RELATIONSHIP BETWEEN SURFACE OZONE OVER
SOUTH AFRICAN HIGHVELD AND EL NIÑO – SOUTHERN OSCILLATION

A Thesis in
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by
Nikolai Balashov

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The thesis of Nikolai Balashov was reviewed and approved* by the following:

*Signatures are on file in the Graduate School

Anne M. Thompson  
Professor of Meteorology  
Thesis Advisor

Chris E. Forest  
Associate Professor of Climate Dynamics

George Young  
Professor of Meteorology and GeoEnvironmental Engineering

Johannes Verlinde  
Professor of Meteorology  
Associate Head, Graduate Program in Meteorology
ABSTRACT

Surface ozone variability due to El-Niño Southern Oscillation (ENSO) during 1990-2007 is examined at the Highveld – a heavily populated region in South Africa with numerous industrial facilities. The meteorological perturbations of the region are significantly affected by the variability in the sea surface temperature (SST) anomalies of the tropical eastern Pacific Ocean (ENSO). Surface ozone is sensitive to the meteorological conditions such as clouds because its production depends on the solar radiation to photolyse NO₂. We use generalized linear regression model to establish any linear relationship that may exist between the Highveld ozone, measured at 5 ESKOM air quality monitoring stations, and ENSO. Our results find that 4 out of 5 stations are sensitive to the ENSO in the January-July period where El Niño with dry and warm anomalies acts to amplify the ozone, while La Niña with wet and cool anomalies act to reduce the ozone. The most consistent enhancement at these 4 stations is 4-6 ppbv in February-April period of 1998. The most consistent reduction is -3-5 ppbv in January-May of 1999 and 2000. In addition over the study period of 18 years three stations display negative ozone trend and two stations show no significant change in ozone.
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Chapter 1
INTRODUCTION

The South African provinces of Mpumalanga, Gauteng and Free State partially comprise a region known as the Highveld (figure 1-1) – a plateau with elevations above 1200 meters (Tooth et al., 2004). The region is home to the most industrial and populous section of the country containing the majority of South African coal-fired power plants along with close to 35% of its population (Fox and Rowntree, 2000; Freiman and Piketh, 2003; Rorich and Galpin, 1998; Tyson et al., 1988). Given the combination of the aforementioned characteristics it is reasonable to hypothesize that air pollution is an important issue for the biosphere of Highveld. In fact a number of studies have been published describing this topic in some detail (Emberson et al., 2003; Lee et al., 1996; McGranahan and Murray, 2003; Norman et al., 2007; Stevens, 1987; Terblanche et al., 1998; Tyson et al., 1988; Van Nierop, 1995; von Schirnding et al., 1991; Yach et al., 1991). United States Environmental Protection Agency (EPA) has established six “criteria” air pollutants that present a substantial threat to living organisms: \( \text{O}_3 \) (surface ozone), \( \text{NO}_x = \text{NO} + \text{NO}_2 \) (nitrogen oxides), \( \text{CO} \) (carbon monoxide), \( \text{PM} \) (particulate matter), \( \text{SO}_2 \) (sulfur dioxide), and \( \text{Pb} \) (lead) (United States Environmental Protection, 1970). In this study we concentrate on the surface ozone, which forms through interactions of nitrogen oxides, volatile organic compounds (VOCs), and sunlight (Jenkin and Clemitshaw, 2000). In addition to EPA criteria, research generally agrees that relatively high concentrations of ozone cause a negative effect on human lung functions (Uysal and Schapira, 2003). Understanding the variability of ozone at the Highveld can give us an insight on the role of anthropogenic and natural factors affecting air quality of that region.
Figure 1-1. The map of South Africa approximately indicating the Highveld borders in green as well as the three provinces that comprise an industrial center along with the major living hub of the country.

