Analysis of Surface Ozone Measurements at Cape Point, SANAE and City of Cape Town

By

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Declaration

I declare that this dissertation is my own work to fulfill the requirements of a Master of Science degree at the University of KwaZulu-Natal under the supervision of Dr Lisa Frost Ramsay. All people’s opinions and work has been referenced and acknowledged.

This work has not been submitted for any degree or examination at any other University.

...........................................................

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......29th...day of...November...2013

...........................................................

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Abstract

This study presents an investigation of surface ozone (O$_3$) at SANAE (2002 to 2009), Cape Point (1997 to 2009), Molteno (1997 to 2007) and Goodwood (2000 to 2006). The Cape Point data was statistically separated to background and non-background (anthropogenic) contributions. The main aim of the study was to investigate diurnal cycles, seasonal cycles, the weekend effect, and any long term trends in surface O$_3$, as well as assess meteorological controls on surface O$_3$ at these stations.

The observed O$_3$ concentrations were higher during the day than at night at all stations, with urban stations (Molteno and Goodwood) showing more pronounced peak-to-peak variations relative to the marine stations (SANAE and Cape Point). The ‘weekend effect’ was evident at Molteno and Goodwood with higher O$_3$ and lower NO$_x$ concentrations on ‘weekends relative to weekdays. The weekend effect on O$_3$ was more pronounced in winter at Goodwood and Molteno. Maximum monthly average concentrations were observed in spring at Goodwood and Molteno, with minimum in winter. The SANAE and Cape Point background O$_3$ maxima were observed in winter (June to August) with minima in summer (January to February). The Cape Point non-background O$_3$ maximum was observed in September with a minimum in summer (January). The seasonal cycles at marine sites appear to be driven by O$_3$ photolysis.

Wind speeds played a critical role in O$_3$ concentrations, particularly in the continental environment. At Goodwood, high NO$_x$ levels are associated with low wind speeds. At SANAE, no significant O$_3$ differences were observed between low wind speeds and high wind speeds while at Cape Point, differences were more evident during the winter months. A decreasing O$_3$ trend in monthly averages was observed from 1997 to 2006 at Molteno while Goodwood demonstrated an increase of O$_3$ monthly averages with decreasing NO$_x$ monthly averages from 2000 to 2006.
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Acronyms and Abbreviations

BG | Background
---|---
CH4 | Methane
CO | Carbon monoxide
CO2 | Carbon dioxide
CSIR | Council of Scientific and Industrial Research
EPA | Environmental Protection Agency
IFB-NOx | NOx from industrial activities (I), fossil fuel combustion (F) and biofuel combustion (B)
LSCE | Laboratoire des Sciences du Climat et l'Environnement
MSA | Monosodium acetate
NH3 | Ammonia
NO2 | Nitrogen peroxide
NO3 | Nitrate
NOAA | National Oceanic and Atmospheric Administration
Non-BG | Non-background
NOx | Oxides of nitrogen
N2O5 | Dinitrogen pentoxide
O3 | Ozone
PAN | Peroxyacetyl nitrate
RHUL | Royal Holloway University of London
SANAE | South African National Antarctic Expedition
SAWS | South African Weather Service
SO2 | Sulfur dioxide
SOx | Oxides of sulfur
UEA | University of East Anglia
VOCs | Volatile organic compounds
WCC | World Calibration Centre
CHAPTER 1

1.1 Introduction

Understanding the physical and chemical dynamics of ozone (O\textsubscript{3}) in the troposphere is an important research priority in the context of air pollution and global warming concerns. Surface O\textsubscript{3} is a secondary pollutant which is formed through reactions between oxides of nitrogen (NO\textsubscript{x}) such as nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}), and volatile organic compounds (VOC), including methane, toluene and benzene, in the presence of sunlight. Surface O\textsubscript{3} concentrations have increased in the past century in many urban centres, particularly in the Northern Hemisphere, and O\textsubscript{3} currently is regarded as the third most important contributor to global warming after carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}) due to human development (Intergovernmental Panel on Climate Change (IPCC), 2001). Although O\textsubscript{3} data from the nineteenth century are limited, results suggest that pre-industrial ground level O\textsubscript{3} concentrations were less than 10 ppb (Volz and Kley 1988). According to Vingarzan (2004), present annual average background O\textsubscript{3} concentrations in the mid-latitudes of the Northern Hemisphere range between 20 and 45 ppb, while values range between 23 to 34 ppb at Canadian background stations. In 2008 (Figure 1.1), O\textsubscript{3} annual average concentrations in the Northern Hemisphere varied between 20 to 48 ppb, while in the Southern Hemisphere, values varied between 20.0 to 36.0 ppb (Figure 1.1). According to Ashmore (2005) surface O\textsubscript{3} concentrations are steadily increasing and O\textsubscript{3} is now considered to be the most significant air pollutant affecting vegetation.

Figure 1.1: (a) Modeled global changes in surface O\textsubscript{3} concentrations between pre-industrial times and (b) surface O\textsubscript{3} in 2008 (Science Policy Report, 2008).
There are two main approaches to understanding surface $O_3$ increases, namely trend analysis based on long term data, and climatological analysis of long range transport and transformation (Pochanart et al, 1999). This study incorporates both approaches to understanding $O_3$ concentrations measured at SANAE, Cape Point, Molteno and Goodwood, and their relationship with precursor emissions of $NO_x$ and VOCs. This chapter presents the study’s aims and objectives, followed by a description of the study sites. Chapter 2 commences with $O_3$ chemistry in the troposphere, followed by a review of previous studies conducted at the four stations. Chapter 3 describes the measurement techniques at the four stations, data verification, and the filtering method use to separate Cape Point data into background and non-background datasets. The types of data analysis and statistical approaches are also described in this chapter. Chapter 4 presents the study’s results and a discussion of diurnal cycles, seasonal cycles, and the influence of meteorology on $O_3$ concentrations and a description of long term trends. Chapter 5 commences with a summary of the study, followed by conclusion and recommendations.

1.2 Study motivation

The Cape Point station is primarily exposed to air from the South Atlantic Ocean, which provides background concentrations of trace gases as measured at the station. ‘Background’ refers to air masses arriving at the station without pollutants arising from anthropogenic activities. The Cape Point station, however, also receives polluted air, especially from the Cape Town urban region (Brunke and Scheel, 1998). These air masses contain pollutants from anthropogenic activities and are thus described as ‘non-background air’. Such pollution episodes usually last only for a few hours and are easily recognized by simultaneous peaks in carbon monoxide (CO), methane (CH$_4$) and radon (Rn) concentrations. Non-background pollutant concentrations measured at Cape Point’s three intakes (4m, 14m and 30m) from March 2009 until September 2009 previously were analyzed by Brunke et al. (2009). Results indicated a significant difference of up to 60 ppb between measurements at these three heights during polluted episodes, while differences between background measurements were as low as 5.0 ppb.

The major focus of the World Meteorological Organization Global Atmosphere Watch (WMO_GAW) is trace gas measurements in clean, background air for the assessment of long-term trends. There is little analysis conducted on non-background data. The analysis of air
derived from the north of Cape Point has received some attention from South African Weather Service (SAWS) but constitutes a largely untapped reservoir of information. The current study provides an excellent opportunity to compare background and non-background air sampled at the three ozone intakes, and to determine whether the diurnal and seasonal cycles affecting background and non-background air differ between sites, and if so, to determine possible reasons for their differences.

1.3 Aims of the study
The primary goals of this study are to analyze surface O$_3$ from four stations (Cape Point, SANAE, Goodwood and Molteno) and investigate meteorological controls that lead to either enhancement or decreases in tropospheric ozone concentrations at these sites. The study aims to also identify any temporal trends, including diurnal or seasonal variations, at the various sites, and any differences in these patterns between sites.

This study utilizes data from:
- the 30 m Cape Point monitor (1997 to 2009);
- the 4 m Cape Point monitor (1997 to 2009);
- the 14 m Cape Point monitor (2008);
- the City of Cape Town’s Molteno (1997 to 2007) and Goodwood (2000 to 2006) monitoring stations;
- SANAE in Antarctica (2002 to 2009).

The study objectives include the following:
1) To develop and compare the background and non-background O$_3$ concentration roses for Cape Point, the City of Cape Town stations and SANAE;
2) To analyse the temperature, atmospheric pressure, wind speed and wind direction for both background and non-background air masses;
3) To compare the seasonal and diurnal fluctuations of O$_3$ in the three air intakes at Cape Point (background and non-background), SANAE and the City of Cape Town stations and correlate with ozone concentrations at the study sites;
4) To assess any ‘weekend effect’ in O$_3$ measurements at Cape Point, SANAE, and City of Cape Town over the periods of available data.

1.4 Study area

The City of Cape Town is situated to the north of the Cape Peninsular, which lies between the Indian and Atlantic Oceans and ends at Cape Point. Table Mountain (three kilometers from side to side) forms the background to the City.

The Western Cape region is one of the six regions in the world (and the only one in Africa) with a Mediterranean climate (http://www.grabovrat.com). These regions lie between 30° and 45° of latitude (Figure 1.2). Mainly in winter (June to August), but also in late autumn and early spring, well-developed cold fronts move from the Atlantic Ocean towards the Cape coast, bringing heavy precipitation and strong north-westerly winds to the Peninsula. The winter months are cool and wet, with an average minimum temperature of 7.0°C and maximum of 17.5°C. Most of the city's annual rainfall occurs in winter. Due to the mountainous topography of the city, rainfall levels between sites can vary significantly (Wichmann, 2006). During spring, average temperatures range between 20 and 25°C. Spring (September to November) is associated with intermittent rainfall episodes (usually associated with the persistence of cold fronts) and mild temperatures. The summer months (December to February) are warm and dry. The Peninsula experiences a strong wind from the south-east, known locally as the Cape Doctor because it dissipates pollution episodes and cleans local air. This south-easterly wind is caused by a high-pressure system that lies over the South Atlantic to the west of Cape Town, known as the South Atlantic High (Kruger et al., 2010). Summer temperatures are mild, with an average daily maximum of 28 °C (Wichmann, 2006). During the autumn months (March to May), temperatures are mild with highs averaging in the mid-twenties.
The City of Cape Town’s main polluters include:

- traffic, emitting hydrocarbons, CO, NO\textsubscript{x}, SO\textsubscript{2} and particulates; and
- Caltex Refining in Table View, emitting hydrocarbons, SO\textsubscript{x}, NH\textsubscript{3}, aldehydes, NO\textsubscript{x}, cyanides, CO, and particulates;
- domestic fuel burning within townships and informal settlements, with the main pollutants released including CO, NO\textsubscript{2}, SO\textsubscript{2}, particulates and polycyclic aromatic hydrocarbons;
- Consol Glass in Bellville, emitting mainly particulates, SO\textsubscript{x} and NO\textsubscript{x};
- the airport, emitting hydrocarbons, CO, NO\textsubscript{x}, SO\textsubscript{2} and particulates during airport operations, vehicle traffic, aircraft operation and maintenance, and on-site fuel storage facilities (Walton, 2005).

1.4.4 SANAE IV station

SANAE is located 851 m above sea level at 71° 40' 42'' S, 2° 49' 44'' W. The station is built on solid rock, 170 km inland from the Weddell Sea (Plate 1). Winds blow predominantly from the north-east, east and south-east (Labuschagne et al., 2003).
Temperatures in winter are close to -50°C and the sun is not observable for more than three months of the year. In 2004, SANAE was one of the 43 stations operating south of 60°S (Figure 1.3) and one of the 60 Antarctic stations. In April 2012, the number of Antarctic stations increased to 101 worldwide (http://www.scar.org). There are four research programs associated with SANAE: Physical Sciences, Earth Sciences, Life Sciences and Oceanographic Sciences. Due to severe weather conditions, only the Physical Science program extends all year round at SANAE IV. The other programs are conducted during summer period when the weather permits fieldwork and the sea ice level is at its minimum (http://www.sanap.org.za).

Plate 1: Outside view of SANAE station (http://www.sanap.org.za).
1.4.2 Molteno and Goodwood

The City of Cape Town monitors air quality at 14 stations (Figure 1.4), measuring particulates ($\text{PM}_{10}$ directly), nitrogen dioxide ($\text{NO}_2$), sulphur dioxide ($\text{SO}_2$), carbon monoxide (CO) and ozone ($\text{O}_3$). Ozone measurements commenced in 1992 at Molteno. The City of Cape Town uses instrument caravans for monitoring (Plate 2). The Molteno station is located in Cape Town’s city centre at approximately $31^\circ \ 22' \ S \ 26^\circ \ 22' \ E$. The city bowl is bordered on three sides by mountains, which promotes the accumulation of pollutants throughout the year (Wichmann, 2006).
Figure 1.4: City of Cape Town monitoring stations (http://web1.capetown.gov.za).

Plate 2: Outside view of City of Cape Town monitoring station (City of Cape Town quality monitoring group).
The Goodwood monitoring station is located in a residential area between the southern and the northern suburbs of Cape Town at 33° 55' S, 18° 22' E. It is situated 10 km away from the city centre. The station was located to measure industrial emissions (Wichmann, 2006).

1.4.3 Cape Point

The Cape Point Global Atmosphere Watch (GAW) station, managed and maintained by SAWS, is located on the Cape Peninsula in the South African National Parks (SANParks) nature reserve (34° 35’ S; 18° 48' E), which is about 58 km south of the City of Cape Town (Plate 3). The station is located on the top of a cliff (Plate 4). This station provides a record of more than 30 years (beginning 1978) of chlorofluorocarbons [Freon -11 (CF-11)] and CO. Monitoring has expanded over the years and currently includes measurements of carbon dioxide (CO₂), methane (CH₄), ozone (O₃), nitrous oxide (N₂O), sulphur dioxide (SO₂), total gas mercury (TGM) and further chlorofluorocarbons (including Freon-12, Freon-113, methyl chloroform and carbon tetrachloride). In addition, radon (Rn) is measured and used as a tracer for distinguishing background and non-background air masses. Meteorological parameters such as humidity, pressure, temperature, wind direction and wind speed also are measured at the site.

Plate 3: Cape Point GAW station (Courtesy of SAWS).
Sampling collaborators at the station have included the University of East Anglia (UEA), National Oceanic and Atmospheric Administration (NOAA), Royal University of Holloway (RHUL) and Laboratoire des Sciences du Climat et 'Environnement (LSCE). Flask samples are only taken under background conditions and sent back to the respective institutes for analyses. Passive samplers belonging to North West University measure O₃, SO₂, nitrogen dioxide (NO₂) and ammonia (NH₃). Rain water samples are collected for CSIR and the University of North West. Particulate matter sampling has been conducted at Cape Point with filters sent to France for analysis of acetate, propionate, formate, monosodium acetate (MSA), chloride, nitrate, glutarate, succinate, sulphate, oxalate, phosphate, sodium, ammonium, potassium, magnesium and calcium.

1.5 Conclusion
SANAE and Cape Point stations are located far from the anthropogenic activities compared to urban stations (Molteno and Goodwood) which are likely to be affected by human activities. Although background stations are not more affected by anthropogenic emissions, such emissions can be transported from non-background sites to background sites. The available data from SANAE, Cape Point, Molteno and Goodwood will give a better understanding of O₃ in both background and non-background stations.
CHAPTER 2
(Theoretical Framework)

2.1 Introduction
This chapter presents current understandings of ozone chemistry in the troposphere, ozone sources and sinks and the environmental impacts of high ambient ozone concentrations. A review is also conducted of previous studies on diurnal and seasonal cycles, the weekend effect, long-term trends and the effect of meteorology on ambient ozone levels.

2.2 An Introduction to Ozone Chemistry
Prior to the 1940s, stratospheric O$_3$ was the only known source of tropospheric O$_3$. Haagen-Smit (1952) suggested that the photochemical smog in the Los Angeles area contained O$_3$ concentrations that were too high to originate entirely from stratospheric O$_3$. Since then, further investigations have revealed that O$_3$ in the troposphere can be caused either by transportation of O$_3$-rich air from the stratosphere to the troposphere or from photochemical reactions involving O$_3$ precursors in the troposphere. The chemical formation of O$_3$ depends on ultraviolet (UV) radiation and O$_3$ precursors. In 1930, Chapman proposed the photochemical reaction below for O$_3$ formation.

$$O + O_2 + M \rightarrow O_3 + M$$  \hspace{1cm} (1)

Where M represents any other molecule (usually N$_2$ or O$_2$ since these two molecules constitute 99% of the volume of air).

