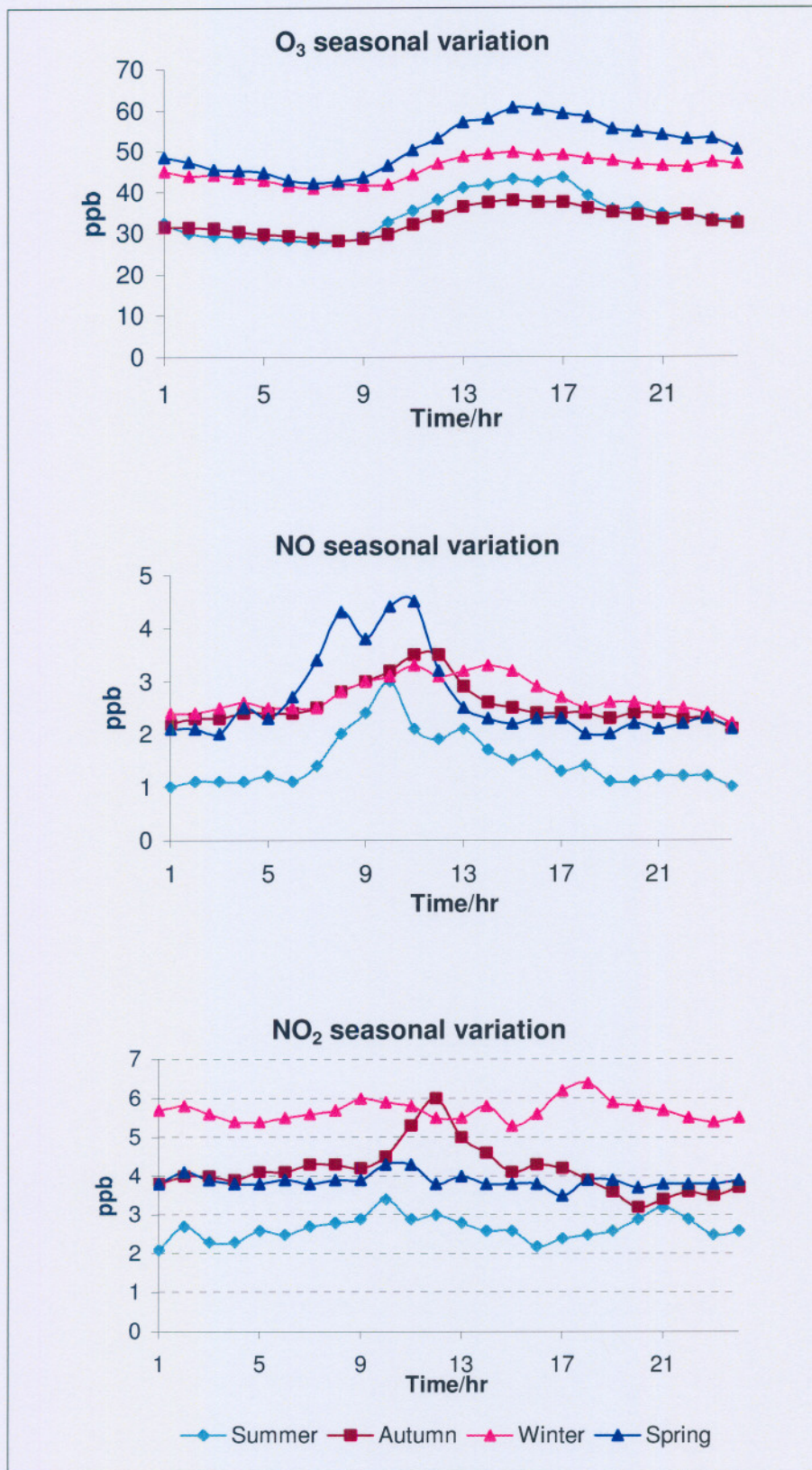


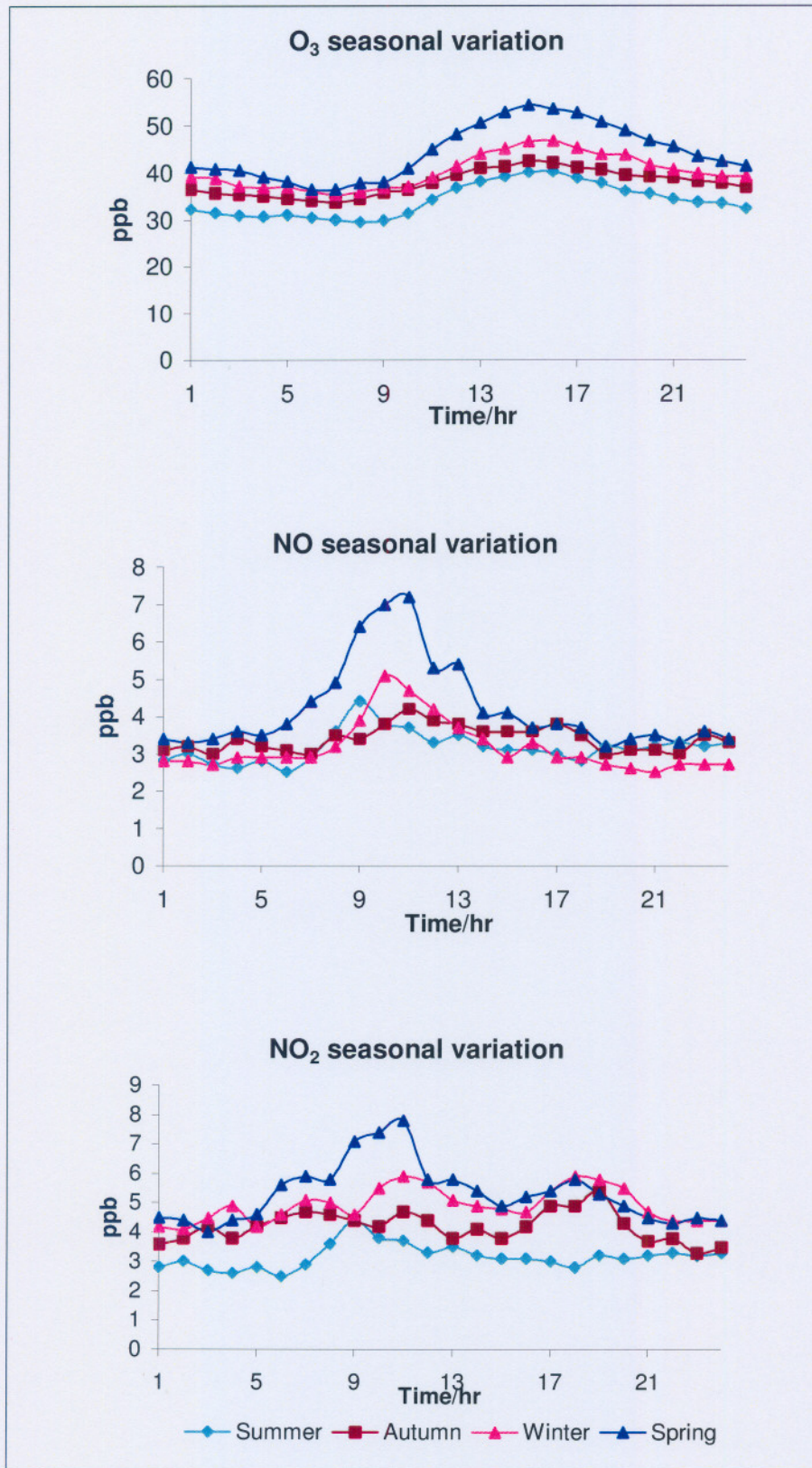
Figure A11: Seasonal variation of air pollutants (2000-2001)