Only a few studies have attempted to analyze Highveld long-term surface ozone variability (Combrink et al., 1995; Martins et al., 2007; Mokgathle, 2006; Rorich and Galpin, 1998; Zunckel et al., 2004). Large year-to-year monthly mean ozone fluctuations in this sector have puzzled the few scientists who analyzed long-term ozone records (Martins et al., 2007; Mokgathle, 2006; Pienaar, 2011). For instance, the financial crisis of late 1990s and early 2000s
in South Africa (Fedderke et al., 2006) has been suggested as a reason for the decline in the pollutants for that period (Pienaar, 2011). We hypothesize that the variability of meteorological parameters, indirectly influencing ozone formation, could be another significant factor modulating the ozone amounts. Studies have shown the pronounced effect of ENSO on the meteorology of eastern South Africa (Cook, 2001; Kanyanga, 2008; Lindesay, 1988). Because we expect that natural parameters play an important role on the observed ozone concentrations, the reasonable assumption then is to compare ENSO oscillations with the Highveld ozone variability. Motivated by the observed teleconnection between meteorology of eastern South Africa and Pacific Ocean sea surface temperature (SST) anomalies we attempt to show that linear relationship exists between ENSO and the Highveld ozone. This chapter discusses background of this study covering ozone chemistry and meteorology relevant to South African Highveld.

1.1 Context

1.1.1 Ozone Chemistry

The atmosphere of Earth has several different mechanisms to produce ozone. Stratospheric ozone forms through the dissociation of molecular oxygen by solar UV radiation and subsequent reaction of oxygen atoms with $O_2$ in the company of another molecule M (commonly $N_2$ or $O_2$). Ozone accumulates in the free troposphere as an outcome of photolysis of $NO_2$ and downward transport from the stratosphere. Variation of the surface or lower tropospheric ozone is also governed by photochemistry of $NO_2$, but principally dependent upon the local environmental conditions. Due to anthropogenic emissions of the ozone precursors urban and developing regions usually allow for greater ozone concentrations than rural and remote places. Exact
pathways leading to the formation of surface ozone; therefore, have been difficult to establish in the continuously changing lower atmosphere (Chapters 5 and 6, Seinfeld and Pandis, 2006).

Without any other contributors the reactions involving NO, NO₂, O, O₃, M, and radiation at wavelength < 424 nm form a null cycle:

\[
\text{NO}_2 + h\nu (\lambda < 424 \text{ nm}) \rightarrow \text{NO} + \text{O} \quad (R1.1)
\]
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (R1.2)
\]
\[
\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (R1.3)
\]

At some point these reactions come to a steady-state, where NO₂ is created and destroyed equally. Given such chemistry, ozone concentrations would only be dependent upon the existing NO₂ concentrations; however, observations show that this is not the case for tropospheric air. It is therefore concluded that other important chemical processes take place in the lower atmosphere (Chapter 6, Seinfeld and Pandis, 2006).

Hydroxyl (OH) radical, which forms through the reaction of excited singlet oxygen atom and water vapor molecule, has an ability to initiate oxidations of carbon monoxide (CO) and volatile organic compounds (VOCs) leading to the production of hydroperoxy radical (HO₂) and organic peroxy radicals (RO₂). The following reactions are now able to proceed:

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (R1.4)
\]
\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad (R1.5)
\]

It is crucial that in this case conversion from NO to NO₂ no longer requires O₃ molecule and resulting NO₂ becomes a net source for additional O₃. In order for the ozone to grow, however, there must be a balance between NOₓ and VOCs as there are possibilities for VOC-limited and NOₓ-limited conditions where the following reactions are responsible for termination of ozone production reaction chain:
VOC-limited:

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  
\hspace{2cm} (R1.6)

NO\textsubscript{x}-limited:

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
\hspace{2cm} (R1.7)

\[ \text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \]  
\hspace{2cm} (R1.8)

Reaction (R1.6) competes against the reaction of OH radical with generic saturated hydrocarbon (RH) that leads to the production of RO\textsubscript{2} needed for NO\textsubscript{2} formation, while the reactions (R1.7) and (R1.8) compete with the reactions (R1.4) and (R1.5) similarly impairing NO\textsubscript{2} production. This is, of course, a simplified description of chemistry but it does show how an environment may significantly influence the ozone concentration at a particular location (Jenkin and Clemitshaw, 2000).

Urban and developing regions are expected to see higher ozone values than rural regions as VOCs and NO\textsubscript{x} are amply available. Rural places tend to have lesser ozone variability due to the absence of local NO\textsubscript{x} emissions even though VOCs are still available. These cases can be called NO\textsubscript{x}-limited. Because ozone formation depends on solar UV to photolyse NO\textsubscript{2} the diurnal ozone cycle could be more erratic for the urban places than for the rural areas. It is for this reason the ozone in the rapidly developing South African Highveld may be sensitive to meteorological properties (see sections 1.1.2 and 1.2.1).