Atomic oxygen is naturally produced when molecular oxygen absorbs UV at wavelengths below 242 nm (Reaction 2), where $h\nu$ represents ultraviolet radiation. Reaction 2 below shows the photolysis of O$_2$ molecule by ultraviolet radiation to two oxygen (O) atoms. These O atoms react simultaneously with O$_2$ molecules to form O$_3$ molecules (Reactions 3 and 4).

$$O_2 + h\nu \rightarrow O + O$$  \hspace{1cm} (2)
$$O + O_2 \rightarrow O_3$$  \hspace{1cm} (3)
$$O + O_2 \rightarrow O_3$$  \hspace{1cm} (4)

**Net reaction:** $3O_2 + h\nu \rightarrow 2O_3$ (Chapman, 1930)  \hspace{1cm} (5)
An increase in solar radiation with higher concentrations of NO\textsubscript{2} and VOCs, encourages the formation of O\textsubscript{3} (Seinfeld and Pandis, 1998). Tropospheric O\textsubscript{3} production increases in urban environments due to anthropogenic activities that emit NO\textsubscript{x}, CO, and VOCs, which are important O\textsubscript{3} precursors. The ratio of VOCs to NO\textsubscript{x} is high in NO\textsubscript{x} sensitive environment whereas the VOC to NO\textsubscript{x} ratio is low in VOC sensitive environments. Ozone production will increase with increasing VOCs in VOC sensitive environments and decrease with increasing NO\textsubscript{x} (Sillman, 1999).

Wavelengths below 310 nm destroy O\textsubscript{3} in the atmosphere, forming an O\textsubscript{2} molecule and O atom (Reaction 6 below). Subsequently the O atom formed reacts with water vapour to form two OH radicals (Levy, 1971).

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} \quad \text{(6)}
\]
\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(7)}
\]

Ozone chemistry at polar sites has been reported to be more complicated (Helmig \textit{et al.}, 2007). Unique photochemical processes at the surface and boundary layer have been reported by Bottenheim \textit{et al.} (1986) and Barrie \textit{et al.} (1988). As a result of these processes, O\textsubscript{3} depletion events (in the range of 20 ppbv/day to 40 ppbv/day) occur during spring time as reported for Barrow in Alaska, Alert in USA, and Neumayer in Antarctica (Kaleschke \textit{et al.}, 2005). On average, however, surface O\textsubscript{3} lifetimes are approximately 100 days in polar regions, which is significantly longer than the average one to two weeks in summer and one to two months during winter in other environments (Liu and Ridley, 1999). The longer lifetime in polar regions is due to weak ozone sinks, low water vapor and low solar radiation. Although lifetimes are generally shorter outside of the polar regions, there is still sufficient time for ambient ozone produced in one polluted region to be transported to another within its lifetime. This can even occur at the scale of continents (Akimoto, 2003). This phenomenon is more likely to occur during winter months when O\textsubscript{3} has a longer lifetime in the atmosphere.
As previously described in this study, there have been significant increases in O\textsubscript{3} concentrations since the commencement of heavy industrial activity. The Intergovernmental Panel on Climate Change (IPCC 2001, 2007) reported a global average radiative forcing of 0.35 W/m\textsuperscript{2} in 2005 due to tropospheric O\textsubscript{3}. The observed positive radiative forcing was comparable to that of halocarbons, higher than N\textsubscript{2}O and lower than CH\textsubscript{4} and CO\textsubscript{2} (Figure 2.1).

![Figure 2.1: Global average radiative forcing in 2005 (IPCC, 2007).](image)

### 2.3 Sources of Tropospheric O\textsubscript{3}

Tropospheric ozone (O\textsubscript{3}) levels are controlled by chemical and physical processes, and its precursors originate from both natural and anthropogenic activities. It is a secondary pollutant formed through the reactions of nitrogen oxides (NO\textsubscript{x}), volatile organic compounds (VOCs), methane (CH\textsubscript{4}), and carbon monoxide (CO) in the presence of sunlight (Seinfeld and Pandis 1998) or through the transportation of O\textsubscript{3}-rich air from the stratosphere to the troposphere. Figure 2.2 shows tropospheric O\textsubscript{3} sources according to geographic location. As evident from the diagram, O\textsubscript{3} in the mid-latitudes is strongly influenced by anthropogenic activities (e.g. urban...
pollution and biomass burning). In the tropics, NO\textsubscript{x} generated during lightning plays an important role in O\textsubscript{3} formation whereas in Arctic and Antarctic regions, snowpack plays a critical role in O\textsubscript{3} formation by releasing NO from the photolysis of nitrate (NO\textsubscript{3}). Cotter \textit{et al.} (2003) observed that NO\textsubscript{3} has a strong absorption of ultraviolet light (260-330 nm) and the concentrations of NO\textsubscript{x} above the ice surface strong correlates with ultraviolet B-band (UVB; 275-320 nm). At the Neumayer station (Antarctica), high NO concentrations were observed in summer and autumn. The occurrence of the annual maximum strongly correlates with maxima in UVB radiation (Weller \textit{et al.}, 2002). A detailed discussion on the sources of tropospheric O\textsubscript{3} is presented in the following sections.

![Figure 2.2: Sources of tropospheric O\textsubscript{3}](www.earthobservatory.nasa.gov)

2.3.1 \textit{Stratospheric/Tropospheric O\textsubscript{3} Exchange}

Although the focus of the current study is on tropospheric O\textsubscript{3}, the influence of stratospheric O\textsubscript{3} cannot be ignored and is briefly discussed here. Stratosphere-troposphere exchange is associated with jet streams and tropopause folds (Newell, 1963; Danielsen, 1968) and large-scale overturning of the stratosphere (Brewer, 1949; Holton \textit{et al.}, 1995). Early studies reported two near tropopause jet streams: the subtropical jet streams found at the pole ward edge of the Hadley circulation and polar jet streams found above the polar front zone (Holton, 1992; Bluestein, 1993). Figure 2.3 shows the location of these jet streams in the atmosphere. It is well
known that stratospheric intrusion events can be identified by a rapid decrease of relative humidity and an increase in O$_3$ concentrations (Cui et al., 2009). Brioude et al. (2006) highlighted the importance of understanding these physical transport processes to contextualise any investigation of the chemistry of trace gases.

Figure 2.3: Location of jet streams (http://www.srh.noaa.gov).

2.3.2 The Influence of Methane

Tropospheric O$_3$ is a precursor of the hydroxyl radical (OH) (Reactions 6 and 7 in Section 2.1 above), which controls the chemical composition of the atmosphere through methane (CH$_4$) and carbon monoxide (CO) reactions (Finnan et al., 1997). Moreover, the hydroxyl radical is known as the major sink of CH$_4$ and NO$_x$, with increases in CH$_4$ concentrations associated with reductions in OH. According to Wild et al. (2001) and West et al. (2007), increasing CH$_4$ concentrations cause a long term increase in O$_3$ concentrations. On the other hand, reductions in global CO emissions cause an increase in OH which causes a reduction in CH$_4$ concentrations, leading to a long term decrease in O$_3$.

Sources of atmospheric CH$_4$ include wetlands, ruminants, energy, rice agriculture, landfills, wastewater, biomass burning, oceans, and termites (Fiore et al., 2008). Anthropogenic emissions are estimated to contribute at least 60% to total CH$_4$ emissions, with individual studies reporting a range of 500 to 610 Tg$^{-1}$ for total CH$_4$ emissions (Fiore et al., 2008). Depending on the
availability of NO concentrations, CH₄ oxidation produces O₃ via reactions of peroxy radicals with NOₓ. The formation of O₃ from CH₄ involves a sequence of nine reactions which is the longest chain of all the O₃ precursors. These reactions were proposed by Crutzen (1973, 1974):

\[
\begin{align*}
\text{OH} + \text{CH}_4 & \rightarrow \text{H}_2\text{O} + \text{CH}_3 \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{O}_2 + \text{M} \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{HCHO} + \text{UVB} & \rightarrow \text{HCO} + \text{H} \\
\text{HCO} + \text{O}_2 & \rightarrow \text{CO} + \text{HO}_2 \\
3 [\text{HO}_2 + \text{NO}] & \rightarrow \text{HO} + \text{NO}_2 \\
4 [\text{NO}_2 + \text{UVA}] & \rightarrow \text{NO} + \text{O}_2 \\
3 [\text{O} + \text{O}_2] & \rightarrow \text{O}_3 \\
\text{Net: CH}_4 + 8\text{O}_2 + 5 \text{ photons} & \rightarrow \text{CO} + 4\text{O}_3 + 2\text{OH} + \text{H}_2\text{O}
\end{align*}
\]

Where M represents any other molecule (usually N₂ or O₂ since these two molecules constitute 99% of the volume of air).

2.3.3 The Influence of Volatile Organic Compounds and Carbon Monoxide

Volatile organic compounds (VOCs) are emitted naturally in biogenic processes by vegetation (e.g. pinene and terpene), forest fires, animals and during anthropogenic activities e.g. use of vehicles and industrial processes (Lemieux et al., 2004; Buzcu and Fraser, 2006). The sequence of O₃ formation from VOCs is initiated by the reaction of a VOC or CO with the OH radical (Haagen-Smit, 1952). Reaction 18 shows the reaction of a VOC with OH and O₂ to form an organic molecule (RO₂) and H₂O. In the absence of VOCs, Reaction 19 takes place with CO reacting with OH and O₂ to form HO₂ and CO₂. These reactions are followed by either Reaction 20 or 21 depending on the availability of RO₂ and HO₂ from Reactions 18 and 19 respectively. In Reaction 22, the NO₂ formed from Reactions 20 or 21 undergoes photolysis to form NO and an O atom. The latter (O atom) is essential to complete O₃ formation through its reaction with an O₂ molecule (Reaction 23).
\[ \text{VOC} + \text{OH} + \text{O}_2 \rightarrow \text{RO}_2 + \text{H}_2\text{O} \]  
\[ \text{CO} + \text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \]  
\[ \text{RO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{VOC (secondary)} + \text{HO}_2 + \text{NO}_2 \]  
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  
\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad (\lambda \leq 400\text{nm}) \]  
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]  

Where \( M \) represents any other molecule (usually \( \text{N}_2 \) or \( \text{O}_2 \) since these two molecules constitute 99% of the volume of air).

\( \text{RO}_2 \) represents any organic molecule with \( \text{O}_2 \) attached:

\[ \text{C}_3\text{H}_8 + \text{OH} \rightarrow \text{C}_2\text{H}_7\text{O}_2 \] (24)  
\[ \text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_4\text{CHO} \] (25)

These reactions depend on the availability of \( \text{NO}_x \). At higher \( \text{NO}_x \) concentrations, the above reactions will occur (Reactions 21 to 23). These reactions occur at a faster rate (4000 times faster) relative to Reactions 26 to 28. At lower \( \text{NO}_x \) levels, the sequence of reactions below occurs (Reactions 26 to 28) resulting in the destruction of \( \text{O}_3 \) (Crutzen, 1973; 1974):

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \] (26)  
\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \] (27)  
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + \text{NO}_2 \] (28)  

Net: \( \text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 \) (29)

2.3.4 The Influence of Nitrogen Oxides

Nitrogen oxides (\( \text{NO}_x \)) are produced in urban areas through man-made activities such as fossil fuel combustion and biomass burning (Martin et al., 2007; Labrador et al., 2005; Boersma et al., 2005). Nitrogen oxides also can be emitted naturally from soils, lightning strikes, forest fires started by lightning strikes and oxidation of atmospheric ammonia, \( \text{NO}_x \) is transported from the stratosphere to the troposphere and can be formed through anthropogenic activities involving complex photochemical reactions.
Reaction 30 below shows the photolysis of NO$_2$ by UV radiation at wavelengths between 300 nm and 400 nm to form nitric oxide (NO) and an O atom. Atomic oxygen reacts with an O$_2$ molecule to form an O$_3$ molecule (Reaction 31). Reaction 31 shows the formation of O$_3$ molecule whereas reaction 32 shows O$_3$ titration by NO in the absence of UV radiation (e.g. during night hours). Ozone titration is strong closer to NO-sources and dominates ozone formation and could be the reason why ozone concentrations are lower in the city than in rural areas (Lelieveld and Dentener, 2000). Therefore, NO$_x$ can either generate or destroy O$_3$, depending on the levels of UV radiation.

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad \text{(between 300nm to 400nm)} \quad (30)
\]
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (31)
\]
\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (32)
\]

M represents any other molecule (usually N$_2$ or O$_2$ since these two molecules constitute 99% of the volume of air) and hv represents ultraviolet radiation.

Other important reactions for tropospheric O$_3$ chemistry include the formation of gaseous nitric acid (HNO$_3$) through the oxidation of NO$_2$ into nitrate (NO$_3$), dinitrogen pentaoxide (N$_2$O$_5$) is formed through the reaction of NO$_2$ and NO$_3$, later N$_2$O$_5$ reacts with water (H$_2$O) to form HNO$_3$. These reactions occur during the night in the absence of NO$_x$ photolysis (Seinfeld and Pandis, 2006).

\[
\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \quad (33)
\]
\[
\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (34)
\]
\[
\text{N}_2\text{O}_5 \text{ (g)} + \text{H}_2\text{O (l)} \rightarrow 2\text{HNO}_3 \text{ (aq)} \quad (35)
\]

M represents any other molecule (usually N$_2$ or O$_2$ since these two molecules constitute 99% of the volume of air).
During the day, HNO$_3$ is formed directly from the reaction of NO$_2$ and OH. Reaction 36 below occur when VOC/NO$_2$ ratio is less than an average of 5.5 in urban areas (Seinfeld and Pandis, 2006).

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (36)$$

2.4 Sources of Ozone Precursors

2.4.1 Biogenic emissions

The role of biogenic emissions (from soil and vegetation) in tropospheric O$_3$ chemistry has been studied since the 1970s. In tropical regions, biogenic emissions are particularly important in O$_3$ chemistry (Aghedo et al., 2007). The most important biogenic emission for tropospheric ozone production is the direct emission of NO from recently wetted-soils. Ludwig et al. (2001) and Delon et al. (2009) reported that NO$_X$ emissions are dependent on precipitation, history of soil type and temperature. Van der et al. (2008) used satellite data and reported summer maximum NO$_X$ emissions in both Hemispheres. This maximum was not correlated with the release of NO$_X$ from biomass burning events in winter. These researchers concluded that approximately 40% of surface NO$_X$ in Africa is due to soil emissions.

2.4.2 Lightning

It is well well-known that lightning can lead to increase in NO$_X$ concentrations in the middle and upper troposphere (Choi et al., 2005; Zhang et al., 2003). Lightning occurrence depends on geographic location with greater frequency in tropical areas relative to mid-latitudes and polar regions due to higher temperatures in the tropics. During the day the land surface is heated, causing convectional currents, cloud formation and potential lightning. These lightning strikes occur frequently in Central Africa (http://www.crh.noaa.gov). The effect of lightning on NO$_X$ production had been extensively studied (e.g. Price et al., 1997; Pickering et al., 1998) and it has been revealed that NO$_X$ production occurs during the high energy return stroke phase of the flash and about 75% to 95% of the produced NO$_X$ is in the form of NO. Nitric oxide is produced through the Zel'dovich mechanism, which breaks down the N$_2$ and O$_2$ molecules (Price et al., 1997) at the high temperatures caused by the lightning stroke. Price et al. (1997) reported that the nature of clouds plays a critical role in NO formation with cloud to ground (CG) flashes
producing $6.7 \times 10^{26}$ molecules of NO per flash whereas intracloud (IC) flashes produces $6.7 \times 10^{25}$ molecules of NO per flash. Pickering et al. (1998) observed that clouds with larger volumes above freezing level have more IC flashes than CG flashes and that the ratio of IC/CG is higher in tropics than in the mid-latitudes.