**Figure A12:** Seasonal variation of air pollutants (2001-2002)





**Figure A13:** Seasonal variation of air pollutants (2002-2003)



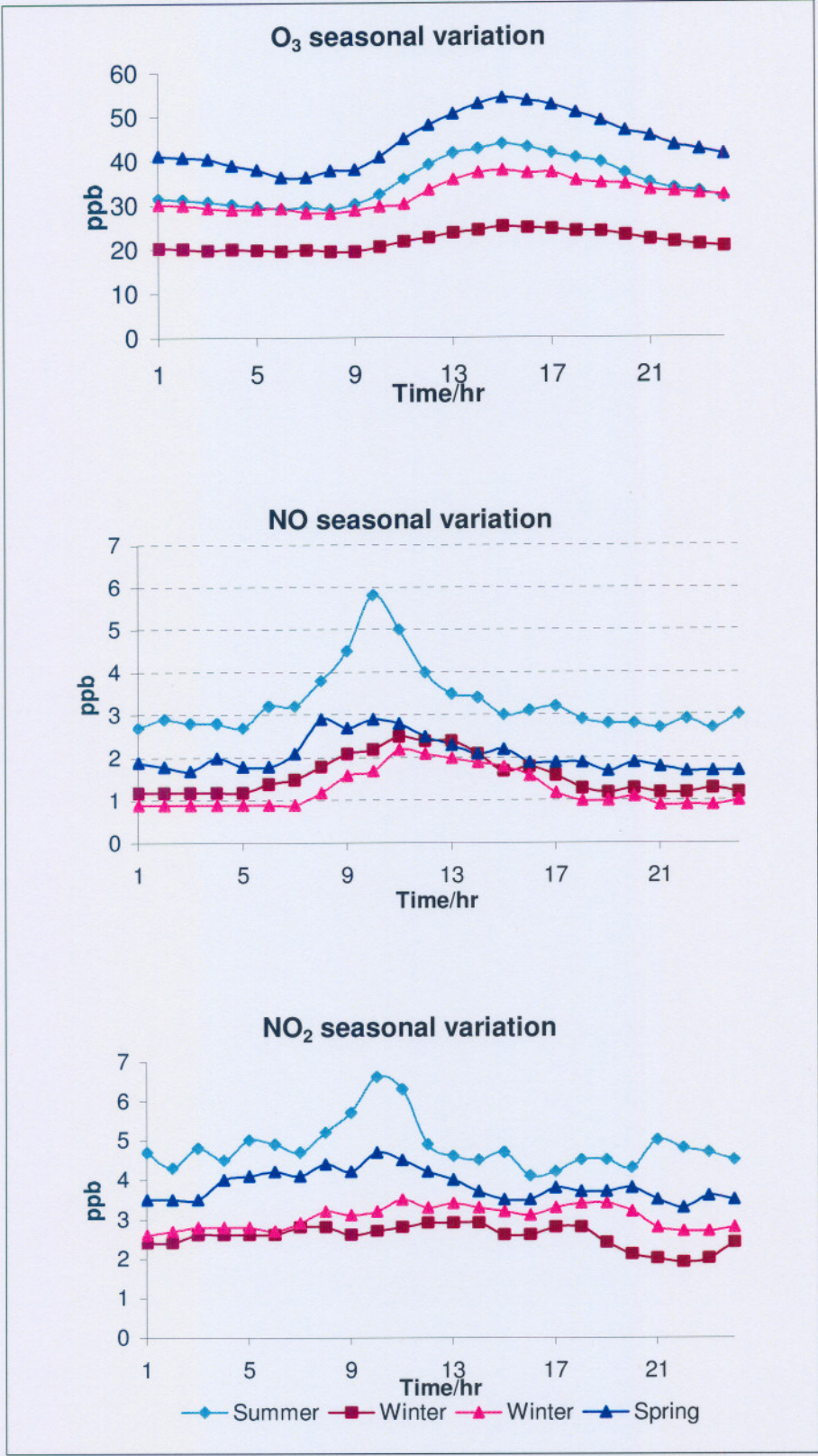
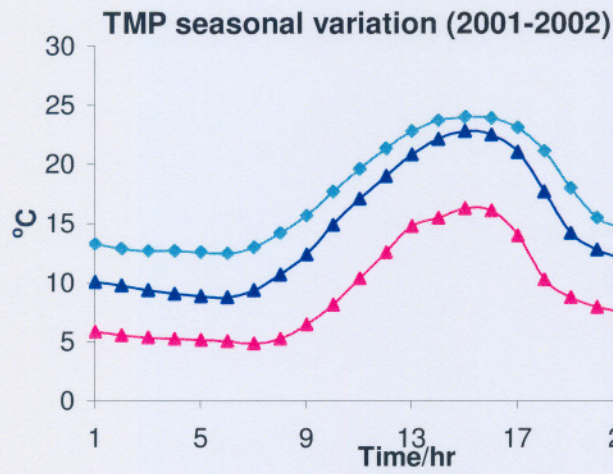
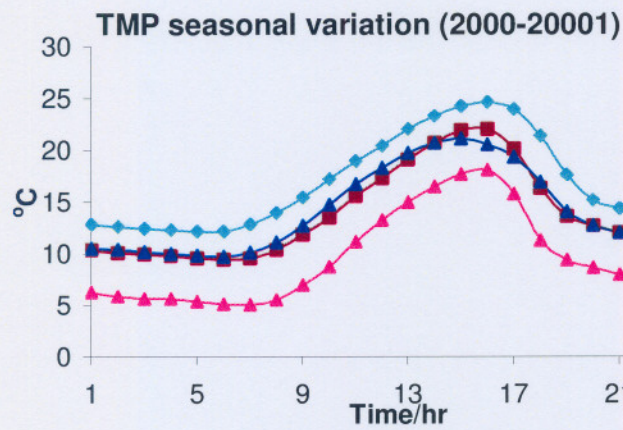
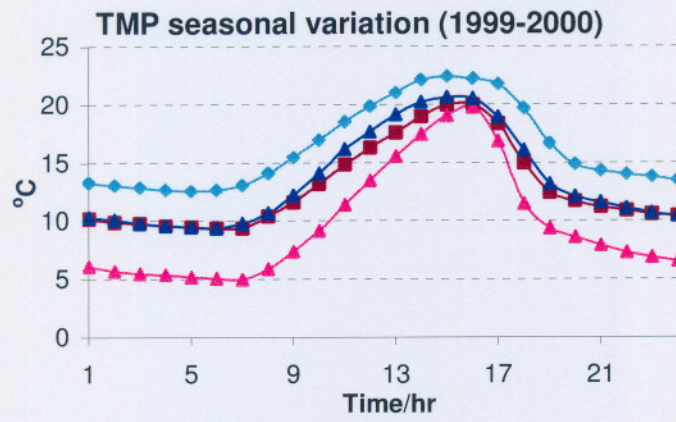