### 1.1.2 Tropospheric Ozone at South African Highveld

South African Highveld exhibits a distinct annual cycle in the tropospheric ozone. Both lower and free tropospheric ozone concentration over the Highveld show maximum values during the spring months of September-October-November (SON) and minimum values in the autumn.
months of March-April-May (MAM) (figure 1-2). The ozone concentration maximum in SON occurs primarily due to stratospheric ozone intrusions caused by the westerly waves (see section 1.1.3) and biomass burning, a process that includes, savannah fires, forest fires, agricultural waste combustion, and domestic biofuel combustion (Diab et al., 2004). These burning processes result in the emission of gases such as CO, CH₄, NOₓ, and non-methane hydrocarbon (NMHC) that are precursors of O₃ (Marufu et al., 2000). Due to the active industry in the region there is generally a consistent source of NOₓ without any clear seasonality. Each location being sensitive to its specific environment (traffic, power plants, etc.) although peaks are possible in the March-June-July period due to the prevailing anticyclonic stability (see section 1.1.3) (Collett et al., 2010). So both seasons MAM and SON seem to produce enough of the NOₓ for the ozone production; however, high availability of CO and VOCs in SON allows these months to maximize their ozone production. Evidence exists for vegetation as a significant isoprene source throughout the year, which makes it unlikely that any of the seasons can be VOC-limited (Guenther et al., 1996). Thus overall ozone production is controlled by either an increase in NOₓ or by an increase in VOCs, which puts meteorological variability as an important factor for the surface ozone generation over the Highveld. Next we will discuss prevalent synoptic patterns and their perturbations over the eastern South Africa.

1.1.3 Meteorological and Climatic Variability in South Africa

Located at the subsiding edge of Southern Hadley and Ferrel cells, eastern South Africa generally experiences mean anticyclonic circulation throughout the year. As the circumpolar vortex strengthens in the winter, westerlies expand, forcing the semi-permanent high pressure in southern Indian Ocean, resulting from the aforementioned subsidence, to move northwestward over the southeastern part of African continent. The resulting synoptic regime generates stable, sunny and cloudless conditions in the region for the most of the austral winter from May to September. Starting in October as heating intensifies westerlies weaken allowing for the easterlies to expand southward leading to the occurrence of easterly waves and lows that bring precipitation and clouds to the region peaking in December-February approximately until the end
of April (figure 1-3). While on a large scale South Africa exhibits major dry and wet periods the day-to-day weather variability can be generalized using specific circulation types (Tyson and Preston-Whyte, 2000).

![Map of southern Africa indicating schematically interaction between westerlies, easterlies and the Indian Ocean anticyclone](image)

**Figure 1-3.** Map of southern Africa indicating schematically interaction between westerlies, easterlies and the Indian Ocean anticyclone [adapted from Diab et al. (2004)].

The most prevalent atmospheric circulation types over the Highveld can be divided into the five synoptic patterns: continental anticyclone, ridging anticyclone, westerly wave/trough,
cut-off low, and tropical easterly disturbance. In turn these five patterns can be categorized into three broader regimes by combining continental and ridging anticyclone, westerly wave/trough and cut-off low, and finally tropical easterly disturbances. Respectively first and third regimes show pronounced out-of-phase annual cycle manifested by dominating anticyclonic circulation from April to September and wet tropical influence from October until March, while the second regime persists throughout the year with maximum activity in October (Garstang et al., 1996). Year-to-year variability in synoptic patterns over the eastern South Africa, however, can be substantial due to the apparent teleconnection of local meteorology with the sea surface temperature (SST) anomalies of Atlantic, Pacific and Indian Oceans (Cook, 2001; Goddard and Graham, 1999; Reason and Jagadheesha, 2005b).