Studies conducted by Tie et al. (2002) and Grewe et al. (2001) using the Goddard Institute for Space Studies (GISS) model show that lightning contributes about 16% (6.5 TgN/yr) of the total NO$_x$ global budget whereas biomass burning and fossil fuel burning contribute about 70% of the NO$_x$ global budget. These figures were collected from Global Emission Inventory Activity (GEIA) dataset (Benkovitz et al., 1996; Olivier et al., 1996). According to Martin et al. (2007); Labrador et al. (2005) and Boersma et al. (2005) global estimates of NO$_x$ emissions from lightning vary between 1 to 20 TgN/yr, whereas 5±3 TgN/yr is applied for most modelling (Schumann and Huntrieser, 2007). In 2001 the Intergovernmental Panel on Climate (IPCC, 2001) highlighted the uncertainty on the estimates applied in models for NO$_x$ emissions from lightning, stating that lightning produced NO$_x$ ranges between 2-20 TgN/yr. A further study is required to reduce this uncertainty. Later, Shindell et al. (2003) used the NASA GISS global carbon model to study the effect of lightning produced NO$_x$ on tropospheric O$_3$, and reported a global radiative forcing of 0.35 W/m$^2$ in June, July and August and 0.26 W/m$^2$ in December, January and February.

2.4.3 Biomass burning

Biomass burning impacts air quality and the carbon budget due to emissions of aerosols trace gases such as CO, hydrocarbons and NO$_x$ (Andreae and Merlet, 2001; Crutzen and Andreae, 1990; Marufu et al., 2000; Thompson et al., 2001). These pollutants can be transported many thousands of kilometres downwind. Annual NO$_x$ emissions of 20.9 TgN/yr were reported from biomass burning (Tie et al., 2002 and Grewe et al., 2001). Africa has been reported as the continent emitting the largest quantity of biomass burning emissions (Figure 2.4). Several researchers (Andreae, 1991; van der Werf et al., 2003; van der Werf et al., 2006) have reported that African fires are responsible for an average of 30 to 50% of the total amount of vegetation burned globally each year, making Africa, on average, the single largest biomass burning emissions source. Tropical countries are affected more by biomass burning compared to mid-latitudes and polar regions because of the greater abundance of vegetation combined with populations reliant of biomass for fuel. It has been estimated that approximately 85% of biomass
burning occurs in tropical countries (Andreae, 1991) and with increasing population the demand for land use is increasing. The main sources of biomass burning reported in previous studies (e.g. Delmas et al., 1999; Crutzen and Andreae, 1990) are man-made activities (such as forest clearance, savannah burning, restoration and land management). These sources of biomass burning are particularly evident during dry and hot season, (e.g. Thompson et al., 2000; Edwards et al., 2003; Jourdain et al., 2007) in late November to early March in Northern Hemisphere and July to October in the Southern Hemisphere. However, the frequency and intensity of fires is also dependent on meteorological and climatic conditions (Palacios-Orueta et al., 2004). Colour coding on the vertical axis in Figure 2.4 shows the global fire frequency for the period 2000 to 2009.

Figure 2.4: Average annual number of fires that occurs from 2000 to 2009 (http://www.gfdl.noaa.gov).

Figure 2.5 shows a biomass burning event that occurred in September 2008 in South Africa, Swaziland and Mozambique. Several studies on biomass burning have been conducted over a long period (e.g. Seiler and Crutzen, 1990; Hao and Liu, 1994) using statistical and inventory data. However these datasets were found to be incomplete and only available for a specific time period. An attempt was made to limit insufficient biomass burning data by starting satellite measurements e.g. Moderate Resolution Imaging Spectroradiometer (MODIS), Global Burned Area (GBA), Global Burn Scar Atlas (GLOBSCAR), Global Fire Emission Database (GFED
3.1) and Global Burn Scar Atlas Lund-Potsdam-Jena Global Dynamic Vegetation model (GLOBSCAR LPJ- DGVM) to improve the estimates of biomass burning emissions.

Seasonal cycles of O$_3$ can be affected by biomass burning. Zunckel et al. (2004) reported O$_3$ maxima in spring in Africa, and this maximum coincides with biomass burning period. In addition, another study on elevated O$_3$ events during spring over Johannesburg (Raghunandan et al., 2007), revealed the impacts of biomass burning, biogenic emissions and lightning precursors on ozone concentrations in this region.

Figure 2.5: Fires burning in Mozambique, South Africa and Swaziland in September 2008 (www.earthobservatory.nasa.gov).

2.4.4 Industrial and Vehicular Emissions

Precursor gases involved in the photochemical O$_3$ production are at higher concentrations in urban areas due to high traffic (automobile emissions) and industrial activities (Baker et al., 2008; Bradley et al., 1999; Warneke et al., 2007). Fossil fuel combustion is higher in developed countries, notably in the Northern Hemisphere (e.g. Lilieveld and Dentener, 2000). The Southern Hemisphere is considerably less polluted than the Northern Hemisphere because of a lower average population density (Figure 2.6), lower levels of industrialisation and fewer land masses.
Although the sources of industrial emissions are lower in the Southern Hemisphere, they still have a significant influence on the levels of urban smog.

Figure 2.6 shows industrial activities (I), fossil fuels (F) and biofuel combustion (B) (collectively known as IFB-NO\textsubscript{x} emissions) for both Hemispheres. Population data used in Figure 2.6 was obtained from United States Central Intelligence Agency (The World Fact Book- CIA, (2007), while emission data was obtained from Olivier and Berdoski (2001). Biofuel burning provides about 15\% of the world’s primary energy (Bhattacharya and Salam, 2002), with 13\% used in developing countries and the remaining 2\% in developed and/or industrialized countries. The Southern Hemisphere has a greater proportion of developing countries compared to the Northern Hemisphere.

![Figure 2.6: (a) Global human population and (b) IFB-NO\textsubscript{x} emissions in 2000 (www.unece.org).](image)

Africa is a continent with a number of developing countries with increasing populations, increasing numbers of automobiles and increasing industrial emissions. Previous studies conducted by United States Environmental Protection Agency (http://www.epa.gov) and Wallington et al. (2008) reported that motor cars release high hydrocarbons, CO, carbon dioxide (CO\textsubscript{2}), NO\textsubscript{x}, nitrous oxide (N\textsubscript{2}O), particulate matter (PM), hydrofluorocarbon-134a (HFC-134a) and CH\textsubscript{4} from incomplete combustion of petroleum-based fuels in motor car engines. These emissions vary according to the automobile type and primary fuel used (http://www.epa.gov).
In 2005, African fossil fuel emissions contributed about 285 TgC, accounting for 3.7% of the global emissions (Canadell et al., 2008). Figure 2.7 shows South Africa as the highest emitter of fossil fuels in Africa with an average of 110.1 TgC/yr from 2000 to 2005 followed by Egypt (38.2 TgC/yr), Nigeria (25.1 TgC/yr) and Algeria (22.4 TgC/yr). In South Africa, coal fired powered stations located in the Highveld and Mpumalanga, timber processing plants, coal and metal mines, smelters, brick factories and petrochemical operations are major sources of carbon emissions (Kirkman et al., 2000). As much as 80% of South Africa’s electricity is generated by coal–fired power station in Mpumalanga making the Highveld an air pollution ‘hotspot’ (Tyson et al., 1988).

Figure 2.7: Annual emissions of carbon (TgC/yr) from the combustion of fossil fuels and land use change and forestry (LUC&F). Top fifteen African countries averaged for the period 2000–2005 (Canadell et al., 2008).
2.5 Ozone Sinks

2.5.1 Dry deposition
Gases and aerosols often adhere to surfaces with which they come into contact. Normally, the rate of dry deposition increases with the reactivity of the gas and depends on the type of surface. Dry deposition on terrestrial and ocean surfaces serves as a physical ozone sink. Ganzeveld et al. (2009) estimated that 200 to 300 Tg/yr of O_3 is deposited to the ocean surface. The deposition velocities ranges between 0.01 to 0.15 cm.s\(^{-1}\) for ocean water and 0.01 to 0.10 cm.s\(^{-1}\) for fresh water. Nightingale and Liss (2003) reported that the deposition velocity is influenced by wind as water turbulence controls the exchange rate. Lower O_3 fluxes are reported for water relative to land surfaces.

2.5.2 Photolysis
Photolysis is another important tropospheric O_3 sink. The destruction of O_3 is caused by short wavelength radiation (\(\lambda < 340\) nm).

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} \quad (37)
\]

The O atom then reacts with water vapour to form two hydroxyl radicals (OH) by Reaction 7 above.

The lifetime of ozone depends on the level of solar radiation and the concentration of water vapour (Zachariasse et al., 2000). In areas with drier atmosphere (middle and upper troposphere), the O_3 lifetime is longer (3 months) relative to the continental or marine boundary layer where ozone molecules survive for 2 to 5 days (Fishman et al., 1990).

2.5.3 \(\text{HO}_2/\text{OH}\) Catalysed Destruction
Ozone is destroyed by OH and \(\text{HO}_2\) (hydroperoxy) radicals (Lelieveld and Dentener, 2000) as shown in Equations 28 above and 38 below:

\[
\text{O}_3 + \text{HO}_2 \rightarrow 2\text{O}_2 + \text{OH} \quad (38)
\]
2.6 Effect of O$_3$ on Humans and the Environment

In different parts of the atmosphere, and at specific concentrations, ozone can have benefits or negative impacts on health and environments. In the stratosphere, ozone absorbs incoming ultraviolet solar radiation, and any weakening or thinning of this ‘ozone layer’ has implications for the health of humans and other animals. On the other hand, ozone in the lower troposphere acts as a strong greenhouse gas and, at concentrations above 60 ppb, O$_3$ affects the respiratory system, causing lung infections, asthma symptoms and premature mortality (Kinney et al., 1996). According to Lacis et al. (1990), Darrall (1989), Bertman and Roberts, (1991) and Derwent (1995), these high O$_3$ levels can affect human and plants directly or through the formation of poisonous gases such as peroxyacetyl nitrate (PAN). Finkelstein and Johnston (2004) reported that young children are more affected than adults since their lung development is not complete and they tend to have a higher breathing rate than adults. Pulikesi et al. (2006) estimated the number of deaths in the Netherlands related to O$_3$ increased from 990 to 1140 to 1400 people in 2000, 2002 and 2003 respectively.

In addition to the impacts on human health, higher levels of O$_3$ above 60 ppb are harmful to forests, natural vegetation and agricultural crops (National Research Council, 1999) as ozone has the potential to oxidise plant tissues. According to Wittig et al. (2009), present tropospheric O$_3$ levels and those estimated for later this century are toxic to trees and have potential to reduce the carbon sink. Ambient O$_3$ enters plant leaves through the stomata during gaseous exchange. Once in the leaves, it limits photosynthesis and other processes necessary for the healthy functioning of the plant (Morgan et al., 2006; Brooker, 2009). Ozone damage to plants was first observed in *Vitis vinifera* in southern California by Richards et al. (1958). Since then, O$_3$ has been reported as the pollutant that most damages vegetation (Gimelo et al., 1995; Penuelas et al., 1999) and cultivate crops (Treshow and Steward, 1973). Plants affected by O$_3$ may show severe injuries within palisade tissue (Paoletti et al., 2009) with black reddish or brownish spots on branches or stems (Fumagalli et al., 2001; Hayes et al., 2007).

O$_3$ has been reported to affect the diameter and size growth relationships in spruce and beech plants (Pretzsch and Dieler, 2011). Delay in flowering and fruit production due to O$_3$ has also be a concern (Hayes et al., 2012). In addition to these impacts, O$_3$ can form toxic compounds such as hydrogen peroxide (H$_2$O$_2$), superoxide (O$_2^-$), atomic oxygen (O) and hydroxyl radical.
Calatayud et al., (2011) concluded that the response to O₃ levels is controlled by genotype, competitors and ontogeny. Studies (e.g. Lyons et al., 2000; Paakkonen et al., 1995) have shown that thick leaves are more tolerant than thinner leaves.

2.7 Cycles and Trends in O₃ Concentrations
Since high concentrations of O₃ in the lower troposphere have implications for the environment (including its inhabitants), it is important to monitor its concentrations so that control measures can be put in place to avoid negative impacts. This section highlights research on these natural cycles and anthropogenic influences on ozone at the sites of focus.

2.7.1 Studies on diurnal cycles at SANAE, Cape Point and City of Cape Town
Ozone levels are at their minimum in the early morning and increase during the day as a result of photochemical processes, reaching their maximum in the early afternoon. During the night, ozone is removed by NO (Reaction 32, section 2.2.4) and remains low until the next morning when sunlight encourages O₃ formation again. Photolysis of ozone results in the formation of oxygen atom (O), which reacts with water vapor to produce the hydroxyl radical (Ramanathan and Dickinson, 1979; Fishman et al., 1979a). This hydroxyl radical (OH) is the most important tropospheric oxidant, removing pollutants and trace gases such as CO, CH₄, other hydrocarbons from the air.

In this study, diurnal cycles of O₃ and NOₓ at all four stations (SANAE, Cape Point background, Cape Point non-background, Molteno and Goodwood) and the NOₓ diurnal cycle at Goodwood are evaluated. The diurnal cycle at Cape Point has been studied extensively, with authors looking at the combined dataset (unfiltered data meaning background and non-background data not separated) (e.g. Labuschagne et al., 2001 and Zunckel et al., 2004) as well as the filtered O₃ background data. According to Zunckel et al. (2004) average minimum values (from 1999 to 2001) occur between 06:00 to 08:00 and maximum values at 15:00. An average peak-to-peak difference of approximately 4.0 ppb was reported for all data (all data refers to all data recorded over the study period with no filtering techniques employed) while an average peak-to-peak difference of less than 1.0 ppb was reported for background data (background refers to data filtered according to radon concentrations). The all data peak-to-peak was suspected to reflect
some of the anthropogenic NO\textsubscript{x} emissions that lead to O\textsubscript{3} formation during the day and O\textsubscript{3} titration during the night (Zunckel \textit{et al.}, 2004). Smaller diurnal ranges have been observed in polar data relative to non-polar datasets (marine and continental), suggesting cleaner air with low NO\textsubscript{x} in the polar regions, most likely due the lack of anthropogenic emissions in these region (Ayers \textit{et al.}, 1997; Monks \textit{et al.}, 1998) sites.

Research conducted by Wichmann (2006) on diurnal cycles in the Cape Town region (Goodwood and Molteno stations specifically) showed higher O\textsubscript{3} concentrations during the day relative to the night and early hours of the day. The same study showed that NO\textsubscript{x} concentrations were inversely proportional to O\textsubscript{3} concentrations at these stations. This inverse relationship between O\textsubscript{3} and NO\textsubscript{x} suggests NO\textsubscript{x} titration.

\textit{2.7.2 Ozone Weekend Weekday Variations}

Higher ozone levels on weekends relative to weekdays at urban stations have been described by several researchers (e.g. Elkus and Wilson, 1977; Debaje and Kakade, 2006; Swamy \textit{et al.}, 2012). As these studies showed, O\textsubscript{3} concentrations are higher over the weekend despite that ozone precursor concentrations tend to be lower at this time of the week. This phenomenon has been termed the ‘weekend effect’ (e.g. Debaje and Kakade, 2006), According to Liu \textit{et al.} (1987), ozone production decreases as the NO\textsubscript{x} concentration increases during the week. Lower NO\textsubscript{x} concentrations on weekends are associated with lower traffic levels. This results in higher O\textsubscript{3} concentrations due to less NO\textsubscript{x} titration (Sadananga \textit{et al.}, 2008; Shutters and Balling, Jr., 2006). According to Swamy \textit{et al.} (2012), black carbon (BC) concentrations are lower on weekends and BC has a similar diurnal cycle to NO\textsubscript{x}. Less BC on weekends is also associated with high O\textsubscript{3} concentrations due to less absorbance of sunlight by BC particle emissions.