Figure A14: Seasonal variation of air pollutants (2003-2004)







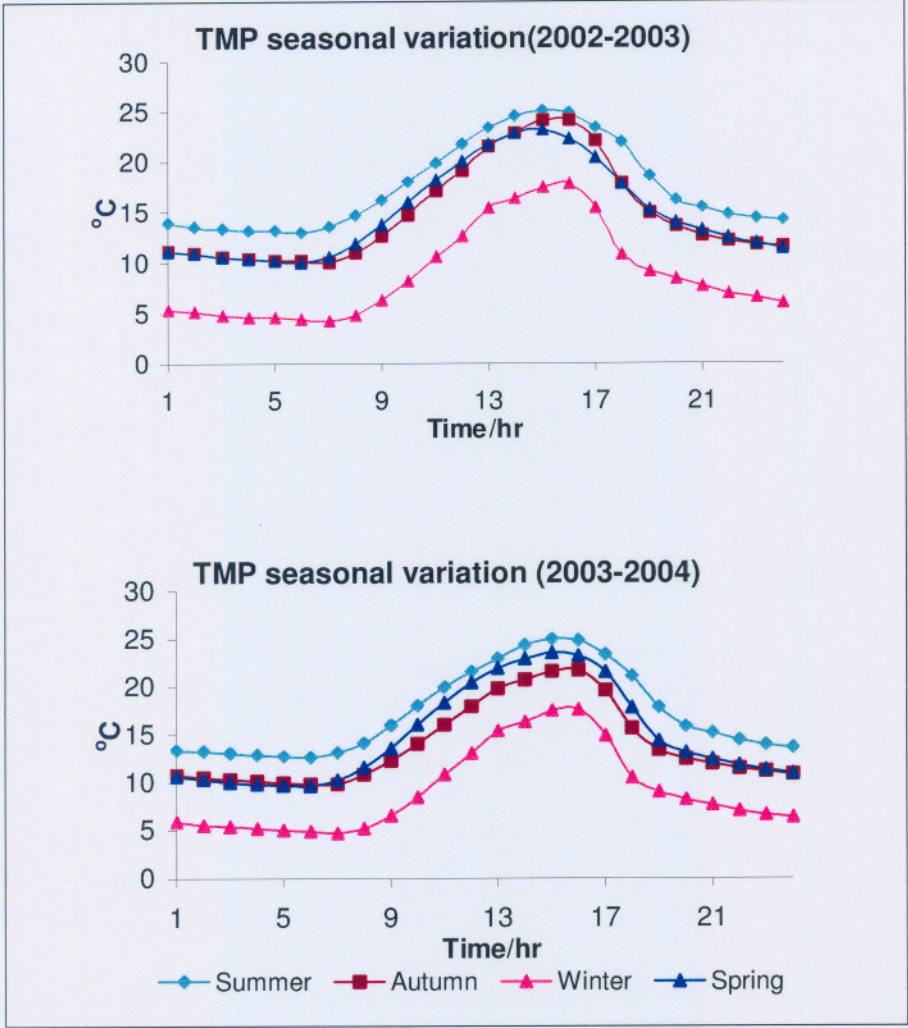


Figure A15: Seasonal variation of