Of the bodies of water mentioned, tropical Pacific and central Indian Oceans have the greatest importance (Goddard and Graham, 1999; Washington and Preston, 2006). SST variability in the tropical Pacific is called ENSO (El Niño–Southern Oscillation) or El Niño/La Niña–Southern Oscillation, where generally El Niño refers to *positive* tropical eastern Pacific SST anomalies and La Niña refers to *negative* tropical eastern Pacific SST anomalies (Trenberth, 1997). When SSTs hover around the climatological mean the condition is known as the normal ENSO phase. Numerous studies have shown a considerable connection between ENSO and October-March precipitation, temperature and wind fields for eastern South Africa, where El Niño usually associates with warm and dry conditions while La Niña is accompanied by cool and wet weather (Kanyanga, 2008; Lindesay, 1988; Reason and Jagadheesha, 2005a; Chapter 8 in Tyson, 1986). It has also been argued that the influence of Indian Ocean SSTs on the precipitation in the region is significant (Goddard and Graham, 1999). Currently it seems reasonable to accept that both oceans have an essential influence on the rainfall over the Highveld and perhaps other weather parameters; whether it is direct, indirect or both remains to be seen. Effects of ENSO on the air flow in the region are extensively discussed in Kanyanga (2008).
Linear correlations between Nino 3.4 (one of the ENSO indices) and major meteorological parameters from NCEP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) reanalysis and CMAP [CPC (Climate Prediction Center) Merged Analysis of Precipitation] enhanced precipitation datasets likewise suggest a strong relation between ENSO and the local meteorology (figure 1-4). Different mechanisms have been proposed to explain this prominent teleconnection.

**Figure 1-4.** Linear seasonal correlations between 6 meteorological parameters over the southern Africa and Nino 3.4 during the regional wet season from October to March. Each panel corresponds to different meteorological parameter: a) 700 mb geopotential height b) surface air temperature c) surface relative humidity d) surface CMAP precipitation e) outgoing long-wave radiation and f) 700 mb zonal wind. Image provided by the NOAA-ESRL Physical Sciences Division, Boulder Colorado from their Web site at http://www.esrl.noaa.gov/psd/.
As eastern and western Pacific Ocean undergoes significant changes in SSTs it unavoidably affects an interrelated series of zonal circulation cells known as the Walker Circulation. In the El Niño regime, the tropical Pacific Ocean SSTs are abnormally high leading to stronger convection over the eastern Pacific as well as to sinking of the air over Indonesia. During La Niña, the tropical eastern Pacific surface ocean water cools below the average leading to convergence of the air over Indonesia and divergence of the air over the eastern Pacific. While the mentioned Walker Circulation cell undergoes significant change so do the other related cells influencing major cloud band formations over Africa (Tyson and Preston-Whyte, 2000). It is believed, however, that the effect is only partial. Jury et al. (1994) found that the Qusi-Biennial Oscillation (QBO), a measure of variability in equatorial stratospheric winds, either enhances or weakens ENSO grip on the regional precipitation. Other studies have suggested mechanisms by which ENSO alters SSTs and wind fields over Indian Ocean (Lau and Nath, 2003; Venzke et al., 2000; Xie et al., 2002), which then in turn may provide a more direct synoptic influence on the Highveld. It is clear that the process by which ENSO affects eastern South African meteorology is complex and requires continual investigation; however, it is important to conclude from the discussion above that there is a significant connection between the regional seasonal weather and Pacific Ocean SST anomalies. It is now possible to discuss how the tropospheric ozone responds to the said climatic and synoptic variability.
1.2 Related Research

1.2.1 Ozone and Meteorology

To improve air quality simulations with atmospheric chemistry models, effects of meteorology on the lower tropospheric ozone have been extensively studied (Civerolo et al., 2007; Cox and Chu, 1996; Dueñas et al., 2002; Lou Thompson et al., 2001; Sistla et al., 1996). Through the alteration of OH concentration, moisture content in the air is able to influence ozone chemistry, where the wetter and cloudy conditions tend to reduce ozone while the dryer conditions tend to favor ozone formation (Klonecki and Levy, 1997; Lelieveld and Crutzen, 1990; Murazaki and Hess, 2006; Tu et al., 2007). Clouds may also significantly reduce photochemical processes vital for the surface ozone production (Flynn et al., 2010; Lelieveld and Crutzen, 1990). Air temperature is typically cited as one of the closest direct associates with the mixed layer ozone as it is able to increase the rate of photolytic chemistry and also reflects the amount of the received surface radiation (Aw, 2003; Klonecki and Levy, 1997; Sillman and Samson, 1995). Calm conditions are typically more advantageous for the ozone build up as the \(O_3\) is not being removed from the location where it has formed; however, ozone advection and transport from the free troposphere may present exceptions to this rule (Tu et al., 2007). Overall, a clear connection exists between meteorology and formation of the surface ozone. This relationship makes scientists to consider the long term ozone variability with respect to the past, present, and future climatic patterns.
1.2.2 Previous Studies

Interactions between different climatic modes and free tropospheric ozone have been documented in different studies (Chandra et al., 1998; Doherty et al., 2006; Thompson et al., 2001). Specifically tropical tropospheric ozone can be very sensitive to the transitions of the Walker Circulation; even to such extent that an ENSO index is devised based on the tropical free tropospheric ozone perturbations (Ziemke et al., 2010). The lower tropospheric ozone response to the climate regimes received much less attention. In this regard, work has mainly focused on the mixed layer ozone sensitivity to the climate change (Holloway et al., 2008; Murazaki and Hess, 2006). Singh and Palazoglu (2012) is the only work known to the author that specifically dealt with effects of the climate variability on the surface ozone. It is therefore exigent to explore this avenue further, especially in the region where the relationship between ground ozone and meteorology can be significant.