Although many studies have been carried out on diurnal cycles at the four stations of focus in this study (SANAE, Cape Point, Molteno and Goodwood), weekend/weekday variations (and their relationship with NO\textsubscript{x} fluctuations) have not been thoroughly investigated before. The effect of other O\textsubscript{3} precursors such as CO and VOCs in O\textsubscript{3} variations over the weekend is not assessed in this study due to the lack of monitoring data in the study areas.
2.7.3 Studies on Seasonal Cycles at SANAE, Cape Point and City of Cape Town

According to Helmig et al. (2007) polar stations show maxima during winter months because of the weakness of ozone sinks during the dark hours when there is no solar radiation. Larger seasonal ranges (approximately 5 ppb) in the Southern Hemisphere polar regions compared to the Northern Hemisphere polar regions are most likely due to less summertime photochemical ozone destruction and more transport of ozone rich air to the Arctic during the Northern Hemisphere spring and summer months (Helmig et al. 2007).

Seasonal cycles have been studied by several researchers at Cape Point (e.g. Oltmans and Levy II, 1994; Brunke and Scheel, 1998; Labuschagne et al., 2001; Zunckel et al., 2004; Brunke et al., 2009). A continuous seasonal cycle with summer minimum and winter maximum was reported at Cape Point and other Global Atmosphere Watch (GAW) stations (SAMOA, Cape Grim, and South Pole) by Oltmans and Levey II (1994). Further investigations conducted by Brunke and Scheel (1998) revealed a similar seasonal trend with a maximum in July/August and minimum in January for Cape Point. Minima were associated with O$_3$ photolysis in summer when the intensity of ultraviolet (UV) light reaches its peak. The study conducted by Labuschagne et al. (2001) using a 1999 to 2001 dataset shows minima ranging between 14.0 to 17.0 ppb (in summer) and maxima ranging between 31.0 to 32.0 ppb (in winter).

A comparative study was done in 2004 for various ozone monitoring sites in southern Africa (Bosjespruit, 5 km from Secunda, Amersfoort, approximately 90 km from Secunda, Cape Point and Maun in Botswana) by Zunckel et al. (2004). Cape Point was the only site experiencing its ozone maximum in winter. Other sites recorded their maxima in late winter or spring (from August to October) and minima in summer months (December and January). Zunckel et al. (2004) also reported results from passive samplers deployed at Cape Point (June 2000 to May 2002). This passive sampling formed part of a collaborative program between Cape Point and North West University (NWU). Results showed maxima between May and July and minima between December and January. Monthly averages calculated from passive samples were in good agreement with in situ monthly averages from June 2000 to May 2002 at Cape Point. Overall, the seasonal cycle is fairly consistent from year to year and typical of the background Southern Hemispheric marine troposphere.
The current study investigates seasonal cycles at SANAE, Cape Point, Molteno and Goodwood. In addition, Cape Point non-background seasonal cycles are investigated. This allows a comparison between seasonal cycles at SANAE and Cape Point background, and between seasonal cycles at Cape Point non-background and seasonal cycles in the urban Cape Town region.

2.7.4 Effect of Meteorology on Surface Ozone Measurements

Meteorological parameters such as wind direction, wind speed, humidity, solar radiation, cloud cover and temperature are the main forces which drive the reactions of O\textsubscript{3} and its transport to surrounding areas. Winds with low speed, high solar radiation, high temperatures, and low humidity generally promote increased ozone. Contrary to this, wet, rainy weather with high relative humidity is typically associated with the low O\textsubscript{3} concentrations provided by wet ozone deposition on the water droplets (Tarasova and Karpetchko, 2003). Associated with the regular cold fronts traversing the Cape coastline in winter, strong north-easterlies and rainfall clean the urban atmosphere over Cape Town. In-between cold fronts episodes, an anticyclonic ridge bring stable conditions and promote the accumulation of pollutants (Jury et al., 1990), often resulting in a brown haze, consisting of O\textsubscript{3}, Peroxyacytyl nitrate (PAN) and other organic compounds, (Wicking–Baird et al., 1997). Stable conditions are further promoted by the onset of surface temperature inversions at night, which only subside when surface temperatures rise after sunrise. Pollutants can be trapped within the surface inversion, or below it as it erodes from the surface up after sunrise (fumigation), which increases local pollutant concentrations.

Polar regions experiences snow in winter months and temperatures are very low during this period. Studies conducted by Domine and Shepson (2002) and Shepson et al. (2003) in the Arctic and Antarctic have demonstrated that snowpacks release NO\textsubscript{x} and there is gaseous exchange between the boundary layer and the atmosphere. This agrees with a previous study by Honrath et al. (1999) that revealed that NO\textsubscript{x} forms during the photolysis of NO\textsubscript{3} in snowpacks and is released to the atmospheric boundary layer (Honrath et al., 1999). According to Domine et al. (2008), controls on the release of NO\textsubscript{x} from snow packs are temperature, pH and ion content. These factors control the chemical and physical properties of NO\textsubscript{x}. 
2.7.5 Studies on long term trends in ozone at SANAE, Cape Point and City of Cape Town

Brunke et al. (2011) reported a small increase of O$_3$ at the 30 m intake of approximately 0.17 ppb/year from 1990 to 2009 in SANAE, Cape Point and Cape Town. Brunke et al. (2011) also reported changes at 4 m and 30 m from 1990 to 1999 and 2000 to 2009. From 1990 to 1999, the measurements at 30 m showed an increase of approximately 0.30 ppb/yr across seasons. From 2000 to 2009, a non-significant decrease of approximately 0.07 ppb/yr and 0.06 ppb/yr for the 4 m and 30 m intakes respectively was reported. Results showed that long term O$_3$ trends are not dependent on the intake height. A continuous increase of approximately 0.4 ppb/yr from 1999 to 2001 was reported by Zunckel et al. (2004). This study showed that O$_3$ is not easily linked to an individual source but is the result of photochemical reactions between the products of a number of source types, with precursor gases potentially transported over great distances. These observations highlight the importance of examining meteorological effects in detail so that the atmospheric transport of precursors can be better understood.

2.8 Conclusion

It can be concluded that there are a number of factors affecting the concentrations of O$_3$. These factors include the influence of industrial and vehicular emissions, lightning, biomass burning, biogenic release, stratospheric-tropospheric exchange, photolytic destruction and dry deposition. These factors can affect both the short and long term trends of O$_3$. Therefore, it is very important to consider such factors when conducting O$_3$ studies. High concentrations of O$_3$ exceeding 60 ppb have a negative effect on human and environment.
(Data and Methodology)

3.1 Introduction
This chapter presents the analytical techniques and calibration methods as applied at SANAE, Cape Point, Molteno and Goodwood. In this chapter, the approach to data analysis is presented for the investigation of diurnal and seasonal cycles, the weekend effect, the effect of meteorology on surface O$_3$ concentrations, and any long term trends.

3.2 Ozone Measurements at Cape Point, SANAE and City of Cape Town
An intake line mounted from the top of a 30 m mast was established for sampling at Cape Point in 1982. In 1996, measurements commenced from a second air intake (at 4 m above ground level). In September 2008, another intake at 14 m above ground level was installed. The SANAE air intake is approximately 11.5 m above ground level while the stations in the City of Cape Town air intakes are approximately 5 m above ground level.

Measurements are continuous at Cape Point, with one minute samples averaged to 30 minute output values. Measurements are made by three Thermo Electron (Teco) analyzers based on an ultraviolet (UV) detection technique. SANAE employs the same Thermo Electron (Teco) analyzer as Cape Point, while each station in the City of Cape Town utilizes an Ozone Analyzer API (Model 400A) with UV absorption. This model is appropriate for analysing ozone in an urban environment.

3.2.1 Validation procedure
An O$_3$ calibrator (TEI 49i-PS) is used to verify the three instruments at Cape Point every two months or when there is analytical suspicion. Daily zero and span sensitivity checks are conducted automatically. Monthly zero-calibration levels are factored into the data processing routine, while the span sensitivity values provide information on long-term instrument stability. Calibrations are performed by World Calibration Centre (WCC-Empa) every four years and the last audit at Cape Point was conducted in August 2011. WCC-Empa audits all stations in the Global Atmosphere Watch (GAW) network and the audit reports are sent to the World
Meteorological Organisation (WMO). With the exception of WCC-Empa audits, SANAE follows the same strategy as Cape Point and has a zero and span sensitivity run each day. The instrument is shipped to Cape Point for verifications with their calibrator, normally after a year or immediately if there are concerns of mal-performance. The Molteno and Goodwood instruments are calibrated with a South African National Accreditation Service (SANAS) calibrator every three months while a portable calibrator (O₃ Calibrator, Model 306) is used at the sites every two weeks.

3.2.2 Validation comparison: Cape Point and City of Cape Town

As part of the current study, the City of Cape Town portable calibrator was used to validate one of the instruments (sampling at 4m intake) at Cape Point. It was decided that a comparison of validation results was necessary when the initial analysis of the monitoring datasets showed that the Cape Town O₃ concentrations generally are lower than Cape Point O₃ concentrations yet it was expected that the urban O₃ concentrations would be higher. This comparison exercise was conducted for two days (22\textsuperscript{nd} and 29\textsuperscript{th} of October 2012). After the verifications, results were compared to the verification results obtained when using Cape Point calibrator. Outcomes (Figures 3.1, 3.2 and 3.3 and Table 3.1 and 3.2) achieved from these tests verified the consistency between Cape Point and Cape Town validation approaches and established that the data from these stations are comparable and representative of ambient concentrations if one assumes that the two calibrators do not have the same degree of error and in the same direction. This is a fair assumption.
Table 3.1 below shows the validation results obtained when verifying the Cape Point analyzer (4 m intake) with the Cape Town calibrator on the 22nd of October 2012. Column 1 shows O₃ concentrations generated from the calibrator (calibrator output to the analyzer), while column 2 shows O₃ readings recorded by the analyzer. During this verification, the Cape Point analyzer reads higher by approximately 7.2 ppb at each level of the calibrator setting (0 ppb to 180 ppb). Column 3 shows actual O₃ concentrations recorded by the analyzer after eliminating the offset (7.17 ppb) of the calibrator. Column 4 shows the difference between the O₃ generated from the calibrator and the O₃ concentrations recorded by the analyzer.
Table 3.1: Validation of Cape Point 4m O$_3$ analyzer using City of Cape Town O$_3$ calibrator on the 22 of October 2012

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Town O$_3$ calibrator [ppb]</td>
<td>Cape Point O$_3$ analyzer (4m intake)</td>
<td>Cape Point O$_3$ analyzer (4m intake) minus offset (7.17)</td>
<td>Calibrator minus Cape Point analyzer (4m intake)</td>
</tr>
<tr>
<td>0.0</td>
<td>7.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>37.4</td>
<td>30.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>60.0</td>
<td>68.4</td>
<td>61.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>90.0</td>
<td>98.8</td>
<td>91.6</td>
<td>-1.6</td>
</tr>
<tr>
<td>120.0</td>
<td>129.2</td>
<td>122.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>150.0</td>
<td>158.9</td>
<td>151.7</td>
<td>-1.7</td>
</tr>
<tr>
<td>180.0</td>
<td>187.9</td>
<td>180.7</td>
<td>-0.7</td>
</tr>
</tbody>
</table>

Figure 3.2: Cape Point 4m O$_3$ analyzer validations using City of Cape Town O$_3$ calibrator on the 29 of October 2012

Table 3.2 below shows the validation results obtained when verifying the Cape Point analyzer (4m intake) with the Cape Town calibrator on the 29$^{th}$ of October 2012. Column 1 shows O$_3$ concentrations generated from the calibrator (calibrator output to the analyzer), while column 2 shows O$_3$ readings recorded by the analyzer. During this verification, the Cape Point analyzer read higher by approximately 3.5 ppb at each level of the calibrator setting (0 ppb to 180 ppb).
Column 3 shows actual O\textsubscript{3} concentrations recorded by the analyzer after eliminating the offset (3.50 ppb) of the calibrator. Column 4 shows the difference between the O\textsubscript{3} generated from the calibrator and the O\textsubscript{3} concentrations recorded by the analyzer. With the exception of the offset, the two verification results are in good agreement.

Table 3.2: Validation of Cape Point 4m O\textsubscript{3} analyzer using City of Cape Town O\textsubscript{3} calibrator on the 29 of October 2012

<table>
<thead>
<tr>
<th>Column 1 (Cape Town O\textsubscript{3} calibrator [ppb])</th>
<th>Column 2 (Cape Point O\textsubscript{3} analyzer (4m intake))</th>
<th>Column 3 (Cape Point O\textsubscript{3} analyzer (4m intake) minus offset (3.5))</th>
<th>Column 4 (Calibrator minus Cape Point analyzer (4m intake))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.5</td>
<td>29.7</td>
<td>0.3</td>
</tr>
<tr>
<td>30.0</td>
<td>33.2</td>
<td>62.9</td>
<td>59.4</td>
</tr>
<tr>
<td>90.0</td>
<td>93.0</td>
<td>89.5</td>
<td>0.5</td>
</tr>
<tr>
<td>120.0</td>
<td>124.1</td>
<td>120.6</td>
<td>-0.6</td>
</tr>
<tr>
<td>150.0</td>
<td>154.2</td>
<td>150.7</td>
<td>-0.7</td>
</tr>
<tr>
<td>160.0</td>
<td>163.7</td>
<td>160.2</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

Figure 3.3: Cape Point 4m O\textsubscript{3} analyzer validations using Cape Point calibrator
3.2.3 Filtering of data to background and non-background at Cape Point

Cape Point is regarded as a background station due to its location and dominant southerly winds, which originate from the Atlantic Ocean. When such air masses arrive at the station, they show the following characteristics: low radon ($^{222}$Rn) concentrations, carbon monoxide (CO) concentration stability over time, and generally low particulate concentrations (measured by a condensation particle counter, CPC), although there are exceptions when particulate measurements are high, possibly due to increased sea salt particulates. Contrary to this, non-background conditions are characterized by higher levels of $^{222}$Rn, higher particulate concentrations, and CO levels are more variable, as a result of non-homogenous air masses arriving from terrestrial sources. In non-background conditions, winds generally have lower speeds and the predominant wind direction is northerly.

Cape Point uses two separation techniques for filtering data into background and non-background categories, namely CO filtering technique Brunke et al. (2004) and $^{222}$Rn filtering technique Brunke et al. (2004). The radon technique reported by Brunke et al. (2004) to be more sensitive and filter data more adequately relative to the CO filtering technique. Radon occurs naturally as a radioactive gas as part of radioactive decay from radiogenic uranium to stable lead. Sources of radon are minerals rocks rich in potassium, thorium and uranium (e.g. granites) and ground water. Radon has a half life span of 3.8 days and after that decays to stable lead (http://www.epa.gov). In this study, the $^{222}$Rn filtering technique was selected to filter O$_3$ data into background (when $^{222}$Rn was less than 250 mBq$^{-3}$) and non-background (when $^{222}$Rn was more than 1200 mBq$^{-3}$) categories. When an air mass has a $^{222}$Rn concentrations between 250 to 1200 mBq$^{-3}$, it is referred to as a mixed mass (containing both background and non-background masses).

3.3 Data analysis

3.3.1. Diurnal analysis

Averages for each hour of the day (e.g. 1:00 am to 2:00 am, 2:00 am to 3:00 am etc.) were calculated for all the records from Sanae, Cape Point, Molteno and Goodwood. Thirty minute averages also were calculated from one minute data recorded at Cape Point and Sanae.
Point, hourly O$_3$ averages were calculated for background and non-background air masses. The background diurnal cycle was compared with the Sanae diurnal cycle while the non-background diurnal cycle was compared with Molteno and Goodwood diurnal cycles. Analysis of diurnal cycles is important for investigating O$_3$ patterns over the course of a 24-hour period and reflects the influence of local activities if wind data is available.