ambient temperature



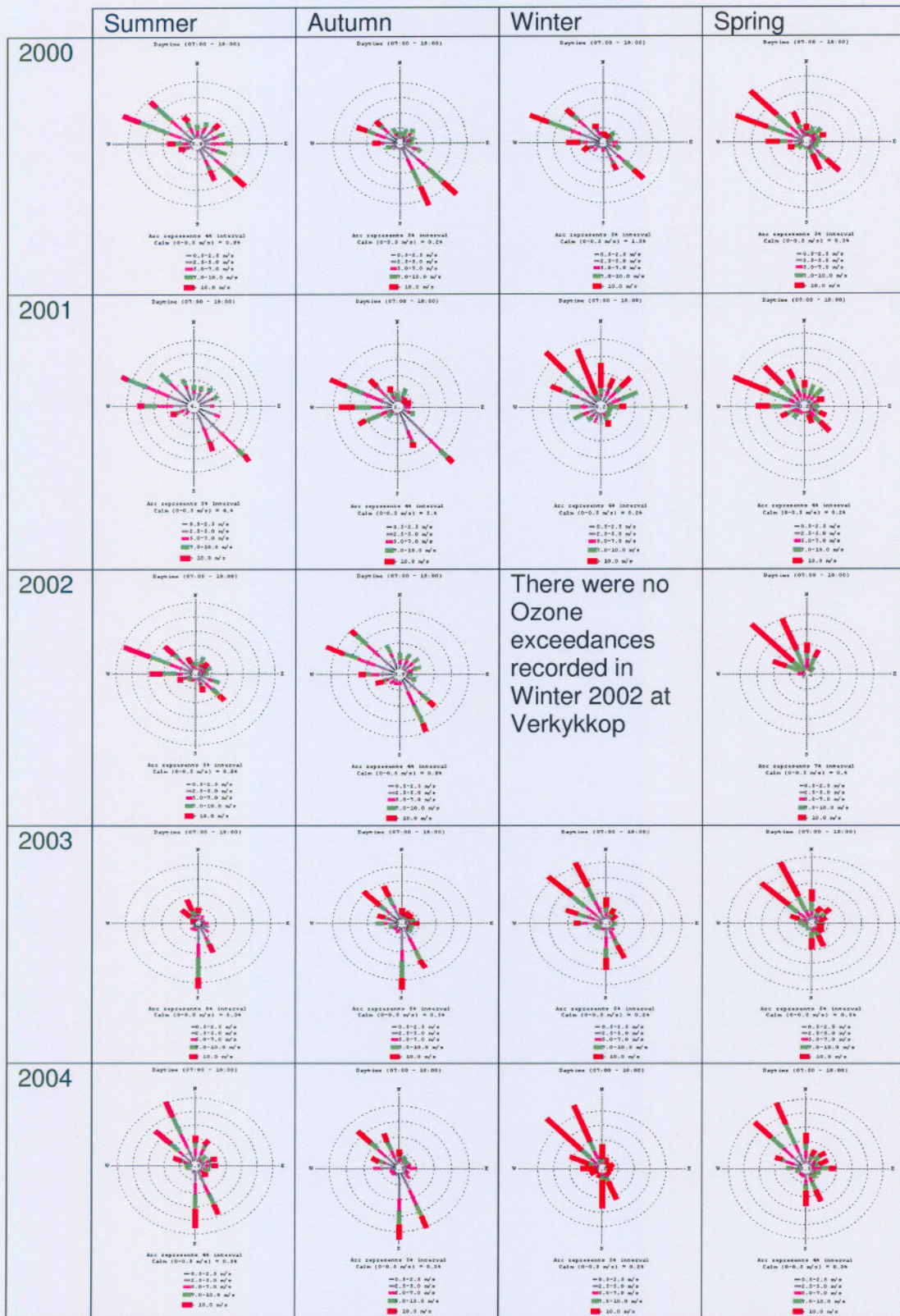


Figure A16: Seasonal wind roses



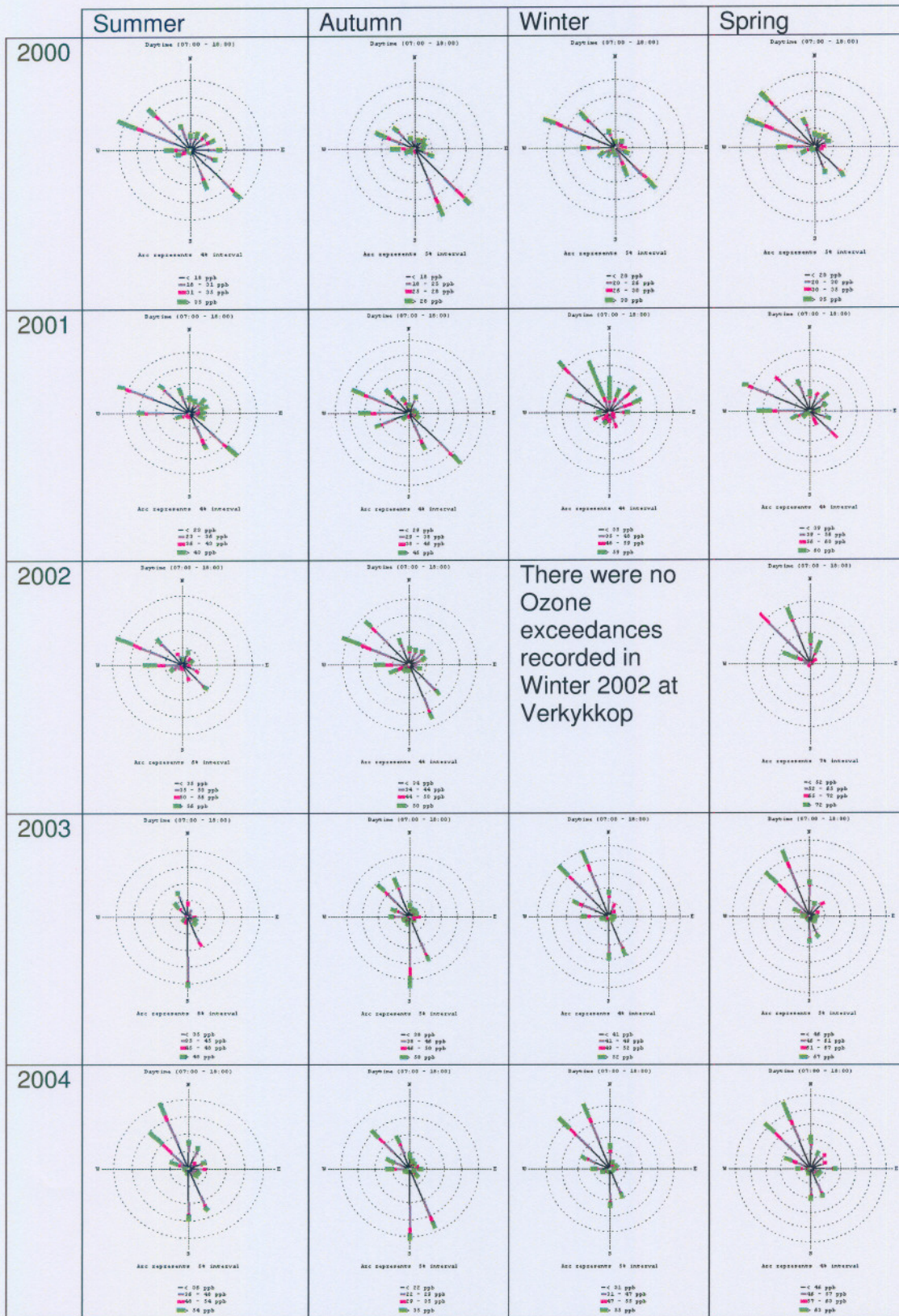