3.3.2. Weekend/weekday diurnal analysis

The hourly O$_3$ averages were calculated for weekdays (Monday to Friday) and weekends (Saturday and Sunday) at Sanae, Cape Point, Molteno and Goodwood to study the effect of vehicular emissions on O$_3$ concentrations. Vehicular emissions of NO$_x$ tends to be higher during the week. As discussed in section 3.1.3, Cape Point data used for this study was categorized into background and non-background categories. For the analysis of weekend and weekday diurnal cycles, hourly O$_3$ averages were calculated for both background and non-background datasets.

3.3.3. Seasonal analysis

Monthly O$_3$ averages were calculated from hourly O$_3$ averages at all four stations (Sanae, Cape Point, Molteno and Goodwood). At Cape Point station, monthly O$_3$ averages were calculated for both background and non-background categories. The main aim of separating Cape Point data is to study seasonal variations in both background and non-background data and to compare the Cape Point background O$_3$ seasonal cycle with O$_3$ seasonal cycle observed at Sanae, and to compare the Cape Point non-background O$_3$ seasonal cycle with the Molteno and Goodwood O$_3$ seasonal cycles.

3.3.4. Weekend/weekday seasonal cycle analysis

Weekday (Monday to Friday) and weekend (Saturday and Sunday) monthly O$_3$ averages were calculated from hourly O$_3$ averages at all four stations in order to investigate weekday O$_3$ seasonal cycles and weekend O$_3$ seasonal cycles. Furthermore, at Cape Point, the weekday and weekend O$_3$ seasonal cycles were calculated for both background and non-background data. As mentioned earlier in this chapter, the separation of O$_3$ and NO$_x$ data into weekday and weekend categories assists in the assessment of the influence of vehicular emissions on ambient O$_3$ concentrations.
3.3.5. Effect of meteorology on surface ozone

The influences of several meteorological parameters on O$_3$ concentrations at the various stations were assessed. The selected meteorological parameters were as follows: temperature (°C), humidity (%), wind speed (m/s) and wind direction (°). These parameters are monitored at Vesleskarvet weather station (closest meteorological station to SANAE), Cape Point, and Cape Town weather office (approximately 19 km from Molteno and approximately 12 km from Goodwood).

To assess the effect of wind speed on surface O$_3$, wind speed was categorized into three categories: i) winds less than 5 m/s, ii) winds between 5 to 10 m/s and iii) winds between 10 to 15 m/s. Surface O$_3$ was filtered according to the wind speed categories mentioned above. Monthly O$_3$ averages were calculated from hourly O$_3$ averages for each wind speed category. For the investigation of the influence of wind on O$_3$ measurements, wind direction was segregated into sixteen azimuth sectors, each being 22.5°, increasing clockwise from N (0°) . Pollution roses were constructed. In addition, monthly O$_3$ averages were calculated for summer (December-February), autumn (March- May), winter (June-August) and spring (September-November) for each wind sector. These data were used to construct O$_3$ pollution roses for all seasons at all four stations. Similarly, a NO$_x$ pollution rose was constructed using Goodwood data by following the same procedure as described above. This analysis is critical for relating wind with NO$_x$ emissions associated with traffic.

3.3.6. Correlation analysis of surface ozone

Correlation analysis between hourly O$_3$ averages at SANAE and hourly O$_3$ averages at Cape Point background were conducted at the 95% confidence level. A similar analysis was done between hourly O$_3$ averages at Cape Point non-background and hourly O$_3$ averages at Molteno and hourly O$_3$ averages at Goodwood. The correlation between hourly NO$_x$ averages and hourly O$_3$ averages at Goodwood offered a further perspective on the influence of vehicular emissions on O$_3$ concentrations. Additional correlation analyses were conducted for monthly O$_3$ averages and monthly averages of meteorological parameters (temperature and humidity).
3.3.7. Long term trends of surface \(O_3\)
Long term trends in \(O_3\) concentrations were assessed by calculating annual \(O_3\) averages for all stations and plotting these on a graph. Average trend lines were then added to these graphs and their slopes were calculated for 2002 to 2009 at SANAE, 1997 to 2009 at Cape Point, 1997 to 2007 at Molteno and 2000 to 2006 at Goodwood). The same approach was used to calculate the trend in annual \(NO_x\) concentrations at Goodwood. All the stations used in this study offered more than seven years of data, which allowed for some analysis of changes in annual average \(O_3\) concentrations over time. It is critical to know whether surface \(O_3\) concentrations are increasing, decreasing or stabilizing. The Cape Town region (Molteno and Goodwood stations) indicates the influence of anthropogenic activities on \(O_3\) concentrations over time. The \(NO_x\) record from Goodwood helped contextualize this trend analysis with respect to vehicular emissions.

3.4. Conclusion
It is very important to separate Cape Point data into background and non-background dataset because Cape Point is affected by both wind regimes. Although the SANAE dataset is not enough for long term trend analysis, all stations provided enough data for the analysis of diurnal, seasonal and weekend effect. Diurnal analysis are important to determine the effect of local pollution on \(O_3\) concentrations. While weekend/weekday analysis gives a better understanding on the effect of vehicular emissions.
CHAPTER 4

Results and Discussion

4.1 Introduction
This chapter presents the results of the analysis of ozone (O$_3$) concentrations of the three air intakes at Cape Point. Cape Point background and non-background concentrations are compared with O$_3$ measurements at SANAE, and the Molteno and Goodwood stations respectively. Diurnal and seasonal cycles, weekend effects and long term O$_3$ trends are also discussed for all stations.

4.2 Diurnal Cycles
This analysis focuses on the averages for each hour of the day across the records. These averages show that O$_3$ levels increase once solar radiation increases in the morning with sunrise, reaching a maximum in the afternoon. This can be explained by the increase in photolysis reactions as well as the emission of oxides of nitrogen (NO$_x$) by traffic and industry as the daytime progresses. The photolysis of ozone precursors to form ozone (Equations 30 and 31) occurs as UV radiation increases and the temperature rises in the morning, peaking in the afternoon. As UV radiation decreases, O$_3$ production decreases and more O$_3$ is destructed by NO titration (Equation 32) than produced. O$_3$ levels remain low until the next morning (Seinfeld and Padis, 2006).

Zunckel et al. (2004) reported O$_3$ minima occurring between 06:00 to 08:00 and maxima at 15:00 at Cape Point under background conditions. Current findings agree with these results with diurnal minima experienced between 08:00 and 09:00 for all three air intakes (Figure 4.1). Peak-to-peak values (i.e. difference between maxima and minima) for the 4 m, 14 m and 30 m background intakes are 1.81 ppb, 2.44 and 1.26 ppb respectively.
The non-background diurnal cycle (Figure 4.2) shows minima and maxima at similar times to the background diurnal cycle, but with different peak-to-peak values. Non-background peak-to-peak values for 4 m, 14 m and 30 m are 6.00 ppb, 6.13 ppb and 4.73 ppb respectively. Labuschagne et al. (2001) reported a peak-to-peak value of 4.00 ppb at Cape Point for the period of 1999 to 2001 when conducting a similar study. This value incorporated both background and non-background concentrations and it is expected that the non-background concentrations would have a higher peak-to-peak value because of greater NO\textsubscript{x} variations relative to background air.
Figure 4.3a illustrates a weak diurnal cycle in the Cape Point background data. There is small peak observed at 15:00 for Cape Point background. The peak-to-peak value of this cycle (1.81 ppb) is low but greater than that at SANAE (0.2 ppb). As Figure 4.3a reveals, there is no distinct diurnal cycle at SANAE over this period of study. This amplitude of 0.2 ppb at SANAE falls within the range of 0.00 to 1.5 ppb reported by Helmig et al. (2007) for polar regions. The strong correlation between the SANAE and Cape Point records (Figure 4.3b bottom) is not significant at the 95% confidence level ($p = 0.124$, $r = 0.7678$, $r^2 = 0.5896$).
Figure 4.3: (a) Average background O$_3$ diurnal cycles at SANAE and Cape Point from 2002 – 2009 and (b) Correlations between the background O$_3$ diurnal cycles at SANAE and Cape Point from 2002 – 2009.

The Cape Point non-background diurnal cycle resembles those of Molteno and Goodwood with the exception that cycles at the latter stations are more pronounced than at Cape Point, with a peak-to-peak value of 6.00 ppb at Cape Point in contrast to 12.16 ppb and 16.80 ppb for Molteno
and Goodwood respectively (Figure 4.4). Maxima occur between 14:00 and 15:00 and minima between 08:00 and 09:00 at Cape Point, Molteno and Goodwood. The morning peak between 04:00 and 08:00 is not visible in the Cape Point non-background record. A previous study (Wichmann, 2006) associated the morning peak with traffic emissions and this could explain its absence at Cape Point since this is not an urban station.

Figure 4.4 illustrates the O$_3$ and NO$_x$ diurnal cycles. The O$_3$ trend lags by five to six hours relative to the NO$_x$ trend. This delay has been observed by Pudasainee et al. (2006) for sites in the Northern Hemisphere. Figure 4.4 reveals an inverse relationship between NO$_x$ and O$_3$ concentrations at Goodwood. At Goodwood the diurnal range in O$_3$ and NO$_x$ is greater relative to non-industrial sites. Molteno and Goodwood diurnal trend is comparable with peak-to-peak values of 12.16 ppb and 15.02 ppb respectively. These results illustrate a greater variation in O$_3$ at Molteno and Goodwood, where more anthropogenic activities occur such that more NO$_x$ and other O$_3$ precursors are produced.

![Figure 4.4: Average O$_3$ diurnal cycles for Cape Point non-background, Goodwood, Molteno and NO$_x$ diurnal cycle for Goodwood (2000 – 2006).](image)
Figure 4.5a illustrates the positive correlation between average hourly non-background O\textsubscript{3} at Molteno and Cape Point from 2000 to 2006. The strong correlation is not significant at the 95% confidence level (p = 0.061, r = 0.7322, r\textsuperscript{2} = 0.5361). Figure 4.5b demonstrates a positive correlation between average diurnal O\textsubscript{3} experienced at non-background Goodwood and Cape Point from 2000 to 2006. The relationship, however, is not significant at the 95% confidence level (p = 0.1161, r = 0.6472, r\textsuperscript{2} = 0.4189).
Figure 4.5: (a) Correlations between the non-background O$_3$ diurnal cycles at Molteno and Cape Point from 2000 – 2006 (b) and correlation between the non-background O$_3$ diurnal cycles at Goodwood and Cape Point from 2000 – 2006.

Figure 4.6 reflects the inverse relationship between NOx and O$_3$ widely documented in literature. Although there is a relationship between the two variables in Goodwood from 2000 to 2006 hourly average data (Figure 4.6), the correlation is not significant at 95% confidence level ($p = 0.182$, $r = -0.57$, $r^2 = 0.32$).
4.3 Weekday and Weekend Diurnal Cycles

Weekday and weekend surface O$_3$ diurnal cycles were analysed using data for 2002 to 2009 at SANAE and Cape Point, and for 2002 to 2007 at Molteno and Goodwood. Surface ozone concentrations are higher over weekends at Molteno and Goodwood. This is most likely due to lower NO$_x$ emissions. Lower NO$_x$ promotes accumulation of O$_3$ because NO titration is limited.

Figure 4.7 illustrates the weekday and weekend diurnal cycles at SANAE. The O$_3$ trend cycle is similar for both weekdays and weekends although peak-to-peak values are slightly lower during the week (0.85 ppb) relative to weekends (0.94 ppb). Peak-to-peak values increase by only 0.09 ppb on the weekends. It can be concluded that there is no significant weekend effect at SANAE over the study period.
Figure 4.7: Average O₃ diurnal cycle for weekends and weekdays at SANAE (2002 – 2009).

A weekend effect is also not obvious for the Cape Point background data (Figure 4.8). The O₃ trend at Cape Point background is similar for both weekdays and weekends. Peak-to-peak values are slightly lower during the week (1.52 ppb) relative to weekends (1.66 ppb). The peak-to-peak difference is thus 0.14 ppb.
Figure 4.8: Average O₃ diurnal cycle for weekends and weekdays at Cape Point background station (1997 – 2009).

A weekend effect is not clear for the Cape Point non-background data (Figure 4.9). The O₃ trend at Cape Point non-background is similar for both weekdays and weekends although peak-to-peak values are slightly higher during the week (5.88 ppb) relative to weekends (5.52 ppb). Peak-to-peak difference thus decreases by 0.36 ppb. It can be concluded that Cape Point is not significantly impacted by the weekend effect. This is expected because the Cape Point station is not proximate to vehicular emission sources.
Figure 4.9: Average non-background O\textsubscript{3} diurnal cycle for weekends and weekdays at Cape Point (1997 – 2009).

Figure 4.10 shows the O\textsubscript{3} trend at Molteno. The minimum increases by 2.84 ppb while the maximum increases by 0.84 ppb on weekends. As such, peak-to-peak values are higher during the week (12.10 ppb) relative to weekends (11.56 ppb). Peak-to-peak difference decreases by 0.54 ppb on the weekends.
Figure 4.10: Average O$_3$ diurnal cycle for weekends and weekdays at Molteno (1997 – 2007).

Goodwood shows a clearer variation between weekdays and weekends (Figure 4.11). Here morning levels of O$_3$ are low, decreasing from around 05:00 until 09:00 before increasing to the afternoon peak. The minimum increases by 2.86 ppb and the maximum increases by 0.70 ppb on weekends. The peak-to-peak values decreases from 17.56 ppb during the week to 15.41 ppb for weekends. The peak-to-peak difference thus decreases by 2.15 ppb on weekends. The observed weekend effect is most likely related to the decreased number of automobiles on roads on weekends relative to weekdays resulting in lower NO$_x$ emissions on weekends. Therefore, there is less O$_3$ titration by NO$_x$ in the mornings on weekends.
Figure 4.11: Average O$_3$ diurnal cycle for weekends and weekdays at Goodwood (2000 – 2006).

Figure 4.12 illustrates NO$_x$ concentrations on weekends and weekdays at Goodwood. The times when NO$_x$ levels are low coincide with high O$_3$ levels and vice versa, suggesting O$_3$ titration by NO$_x$. The trend is similar to that found by researchers at stations where NO$_x$ is the main control on the weekend effect (e.g. Sadanaga et al. 2008). According to Debaje and Kakade (2006) higher O$_3$ on weekends is due to decreased NO$_x$ emissions resulting in less NO$_x$ titration of O$_3$. Jenkin et al. (2002), Palombo et al. (2006) and Sadanaga et al. (2012) reported that the VOC/NO$_x$ ratio plays a critical role in weekend effect. On weekends O$_3$ concentrations are higher while NO$_x$ and VOC emissions are lower, however it is hypothesised that there is more NO$_x$ reduction than VOC reduction on weekends and the ratio of VOC to NO$_x$ in the ambient air is likely to be greater on weekends relative to weekdays.
4.4 Seasonal Cycles

This analysis is based on monthly average concentrations across the records. Three air intakes at Cape Point (Figure 4.13) demonstrate similar seasonal cycles with minima occurring between January and February and maxima between July and August for background measurements. This pattern of summer minima and winter maxima is seen in many locations both in the Northern and Southern Hemispheres, e.g. Barbados (13°N; 59°W) (Oltmans and Levy III, 1994) and Cape Grim (41°S; 145°E) (Ayers et al., 1997). Other studies confirming this pattern include Logan (1985; 1999), Oltmans and Komhyr (1986) and Janach (1989).

The 14 m intake shows lower O₃ levels (by approximately 1 ppb relative to the 4 m and 30 m air intakes) in June (Figure 4.13a). In July 2009, the 14 m intake recorded approximately 1 ppb higher than the other two intakes. The 14 m intake data is for 2009 only, whereas the data for the other two intakes covers the period from 1997 to 2009, and this could explain the observed variations. Figure 4.13b shows a similar trend for all three intakes with an average deviation of 0.24 ppb between the 4 m and 14 m intake and 0.05 ppb between the 4 m and 30 m intakes when analyzing only the 2009 datasets for each intake height.
Figure 4.13: Average background O$_3$ monthly values at (a) 4 m, 30 m (1997 to 2009) and 14 m (2009) at Cape Point and (b) average O$_3$ monthly values at 4 m, 14 m and 30 m (2009) at Cape Point.

Figure 4.14 illustrates non-background O$_3$ monthly averages observed from the three air intakes at Cape Point. As reported for the Cape Point background data, the 14 m dataset shows some differences to the 4 m and 30 m intakes. Higher O$_3$ values of approximately 3 ppb in March are
observed for the 14 m intake relative to other two intakes while in May, the 14 m intake reads lower by approximately 3 ppb relative to other intakes (Figure 4.14a). When analysing only 2009 data (Figure 4.14b), all three intakes show a similar trend. It is thus suggested that these differences are a result of the differences in the lengths of the records (i.e. 14 m is only one year long while the others are thirteen years long allowing for greater variation).

The analysis below is based on the 2009 data where all intakes show a similar seasonal trend. An increase of 8.57 ppb, 11.15 ppb and 8.57 ppb from January to March observed for the 4 m, 14 m and 30 m intakes respectively. A decrease in O₃ levels is observed for all three intakes in April, followed by a sustained increase of 7.43 ppb, 7.72 ppb and 8.53 ppb to July for the 4 m, 14 m and 30 m intakes respectively (Figure 4.14b).
Figure 4.14: Average non-background O$_3$ monthly values at Cape Point (a) 4 m, 30 m (1997 to 2009) and 14 m (2009) and (b) at 4 m, 14 m and 30 m (2009).

Figure 4.15 illustrates monthly NO$_x$ concentrations at Goodwood. A minimum of 27.5 ppb is observed in summer (January) while a maximum of 148.6 ppb is observed in winter (June). The effect of vehicular traffic and cold weather could be the reason of winter NO$_x$ maxima although a narrower atmospheric mixing depth over this time is likely to play a significant role in increasing concentrations.
Cape Point background station and SANAE experience their minima in summer (January) and maxima in winter (July or August). In late spring and winter months (April to August), concentrations at SANAE are higher by an average of approximately 2 ppb relative to Cape Point background concentrations (Figure 4.16). A minimum of 16.32 ppb is observed at SANAE and 16.70 ppb at Cape Point background, while the maximum at SANAE is 33.20 ppb and 31.05 ppb at Cape Point background. These result in peak-to-peak values of 16.88 ppb at SANAE and 14.36 ppb for Cape Point background. The SANAE peak-to-peak value falls within the range of 9 to 20 ppb as reported by Helmig et al. (2007) for polar stations in the Southern Hemisphere.
The urban sites show maxima in October, and minima in May and June for Molteno and Goodwood respectively (Figure 4.17). The Cape Point non-background seasonal cycle is comparable to the Molteno and Goodwood sites except that the minimum occurs in summer with a peak-to-peak value of 12.31 ppb compared to 8.79 ppb for Molteno and 6.11 ppb for Goodwood. Results thus reveal lower O$_3$ peak-to-peak values for the Cape Town region relative to Cape Point. These results highlight the importance of NO$_x$ in O$_3$ formation. At Molteno and Goodwood O$_3$ levels decrease during the autumn/winter months (April to June) but this trend is not clearly visible in the Cape Point non-background data. During this period, NO$_x$ levels are at their highest at Goodwood (Figure 4.15 above). A spring O$_3$ maximum (October) is evident in all three records (Figure 4.17). The reason for this maximum is not clear. There is debate on the causes of this peak but various studies have suggested that PAN and NO$_x$ also peak at this time (e.g. Bottenheim et al., 1994; Sirois and Bottenheim, 1995; Sorteberg et al., 1998; Solberg et al., 1997; Fenneteaux et al., 1999). At Goodwood, a NO$_x$ maximum is not linked to the O$_3$ spring maximum as NO$_x$ shows its maximum in winter. Liu et al. (1987) proposed that the observed O$_3$ spring maximum is due to the long O$_3$ winter lifespan of 200 days and he concluded that the observed spring amplitude could be the result of O$_3$ accumulation during the winter months.
Other studies (e.g. Wang et al., 1998; Jaffe et al., 2003) in the Northern Hemisphere have associated spring maxima with the intercontinental transport of pollution.

**4.5 Weekday and Weekend Seasonal Cycles**

Average monthly O$_3$ levels at SANAE (Figure 4.18) are similar on weekends and weekdays with insignificant differences occurring in late summer and springtime (Feb-May) when average weekend values are slightly higher than weekday values. The ‘weekend effect’ thus does not have a significant influence on this record.
Cape Point background monthly average concentrations (Figure 4.19) on the weekend are either similar or higher than average weekday concentrations for most months of the year, except for August, October and December when average weekday concentrations are higher. It is suspected that some of the higher weekend concentration months are an artifact of the separation process into background and non-background values rather than indicators of the influence of the ‘weekend effect’.

Figure 4.18: Monthly O₃ concentrations for weekdays and weekends at SANAE (2002 – 2006).
At Cape Point non-background (Figure 4.20), average weekend concentrations of $O_3$ are higher than weekdays during January, February, June, July and August, while average weekday concentrations are higher during the rest of the year. The ‘weekend effect’ may explain elevated weekend concentrations in the winter months of June to August. The differences between weekend and weekday concentrations are less pronounced during the summer months of January and February. NO$_x$ is the driving factor for the weekend effect. At Goodwood (Figure 4.21), average monthly weekday NO$_x$ concentrations are higher than average weekend concentrations throughout the year. In winter months, however, the difference between weekends and weekday concentrations can reach more than 20 ppb. This is likely to be related to two key factors. First, and most importantly, increased temperatures during summer increases atmospheric turbulence and the dilution of pollutants, thereby decreasing their concentrations. Thus vehicular emissions of NO$_x$ will be more diluted and have less effect. Second, the average number of vehicles on the roads are likely to be lower during the warmer (and drier) months as conditions are more conducive to walking, cycling or waiting outside for public transport. A further investigation is required with vehicular statistics in summer and winter.
At Molteno, average monthly weekday concentrations are lower than average monthly weekend concentrations except during July and December (Figure 4.22). The weekend effect may explain the more pronounced differences between higher weekend and lower weekday values during
March, April, June and September. The weekend effect is least evident during the summer
months (December to February) due to the seasonal pattern in weekday and weekend NO\textsubscript{x} described above with greater differences between weekday and weekend NO\textsubscript{x} concentrations during winter.

![Figure 4.22: Monthly O\textsubscript{3} concentrations for weekdays and weekends in Molteno (2002 – 2006).](image)

At Goodwood (Figure 4.23), average monthly weekday concentrations are lower than average weekend concentrations during all months except for January, September, October and December. The weekend effect may explain the particularly pronounced differences between higher weekend concentrations and lower weekday concentrations for April, June and August. The weekend effect is least apparent during some spring and summer months (September, October, December and January). It is suggested that the reasons for this follow the explanation described for Molteno above.
Figure 4.23: Monthly O$_3$ concentrations for weekdays and weekends in Goodwood (2000 – 2006).

Figure 4.24a illustrates the positive correlation between the weekday monthly averages at Cape Point non-background and Molteno. The relationship is significant at the 95% confidence level ($p = 0.01$, $r = 0.62$, $r^2 = 0.38$). Figure 4.24b shows the positive correlation between the weekday monthly averages at Cape Point non-background and Goodwood. The relationship is not significant at the 95% confidence level ($p = 0.191$, $r = 0.41$, $r^2 = 0.16$).
Figure 4.24: Correlations between average weekday concentrations of non-background $O_3$ at (i) Cape Point and Molteno and at (b) Cape Point and Goodwood from 2000 – 2006.

Figure 4.25a illustrates the strong positive correlation between the weekend monthly averages at Cape Point non-background station and Molteno. The relationship is significant at the 95% confidence level ($p = 0.00$, $r = 0.80$, $r^2 = 0.64$). Figure 4.25b shows the positive correlation between the weekend monthly averages at Cape Point non-background and Goodwood. The relationship is significant at the 95% confidence level ($p = 0.04$, $r = 0.60$, $r^2 = 0.36$). The correlation is higher for weekends than weekdays at Molteno and Goodwood. This observation can be explained by the higher concentrations of NO$_x$ during the week at the urban stations, which influences levels of $O_3$ at Molteno and Goodwood. On weekends, lower NO$_x$ at Molteno and Goodwood means that these stations show an increasing similarity with the Cape Point Station (non-background data), which is located some distance from traffic sources.
Figure 4.25: Correlations between average weekday concentrations of O$_3$ at (a) Cape Point non-background data and Molteno from 1997 – 2007 and at (b) Cape Point non-background and Goodwood from 2000 – 2006.
4.6 Angular Distribution of O$_3$

Angular distribution of ozone was worked out in this study as a function of wind direction. The closest station to SANAE that measures wind direction is Vesleskarvet station. Figure 4.26 illustrates the seasonal angular distribution of O$_3$ at SANAE as a function of wind direction measurements at Vesleskavet. Each sectoral component is the average ozone concentration measured during winds from that sector over the season of focus. SANAE is dominated by winds originating from the east with lowest frequencies from the north and north-east.

In summer (Fig. 4.26a), average O$_3$ levels are lower relative to other seasons. A somewhat uniform O$_3$ distribution is observed during this season with a maximum sectoral average concentration of 17.43 ppb from south-west and a minimum sectoral average of 16.06 ppb from the north-north-east. A difference of 1.37 ppb between maximum and minimum sectoral averages is recorded in summer.

Autumn is the season with the second lowest seasonal average (Fig. 4.26b). During this season, highest average concentrations are observed from the north with an average of 26.71 ppb while the sectoral minimum (22.46 ppb) is from the south. A difference of 4.26 ppb between maximum and minimum sectoral averages is recorded in autumn.

In winter, a more uniform O$_3$ distribution is observed with the lowest sectoral average of 30.20 ppb from the west and the highest sectoral average average levels of 33.00 ppb from the south-east (Fig. 4.26c). A difference of 2.80 ppb between maximum and minimum sectoral averages is recorded during this season.

Minimum concentrations observed in spring (22.48 ppb) (Fig. 4.26d) are similar to those recorded in autumn but are from the north. The maximum sectoral average of 30.79 ppb is observed from south-south-east. A difference of 8.30 ppb between maximum and minimum sectoral averages is recorded in spring. This sudden decrease of O$_3$ from the north (with an average of 8 ppb) was reported previously by Labuschagne et al. (2003).
Figure 4.26: Seasonal angular distribution of O$_3$ (ppb) as a function of wind direction at SANAE (2002 – 2009).

Figure 4.27 illustrates seasonal angular distribution of O$_3$ as a function of wind at Cape Point background.

In summer (Figure 4.27a), a somewhat uniform distribution of O$_3$ concentrations is evident, with a maximum sectoral average of 17.00 ppb from the south-east and a minimum sectoral average of 16.21 ppb from the north-north-west. A difference of 0.80 ppb between maximum and minimum sectoral averages is recorded during this season.

In autumn, a maximum sectoral average of 22.88 ppb is recorded from the west-north-west with and a minimum sectoral average of 21.40 ppb is observed from the south-south-east (Figure
4.27b). A difference of 1.47 ppb between maximum and minimum sectoral averages is recorded during this season.

In winter, minimum sectoral average concentrations (29.88 ppb) are observed from the north-north-west with a maximum sectoral average of 31.06 ppb from the west (Figure 4.27c). A difference of 1.18 ppb between maximum and minimum sectoral averages is recorded during this season.

Higher concentrations are observed in spring from the west and west-north-west with a maximum sectoral average of 27.32 ppb. The lowest sectoral average of 26.00 ppb is recorded from the east (Figure 4.27d). A difference of 1.33 ppb between maximum and minimum sectoral averages is recorded during this season.

Figure 4.27: Seasonal angular distribution of O₃ (ppb) as a function of wind direction in Cape Point background (1997 – 2009).
Figure 4.28 illustrates seasonal angular distribution of $O_3$ as a function of wind at Cape Point non-background.

In summer (Figure 4.28a), a somewhat uniform distribution of $O_3$ concentrations is evident, with a maximum sectoral average of 19.58 ppb from the west-north-west and a minimum sectoral average of 17.83 ppb from the east. A difference of 1.75 ppb between maximum and minimum sectoral averages is recorded during this season.

In autumn, a maximum sectoral average of 25.02 ppb is recorded from the west-north-west and a minimum sectoral average of 22.95 ppb is observed from the south-south-east (Figure 4.28b). A difference of 2.07 ppb between maximum and minimum sectoral averages is recorded during this season.

In winter, the minimum sectoral average concentration (26.22 ppb) is observed from the north-north-east while a maximum sectoral average of 31.38 ppb is observed from the west-south-west to west (Figure 4.28c). A difference of 5.17 ppb between maximum and minimum sectoral averages is recorded during this season.

Higher concentrations are observed in spring from the west and west-north-west with a maximum sectoral average of 31.03 ppb (Figure 4.28d). The lowest sectoral average of 26.98 ppb is recorded from the east. A difference of 4.04 ppb between maximum and minimum sectoral averages is recorded during this season.
Figure 4.28: Seasonal angular distribution of O₃ (ppb) as a function of wind direction in Cape Point non-background (1997 – 2009).

Figure 4.29 illustrates seasonal angular distribution of O₃ at Molteno as a function of wind direction measurements at Cape Town weather office.

In summer (Figure 4.29a), the maximum sectoral average of 19.42 ppb occurs from the south-south-east while the minimum sectoral average of 11.29 ppb is observed from the north-north-east and south-east. A difference of 8.13 ppb between maximum and minimum sectoral averages is recorded during this season.

In autumn, a maximum sectoral average of 19.52 ppb is recorded from the south and a minimum sectoral average of 11.15 ppb is observed from the east-south-east (Figure 4.29b). A difference of 8.37 ppb between maximum and minimum sectoral averages is recorded during this season.

In winter, minimum sectoral average concentrations (15.61 ppb) are observed from the north-east with a maximum sectoral average of 23.84 ppb from the north-west (Figure 4.29c). A difference of 8.23 ppb between maximum and minimum sectoral averages is recorded during this season.

Higher concentrations are observed in spring from the west with a maximum sectoral average of 24.38 ppb (Figure 4.29d). The lowest sectoral average of 16.67 ppb is recorded from the north-east. A difference of 7.71 ppb between maximum and minimum sectoral averages is recorded during this season.
Figure 4.29: Seasonal angular distribution of O$_3$ as a function of wind direction in Molteno (1997 – 2007).

Figure 4.30 illustrates seasonal angular distribution of O$_3$ and NO$_x$ at Goodwood as a function of wind direction measurements at Cape Town weather office.

In summer (Figure 4.30a), a maximum sectoral average of 15.49 ppb is observed from the south-south-east and a minimum sectoral average of 6.30 ppb is observed from the north-east. A difference of 9.20 ppb between maximum and minimum sectoral averages is recorded during this season.

In autumn, a maximum sectoral average of 16.10 ppb is recorded from the south and a minimum sectoral average of 6.20 ppb is recorded from the east-south-east (Figure 4.30b). A difference of 9.89 ppb between maximum and minimum sectoral averages is recorded during this season.
In winter, minimum sectoral average concentrations (5.74 ppb) are observed from the east while the maximum sectoral average of 17.60 ppb is observed from the west-north-west (Figure 4.30c). A difference of 11.86 ppb between maximum and minimum sectoral averages is recorded during this season.

Higher concentrations are observed in spring from the west-north-west with a maximum sectoral average of 19.72 ppb. The lowest sectoral average of 6.43 ppb is recorded from the east-north-east (Figure 4.30d). A difference of 13.29 ppb between maximum and minimum sectoral averages is recorded during this season.

Sectors with higher O₃ concentrations coincide with lower NOₓ concentrations and vice versa. Thus stations with greater differences between sectoral maxima and minima values indicate the influence of NOₓ sources in the direction of the O₃ minima. These observations are a reflection of theory (Section 4.1, Equation 3). Equation 3 shows O₃ titration by NOₓ, with higher levels of NOₓ causing decreases in O₃ concentrations. Higher NOₓ levels from north-east to east can be related to traffic peaks from surrounding areas. Neighbourhood sources of NOₓ in Goodwood include traffic at the Shell Petrol Station, traffic on Hugo Street, traffic on the corner of Milton Street, traffic at neighbouring schools (Fairbarn College, Hoerskool President), traffic at the proximate vehicle testing station, traffic at the Municipal buildings on Hugo Street, traffic on the N1, traffic on Giel Basson Road, and traffic on Frans Conradie Road. These sources of NOₓ are listed in order of proximity to the Goodwood station.