Figure A17: Seasonal ozone pollution roses



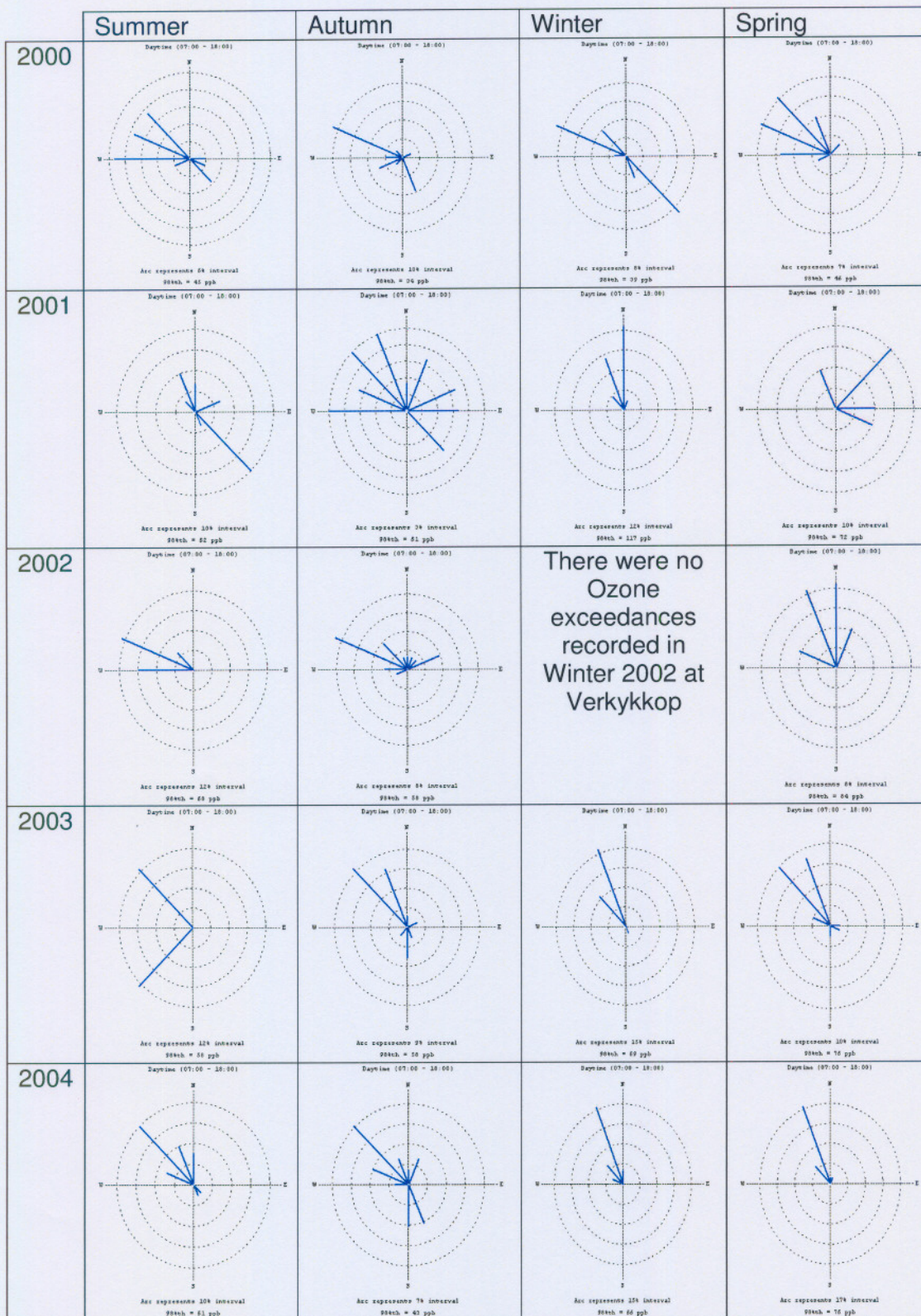


Figure A18: Seasonal 98 percentile ozone exceedance roses