(a)  
(b)
Figure 4.30: Seasonal angular distribution of O$_3$ and NO$_x$ as a function of wind direction in Goodwood (2000 – 2006).

Figure 4.31 illustrates the angular distribution of NO$_x$ at Goodwood as a function of wind direction measurements at the Cape Town weather office. Data was filtered according to time, specifically morning traffic hours (06:00 to 09:00) and other times (20:00 to 05:00 and 10:00 to 15:00). During morning traffic hours, higher values of NO$_x$ are observed in all sectors relative to other times. These high values are related to a number of factors including increased traffic emissions and the persistence of an early morning inversion layer. The inversion layer is more evident in the morning hours and in winter months. The morning traffic maximum is much higher (by 133.95 ppb) than the other times. Outside of the traffic period, NO$_x$ levels decrease due to fewer vehicular sources. Atmospheric instability also generally increases during the course of the day after the morning inversion is lifted.
Figure 4.31: Angular distribution of NO\textsubscript{x} at Goodwood as a function of wind direction for morning traffic and other times (2000 – 2006).

Figure 4.32 illustrates the angular distribution of NO\textsubscript{x} at Goodwood as a function of wind direction measurements at Cape Town weather office. Data was filtered according to time, afternoon traffic hours (16:00 to 19:00) and other times (20:00 to 05:00 and 10:00 to 15:00). During the afternoon traffic hours, higher values of NO\textsubscript{x} are observed. The difference between afternoon maximum NO\textsubscript{x} and the maximum at other times is 32.16 ppb. The afternoon maximum is much lower (by 101.79 ppb) than the morning traffic maximum. One possible explanation for this is that the afternoon peak traffic period occurs after much of the school traffic whereas in the mornings, school traffic occurs at the same time with other traffic. A more pertinent explanation is that atmospheric instability and thus dispersion and dilution is stronger in the afternoons relative to the mornings.
4.7 Effect of Meteorology on Seasonal Cycles

Global radiation tends to be lower at Cape Point during the winter months because of higher cloud cover. Ozone is limited by UV (Figure 4.33) since surface $O_3$ is broken down by photolysis as described in equation 6 above:

Figure 4.33 shows the relationship between monthly average $O_3$ and global radiation at Cape Point background. The monthly average $O_3$ maximum is recorded in winter months when global radiation is at minimum. The global radiation maximum at Cape Point is observed in December (monthly average of 272.02 W/m²) while the minimum occurs in June (85.28 W/m²). The monthly average peak-to-peak value of global radiation is 186.79 W/m² from 1997 to 2009.
Figure 4.33: Monthly average global radiation at Cape Point and monthly average background O$_3$ Cape Point station (1997 to 2009).

Figure 4.34 illustrates negative relationship between monthly average O$_3$ at Cape Point background and monthly average global radiation experienced at Cape Point from 1997 to 2009. The strong negative correlation is significant at a 95% confidence level ($p = 0.00079$, $r = -0.81$, $r^2 = 0.65$). Global radiation decreases from January and reaches its minimum in June before increasing to December. On the other hand, O$_3$ increases from January to July and decreases from August to December. At Cape Point, global radiation is inversely related to O$_3$.

Figure 4.34: Relationship between monthly average O$_3$ concentrations and global radiation at Cape Point (1997 - 2009).
At SANAE, minimum monthly average temperatures occur in late winter and early spring (Figure 4.35) with temperatures falling below -20°C. Monthly average temperature maxima are observed during summer months; these maxima are, however, still below 0°C. The monthly average temperature and O₃ at SANAE reveal that O₃ and temperature are inversely related. However, the temperature minimum occurs in September while the O₃ maximum occurs in July.

Figure 4.35: Relationship between monthly average temperature at SANAE and monthly average SANAE (2002 – 2009).

Figure 4.36 illustrates the strong negative correlation between monthly average O₃ at SANAE and monthly average temperature experienced at SANAE from 2002 to 2009, significant at the 95% confidence level (p = 0.00018, r = -0.958, r² = 0.918). The relationship between O₃ and temperature at SANAE is negative because temperature minima are recorded in winter and maxima in summer while SANAE experience O₃ maxima in winter and minima in summer. The observed inverse relationship is evident in Figure 4.36.
Mean monthly atmospheric pressure and monthly average O$_3$ at SANAE (Figure 4.37) are not clearly related. Atmospheric pressure increased from January (884.24 hPa) to February (894.52 hPa) while a small decrease of 0.56 hPa was observed in March. Average monthly values are 892.66, 892.47 and 893.17 hPa from April to June respectively, followed by a decrease of 18.32 hPa in August. From August to December there is an increasing pressure trend of 8.85 hPa.
Figure 4.38 illustrates the negative relationship between monthly average O$_3$ at SANAE and monthly average pressure experienced at SANAE from 2002 to 2009. The correlation is not significant at the 95% confidence level ($p = 0.536$, $r = -0.259$, $r^2 = 0.067$). According to Simpson et al. (1995), elevated levels of O$_3$ are found in high pressure systems. At SANAE, however, pressure variation is low, and this could explain the lack of any clear relationship between the two variables.

![Figure 4.38: Correlation between monthly average O$_3$ and pressure at SANAE (2002 – 2009).](image)

Figure 4.39 shows the relationship between monthly average O$_3$ and atmospheric pressure at Cape Point background. The monthly average O$_3$ maximum is recorded in winter months for both variables. Atmospheric pressure at Cape Point is at its maximum in July (monthly average of 993.99 hPa) and decreases from August to January (987.00 hPa). The monthly average peak-to-peak value is 6.99 hPa over this period while a maximum of 30.80 ppb and a minimum of 16.43 ppb are recorded for O$_3$. 

![Figure 4.39](image)
Figure 4.39: Monthly average atmospheric pressure at Cape Point (background) and monthly average O$_3$ at Cape Point (background) from 1997 – 2009.

Figure 4.40 illustrates positive relationship between average monthly O$_3$ concentrations at Cape Point background station and average monthly pressure experienced at Cape Point from 1997 to 2009. The relationship is significant at 95% confidence level ($p = 0.0000018$, $r = 0.94$, $r^2 = 0.89$). It is in agreement with observations by Simpson et al. (1995) that elevated levels of O$_3$ are found in high pressure meteorological conditions. Ozone formation is driven by photochemical initiated reactions and these correlate with high atmospheric pressure because of the prevalence of clear (cloudless) skies under high pressure conditions. Thus a positive relationship between pressure and O$_3$ is observed. Higher levels of O$_3$ and pressure are recorded in winter while lower levels of O$_3$ and pressure are observed in summer.
Figure 4.40: Correlation between monthly average $O_3$ and pressure at Cape Point background station (1997 – 2009).

Figure 4.41 illustrates monthly average temperature and $O_3$ at Molteno and Goodwood. Temperature decreases from January and reaches a monthly average minimum of 12.53 °C in July, followed by an increase to 20.29 °C in December. A decrease of $O_3$ for both stations (Molteno and Goodwood) is observed from January to June. In July, $O_3$ increases and reaches a peak in October of 23.99 ppb and 18.48 ppb at Molteno and Goodwood respectively. Monthly average $O_3$ concentrations are not clearly related to atmospheric temperature at these stations.

Figure 4.41: Monthly average temperature at Cape Town and monthly average $O_3$ concentrations at Molteno and Goodwood (2000 – 2006).
Figure 4.42 illustrates an inverse relationship between monthly average O₃ emissions and monthly average temperature recorded in Molteno from 2002 to 2007. The relationship is not significant at 95% confidence level ($p = 0.407$, $r = -0.42$, $r^2 = 0.18$) at this station. Temperature minima occur in winter months whereas maxima are recorded in summer months. On the other hand, O₃ maxima are observed in spring and minima occur in summer. Hence, the relationship between monthly O₃ averages and monthly average temperature is not significant at 95% confidence level. Further investigation of the seasonal cycles is recommended at Molteno. The relationship between O₃ and temperature is not significant at the 95% confidence level. It can be suggested that the observed O₃ maxima at Molteno is not related to monthly average temperatures.

Figure 4.43 shows monthly average O₃ at Molteno and Goodwood as well as monthly average atmospheric pressure. The monthly average O₃ maximum occurs in October while the average monthly atmospheric pressure maximum occurs in July. Figures 4.39 and 4.41 suggest that the mechanism driving seasonal changes in O₃ at these sites is neither temperature nor atmospheric pressure related. The influences of $\Delta T/ \Delta Z$ (i.e. change of temperature with height, which is an
indicator of inversion conditions (when positive) and thus atmospheric stability) and the wind regime are worthy of further investigation to explain this cycle.

Figure 4.43: Monthly average atmospheric pressure at Cape Town and monthly average O$_3$ at Molteno and Goodwood (2000 – 2006).

Figure 4.44 illustrates an inverse relationship between monthly average O$_3$ emissions and monthly average temperatures recorded at Goodwood from 2000 to 2006. The relationship between these variables is not significant at 95% confidence level ($p = 0.925$, $r = 0.044$, $r^2 = 0.002$) at this site. In summer months, higher temperatures are observed while higher O$_3$ averages are recorded in spring. Minima temperatures are observed in winter whereas lowest O$_3$ concentrations are recorded in summer. Therefore, there is no clear relationship between monthly average temperature and monthly average O$_3$. As indicated above, the observed O$_3$ maxima in spring is not related to temperature.
Figure 4.45 illustrates monthly average O$_3$ concentrations and atmospheric pressure at Molteno from 2002 to 2007. A positive relationship between temperature and pressure is observed. However, the relationship between these variables is not significant at 95% confidence level ($p = 0.432$, $r = 0.4$, $r^2 = 0.16$). Pressure maxima occur in winter months whereas O$_3$ maxima occur in spring. The literature suggest higher levels of O$_3$ are expected under high pressure meteorological conditions, but the timing of the O$_3$ maximum at Molteno does not coincide with high atmospheric pressure.

Figure 4.45: Correlation between monthly average O$_3$ and pressure at Molteno (1997 – 2007).
Figure 4.46 illustrates the relationship between monthly average $O_3$ concentrations and pressure at Goodwood from 2000 to 2006. The relationship between these variables is not significant at the 95% confidence level. As discussed in section 4.3, Goodwood recorded $O_3$ maxima in spring and minima in summer. On the other hand, atmospheric pressure is lower in summer and higher in winter (June and July). Therefore, there is no significant relationship detected between $O_3$ concentrations and atmospheric pressure.

![Graph](image)

Figure 4.46: Correlation between monthly average $O_3$ and pressure at Goodwood (2000 – 2006).

Figure 4.47 illustrates a strong inverse relationship between monthly average NO$_x$ concentrations at Goodwood and monthly average temperature experienced in Cape Town from 2000 to 2006. The relationship between NO$_x$ and temperature is significant at the 95% confidence interval ($p = 0.031$, $r = -0.80$, $r^2 = 0.64$). At Goodwood, the NO$_x$ maxima are recorded in winter while minima are recorded in summer. Low temperatures are observed in winter and high temperatures are observed in summer. Therefore, the relationship between monthly NO$_x$ averages and temperature is inversely proportional. The observed results of NO$_x$ maxima in winter can be related to a number of factors as discussed above, including vehicular traffic increases in winter and increased fuel use for heating in winter.
4.8 Effect of wind speed on seasonal cycles

The O₃ data was filtered according to wind speed categories (less than 5 m/s, 5 to 10 m/s and 10-15 m/s) for SANAE (Figure 4.48), Cape Point background (Figure 4.49), Cape Point non-background (Figure 4.50), Molteno (Figure 4.51) and Goodwood (Figure 4.52). Monthly average O₃ was calculated for each wind speed category for each month. A description of each site follows. These results are then interpreted at the end of the section.

Figure 4.48 illustrates O₃ concentrations as a function of wind speed at SANAE. The data can be summarized as follows:

An O₃ minimum of 16.18 ppb is observed in February while a maximum of 33.86 ppb is observed in July for wind speed less than 5 m/s. This results in a peak-to-peak value of 16.68 ppb. For wind speed between 5 to 10 m/s, an O₃ minimum of 16.22 ppb is observed in January while a maximum of 33.15 ppb is observed in July. This results in a peak-to-peak value of 16.93 ppb. Furthermore, an O₃ minimum of 16.39 ppb is observed in January while a maximum of 33.11 ppb is observed in July for wind speed between 10 to 15 m/s. This results in peak-to-peak value of 16.72 ppb.

Literature suggests that winds with lower speeds result in high NOₓ concentration and low O₃ concentrations compared to winds with higher speeds. There is no clear relationship between
monthly O$_3$ averages and wind speed categories at SANAE, and this is likely to be related to the lack of NO$_x$ pollution at SANAE.

Figure 4.48: Monthly average O$_3$ for specific wind speed categories at SANAE (2002 – 2009).

Figure 4.49 illustrates O$_3$ concentrations as a function of wind speed at Cape Point background.

The data can be summarized as follows:

An O$_3$ minimum of 18.30 ppb is observed in January while a maximum of 28.77 ppb is observed in September. This results in a peak-to-peak value of 10.47 ppb. For wind speed between 5 to 10 m/s, an O$_3$ minimum of 17.97 ppb is observed in February while a maximum of 30.23 ppb is observed in August. This results in a peak-to-peak value of 12.26 ppb. Furthermore, an O$_3$ minimum of 16.94 ppb is observed in January while a maximum of 31.24 ppb is observed in July for wind speed between 10 to 15 m/s. This results in a peak-to-peak value of 14.29 ppb.

Although peak-to-peak values increase with increasing wind speed categories, only winter months show lower O$_3$ concentrations for winds with low speed. In other months there is no clear relationship between O$_3$ and wind speed. The observed O$_3$ relationship with wind speed in winter could be an artefact of the data filtering into background and non-background air masses.
Figure 4.49: Monthly average $O_3$ for specific wind speed categories at Cape Point background station (1997 – 2009).

Figure 4.50 illustrates $O_3$ concentrations as a function of wind speed at Cape Point non-background. The data can be summarized as follows:

An $O_3$ minimum of 19.47 ppb is observed in January while a maximum of 28.49 ppb is observed in September. This results in a peak-to-peak value of 9.02 ppb. For wind speed between 5 to 10 m/s, an $O_3$ minimum of 20.73 ppb is observed in February while a maximum of 30.39 ppb is observed in October. This results in a peak-to-peak value of 9.66 ppb. Furthermore, An $O_3$ minimum of 16.82 ppb is observed in January while a maximum of 30.41 ppb is observed in August for wind speed between 10 to 15 m/s. This results in a peak-to-peak value of 13.59 ppb.

Although there is no clear relationship between $O_3$ and speed in winter, $O_3$ maximum is increasing with increasing wind speed while minimum is decreasing with increasing wind speed. This results in peak-to-peak values of 9.02 ppb, 9.66 ppb and 13.59 ppb for < 5 m/s, 5 – 10 m/s and 10 – 15 m/s respectively.
Figure 4.50 illustrates $O_3$ concentrations as a function of wind speed at Molteno. The data can be summarized as follows:

An $O_3$ minimum of 13.49 ppb is observed in January while a maximum of 21.65 ppb is observed in October. This results in a peak-to-peak value of 8.16 ppb.

For wind speed between 5 to 10 m/s, an $O_3$ minimum of 17.88 ppb is observed in January while a maximum of 25.60 ppb is observed in October. This results in a peak-to-peak value of 7.71 ppb. Furthermore, an $O_3$ minimum of 18.10 ppb is observed in January while a maximum of 28.23 ppb is observed in September for wind speed between 10 to 15 m/s. This results in a peak-to-peak value of 10.14 ppb.

The relationship between monthly $O_3$ averages and wind speed in Figure 4.51 reflects theory (e.g. Dapeng et al., 1996; Dabdub et al., 1999; Rodriguez and Guerra, 2001) in that lower speeds occur with lower $O_3$ concentrations while higher wind speeds occur with higher $O_3$ concentrations. Lower wind speeds promote accumulation of NO$_x$ and lower levels of $O_3$ because of $O_3$ titration by NO$_x$, on the other hand, higher wind speeds promote the transportation of air masses and result in lower $O_3$ concentrations.
Figure 4.51 illustrates $O_3$ concentrations as a function of wind speed at Goodwood. The data can be summarized as follows:

An $O_3$ minimum of 11.51 ppb is observed in January while a maximum of 15.90 ppb is observed in October for wind speed less than 5 m/s. This results in a peak-to-peak value of 4.39 ppb.

For wind speeds between 5 to 10 m/s, an $O_3$ minimum of 13.45 ppb is observed in January while a maximum of 21.21 ppb is observed in October. This results in a peak-to-peak value of 7.75 ppb. Furthermore, an $O_3$ minimum of 13.11 ppb is observed in January while a maximum of 23.11 ppb is observed in October for wind speed between 10 to 15 m/s. This results in peak-to-peak value of 10.00 ppb.

As discussed previously, winds with low speed result in high $O_3$ concentrations while high wind speed promoted low $O_3$ concentrations. Results in Figure 4.52 suggest that the relationship between wind speed and $O_3$ monthly averages is most clearly evident in stations located in urban areas (Molteno and Goodwood).
Figure 4.52 illustrates NO\textsubscript{x} concentrations as a function of wind speed at Goodwood. The data can be summarized as follows:

A NO\textsubscript{x} minimum of 15.00 ppb is observed in January while a maximum of 98.29 ppb is observed in June for wind speed less than 5 m/s. This results in a peak-to-peak value of 83.29 ppb. For wind speeds between 5 to 10 m/s, a NO\textsubscript{x} minimum of 9.91 ppb is observed in January while a maximum of 23.55 ppb is observed in June. This results in a peak-to-peak value of 13.63 ppb. Furthermore, a NO\textsubscript{x} minimum of 9.03 ppb is observed in January while a maximum of 28.91 ppb is observed in June for wind speed between 10 to 15 m/s. This results in a peak-to-peak value of 19.88 ppb.

With the exception of 5 – 10 m/s maximum, the observed results are in agreement with the findings reported in the literature (Dapeng et al., 1996; Dabdub et al., 1999; Rodriguez and Guerra, 2001), more especially in urban sites where NO\textsubscript{x} levels are higher.

In summary, at Goodwood and Molteno, higher wind speed categories show lower O\textsubscript{3} concentrations while lower wind speed categories show higher O\textsubscript{3} concentrations. At SANAE and Cape Point the relationship between monthly O\textsubscript{3} averages and monthly speed averages is not clear.
4.9. Long Term Trends of $O_3$ at Various Sites

Monthly $O_3$ averages were calculated from the hourly dataset from 1997 to 2009. The figures below (Figure 4.54, 4.55, 4.56, 4.57 and 4.58) show the monthly average $O_3$ at SANAE, Cape Point background, Cape Point non-background, Molteno and Goodwood respectively. Twelve month moving averages were calculated to investigate trends. Visual analysis of the figures below indicates a general increase, decrease or stabilization in ozone concentrations. Slope (in ppb/yr) is reported for each station.

At SANAE (Figure 4.54) and Cape Point background (Figure 4.55) a clear seasonal cycle is evident with minima in summer and maxima in winter. SANAE shows a slight increasing trend of 0.11 ppb/yr from 2002 to 2009.
At Cape Point background (Figure 4.55) ozone levels are stable (an average trend of -0.02 ppb/yr) from 1997 to 2009. An increasing slope of 0.18 ppb/yr is calculated from 1997 to 2003 followed by stable levels (-0.02 ppb/yr) from 2004 to 2009. When calculating trends, it is important to calculate slope for years which show similar trend behaviour (increase, decrease or stabilization) so that changing trends are not averaged out over longer time periods.
At Cape Point non-background (Figure 4.56) a negative trend of -0.14 ppb/yr is observed from 1997 to 2009. An increasing trend of 1.76 ppb/yr is calculated from 1997 to 2000 followed by a negative trend of -0.10 ppb/yr from 2001 to 2009. At Cape Point non-background, Molteno and Goodwood, monthly O$_3$ averages show high variability. Molteno and Goodwood show more monthly O$_3$ variation compared to Cape Point non-background data. At SANAE and Cape Point background, there is a steady increase from January to June and steady decrease from July to December.

![Figure 4.56](image)

Figure 4.56: Trend in monthly average O$_3$ at Cape Point non-background with twelve month running average (1997-2009).

At Molteno (Figure 4.57) a negative trend of -0.46 ppb/yr is observed from 1997 to 2007. An increasing trend of 0.86 ppb/yr is observed from 1997 to 2000 followed by a negative trend of -0.44 ppb/yr from 2001 to 2007.
At Goodwood (Figure 4.58), an increasing O$_3$ trend of 0.16 ppb/yr is observed from 2000 to 2006. However, NO$_x$ shows a negative trend during from 2000 to 2006 (Figure 4.59).
Figure 4.59: Trend in monthly average NOx at Goodwood with twelve month running average (2000-2006).
CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary

This chapter summarizes the analysis of surface O$_3$ at SANAE (2002-2009), Cape Point background and Cape Point non-background (1997-2009), Molteno (1997-2007) and Goodwood (2000-2006). Diurnal and seasonal cycles, weekend effect and long term trends in these data were assessed.

At SANAE and Cape Point background, diurnal peak-to-peak values are lower relative to non-background stations. Goodwood shows a peak-to-peak value of 16.80 ppb while a peak-to-peak value of 12.16 ppb is recorded at Molteno. The Cape Point non-background station peak-to-peak value (6.00 ppb) is higher than the SANAE (0.24 ppb) and Cape Point non-background data (1.26 ppb) peak-to-peak values. The Cape Point non-background data resembles the Cape Town region (Molteno and Goodwood) with respect to diurnal and seasonal cycle trend but with lower diurnal variation. The correlation between Cape Point non-background O$_3$ and Molteno O$_3$ was not significant ($p = 0.061$, $r = 0.732$, $r^2 = 0.54$) at the 95% confidence level, but significant at the 90% confidence level. The correlation between Cape Point non-background and Goodwood was not significant at the 95% or 90% confidence level ($p = 0.116$, $r = 0.647$, $r^2 = 0.42$). The diurnal variation on weekends and weekdays showed higher peak-to-peak values on weekdays compared to weekends at Molteno and Goodwood. This is most likely due to the well-established ‘weekend effect’ in O$_3$ concentrations at urban stations associated with increased vehicular NO$_x$ emissions during the week. This is supported by NO$_x$ measurements at Goodwood.

Monthly average maxima of 33.20 ppb and 30.80 ppb were observed in winter at SANAE and Cape Point background respectively, while monthly average minima of 16.47 ppb and 16.43 ppb occurred during summer at SANAE and Cape Point background respectively. Monthly average peak-to-peak values are much lower in the Cape Town region (Molteno and Goodwood) relative to those observed at SANAE and Cape Point. At Molteno (16.62 ppb) and Goowood (12.38 ppb), monthly average minima are observed in winter, while monthly average maxima are observed in spring. These maxima do not coincide with NO$_x$ or temperature extremes. The Cape
Point non-background data reveals a monthly average minimum of 17.69 ppb in summer and monthly average maximum of 30.24 ppb in spring.

The ‘weekend effect’ is clearly evident at Molteno and Goodwood but not at SANAE, Cape Point background and Cape Point non-background. On weekends, correlation between Molteno monthly average \(O_3\) and Cape Point non-background monthly average \(O_3\) is strong and significant at the 95% confidence level \((p = 0.00, r = 0.80, r^2 = 0.64)\) while a non-significant correlation is observed between Goodwood monthly average \(O_3\) and Cape Point non-background monthly average \(O_3\) is observed on weekends \((p = 0.191, r = 0.41, r^2 = 0.16)\). On weekdays, monthly averages \(NO_x\) is higher at Goodwood, particularly during the winter months (maximum in June), with a difference of 132.9 ppb observed between monthly \(NO_x\) maxima on weekends and monthly \(NO_x\) minima on weekdays.

Correlation results of monthly average \(O_3\) with monthly average temperature and monthly average pressure show both significant and non-significant relationships. At SANAE, the correlation between monthly average temperature and monthly average \(O_3\) is very strong and significant at the 95% confidence level \((p = 0.00018, r = -0.958, r^2 = 0.918)\) but at Molteno \((p = 0.407, r = -0.42, r^2 = 0.18)\) and Goodwood \((p = 0.925, r = 0.044, r^2 = 0.002)\), the correlation between monthly average temperature and monthly average \(O_3\) is not significant at the 95% confidence level. At SANAE, Molteno and Goodwood, the correlation between monthly average pressure and monthly average \(O_3\) is not significant at the 95% confidence level however at Cape Point background the correlation is strong and significant at the 95% confidence level \((p = 0.0000018, r = 0.94, r^2 = 0.89)\).

Pollution roses at Molteno and Goodwood show higher sectoral average \(O_3\) concentrations during winds from the south-east and north-west relative to other sectors. However, \(NO_x\) pollution roses show lower concentrations from these sectors. Higher \(NO_x\) sectoral average concentrations are observed from east-north-east relative to other sectors. On the other hand, \(O_3\) concentrations are lower during winds from the east-north-east relative to other sectors. These results show more \(O_3\) titration by \(NO_x\) from east-north-east relative to other sectors. The observed maximum sectoral average \(NO_x\) concentrations are 34.53 ppb, 136.79 ppb, 132.70 ppb,
and 59.29 ppb during summer, autumn, winter and spring respectively. Generally, the maximum sectoral average NO\textsubscript{x} originates from the north-east to east directions, and these high levels are associated with vehicular emissions. At SANAE, the minimum sectoral average is observed from the northern sector in spring with a difference of 8.00 ppb relative to the maximum sectoral average. At Cape Point non-background, the sectoral average minimum is observed from the northern sector (Cape Town region) in winter.

At Molteno and Goodwood, an increase in wind speed results in an increase in transportation of air masses, promoting lower levels of NO\textsubscript{x} and higher levels of O\textsubscript{3}. On the other hand, lower wind speeds promotes accumulation of NO\textsubscript{x} and lower levels of O\textsubscript{3}.

An increasing trend of 0.11 ppb/yr of O\textsubscript{3} is observed at SANAE from 2002 to 2009. At Cape Point background an increasing trend of 0.18 ppb/yr is observed from 1997 to 2003 followed by stable values (0.02 ppb/yr) from 2004 to 2009. On the other hand, Cape Point non-background shows an increasing trend of 0.21 ppb/yr from 1997 to 2000 followed by a negative trend of 0.12 ppb/yr from 2001 to 2009. Similarly, Molteno shows an increasing trend of 0.86 ppb/yr from 1997 to 2000 followed by a negative trend of 0.42 ppb/yr from 2001 to 2007. The Goodwood trend deviates from that of Molteno and Cape Point non-background. A continuous increase of 0.26 ppb/yr from 2000 to 2006 is recorded while the NO\textsubscript{x} trend decreased by 2.56 ppb/yr for the same period. The observed O\textsubscript{3} trend increase in Goodwood suggests a decrease O\textsubscript{3} titration by NO\textsubscript{x}.

5.2 Final Comments
The diurnal cycle of O\textsubscript{3} and NO\textsubscript{x} (Figure 4.4) at Goodwood can be subdivided as follows: (a) In the mornings, a NO\textsubscript{x} peak was observed associated with morning traffic, (b) O\textsubscript{3} formation persists between 09:00 and 14:00, (c) afternoon NO\textsubscript{x} accumulation occurs due to traffic peak, (d) balancing of NO\textsubscript{x} and O\textsubscript{3} during night hours (19:00 to 05:00). Although the correlation between O\textsubscript{3} and NO\textsubscript{x} was not significant, 32% of the variation in NO\textsubscript{x} corresponds with the variation in O\textsubscript{3} concentrations at Goodwood. Trends at Cape Point background resemble those of SANAE while trends in Cape Point non-background are almost similar those of the Cape Town region. NO\textsubscript{x} plays a crucial role in the O\textsubscript{3} diurnal cycle at Molteno and Goodwood; O\textsubscript{3} levels
were higher on weekends due to lower NO\textsubscript{x} levels and lower during the week when vehicular emissions of NO\textsubscript{x} levels were elevated.

The geographical location of stations play a crucial role in O\textsubscript{3} concentrations for both short and long term trends. At SANAE and Cape Point background stations, monthly average maxima occur in winter while at Molteno and Goodwood monthly average maxima occur in spring (October or November). Even though the monthly average NO\textsubscript{x} and the monthly average O\textsubscript{3} correlation was not significant (p = 0.202, r = 0.501, \( r^2 = 0.255 \)) at 95\% confidence interval, 25.5\% of the variation in NO\textsubscript{x} corresponds with the variation of O\textsubscript{3}. Molteno and Goodwood are affected more by NO\textsubscript{x} fluctuations than SANAE and Cape Point.

The ‘weekend effect’ on O\textsubscript{3} is more evident at Molteno and Goodwood than at SANAE and Cape Point. Current results indicate higher O\textsubscript{3} concentrations on weekends in all the seasons for both stations (Molteno and Goodwood). Although the monthly average correlation between O\textsubscript{3} and monthly average NO\textsubscript{x} at Goodwood is not significant, 19.5\% of the variation in NO\textsubscript{x} corresponds with the variation of O\textsubscript{3} in weekdays relative to only 0.27\% on weekends.

Wind speed is important for the interpretation of transportation of pollutants from one region to another. An assessment of NO\textsubscript{x} concentrations at different wind speed categories at Goodwood revealed that winds with lower speeds (less than 5m/s) result in higher concentrations of NO\textsubscript{x} relative to higher wind speeds (between 10 to 15 m/s). Current findings show lower monthly O\textsubscript{3} averages at higher wind speeds at Molteno and Goodwood. On the other hand, winds with high wind speed show low NO\textsubscript{x} concentrations and high O\textsubscript{3} concentrations. At SANAE, Cape Point background and non-background stations there is no significant relationship between monthly O\textsubscript{3} averages and wind speed.

Cape Point background shows a similar long-term O\textsubscript{3} trend to that at SANAE, while Cape Point non-background station reflects the Molteno trend. Goodwood shows increase in O\textsubscript{3} while NO\textsubscript{x} concentrations decreased. It is tentatively suggested that Goodwood is a VOC sensitive station but due to the lack of VOC measurements at the station, further investigation needs to be done at a later time when this data is available.
5.3 Limitations of the Study
Nitrogen oxides and other O$_3$ precursor measurements are critical to understand surface O$_3$ changes (seasonal fluctuations and long term trends). The absence of NO$_x$ measurements at Molteno during the period of study limits the conclusions that can be drawn from the observed O$_3$ trends.

5.4 Recommendations
A trend comparison using SANAE data and other polar stations (e.g. Neumayer and South Pole) is recommended since the data used by Helming et al (2007) was not adequate to investigate long term trends at SANAE.

Cape Point is less impacted by human activities than the Cape Town stations due to prevailing south-westerly winds (from the Atlantic ocean). The observed increasing trend at Cape Point background O$_3$ is not related to air masses from Cape Town region. Further investigation is required to find out if the observed trend stabilization from 2004 to 2009 is a regional, hemisphical or global phenomenon.

It is further recommended that analyses of O$_3$ concentrations are conducted at other sites in the Cape Town region (stations under Cape Town provincial government) to allow for further investigation the underlying mechanism involved for spring O$_3$ maximum. Upper air data temperature data could be useful for determining whether the observed phenomenon is linked to temperature inversions.

To further understand the decreasing O$_3$ trend at Molteno and Cape Point non-background data, more detailed investigation and increased monitoring of O$_3$ precursors is necessary. More work remains to be done in the characterization of regional and hemispheric O$_3$ trends.
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