1.3 Objectives

The aim of this study is to understand to what extent meteorological variability, invoked by ENSO and perhaps other climatic modes, influences seasonal surface ozone concentrations over South African Highveld. Above we have presented an array of pathways by which the weather may influence formation of the lower tropospheric ozone assuming sufficient NOx and VOCs environment (see sections 1.1.1 and 1.1.2); additionally we have explored the evident connections between meteorological parameters in the eastern South Africa and ENSO. It is our hypotheses, given the relatively constant or slowly changing chemical ozone precursor environment, that the significant portion of the surface ozone variability over the Highveld can be explained by variations of meteorological parameters such as clouds, precipitation,
temperature, moisture, and wind that in turn correlate strongly with ENSO. Thus La Niña years experiencing anomalously wet, cloudy, and cool summers should observe a drop in the seasonal ozone, while El Niño years tending to be comparatively drier, clearer and warmer in the summers should exhibit a rise in the seasonal ozone. Because the correlation between ENSO and synoptic conditions is not perfect on the Highveld and the local anthropogenic emissions of the surface ozone precursors at times could be erratic, we cannot expect an ideal linear connection between ENSO and the ozone; however, it is reasonable to expect some significant linear relationship between tropical Pacific SSTs and the seasonal ozone amounts, where above average tropical Pacific SSTs should be indicative of the rising seasonal surface ozone concentrations while below average tropical Pacific SSTs should signify the decreasing seasonal surface ozone. The theory could be presented visually (figure 1-6).
Figure 1-6. The diagram indicating an intricate pathway for ENSO to influence surface ozone over the Highveld. ENSO affects Indian Ocean and Walker Circulation, while all of these factors plus the other climate regimes such as Antarctic Oscillation (AAO), Atlantic Ocean SSTs, etc. (not considered here) potentially affect the eastern South African meteorology in the oscillatory behavior such that this meteorology directly impacts the surface ozone precursors and its formation conditions modulating the production of the surface ozone over the Highveld. Therefore the connection between the surface ozone over the Highveld and ENSO can be established.

Climate regimes that are believed to influence meteorology of the Highveld are at the top of the diagram (figure 1-6). ENSO influences Indian Ocean SSTs and the position of the Walker Circulation. Atlantic Ocean SSTs, Antarctic Oscillation (AAO), and perhaps other climate modes may potentially play a role in the weather of the eastern South Africa, but these effects are thought to be of a lesser importance in comparison with the tropical Pacific Ocean SSTs and the Indian Ocean SSTs. These climate patterns are then combined into the single dashed orange box, which affects various meteorological parameters over the Highveld such as temperature, air pressure, clouds, precipitation, air flow, and water vapor represented by the dashed blue box.
Section 1.2.1 describes the effects of these parameters on the ozone precursors, shown in the dashed green box, as summarized here briefly. Temperature affects the rates of ozone producing reactions. Precipitation can reduce NO\textsubscript{x} amounts by the process of wet deposition (Pages 224-227 in Seinfeld and Pandis, 2006). Water vapor impacts oxidation of VOCs. Clouds have significant influence on the Solar Radiation needed to photo dissociate NO\textsubscript{2}. Air flow can bring or remove NO\textsubscript{x} and VOCs from a particular region. Next, the black dashed box denotes uncertain parameters that are sources of NO\textsubscript{x} and VOCs. Although extremely important, these are the effects that we are not able to completely account for in this study. There is a data of NO\textsubscript{x} concentrations at the Highveld, and VOCs and fire counts are not available to us in this region. Biomass burning, however, is typically important only in the winter and spring seasons (mostly dry period) while VOCs concentrations from the vegetation and traffic are assumed to be relatively constant – of course such assumption is erroneous and this factor embodies one of the largest uncertainties of our study. Despite the above-mentioned limitations, the green dashed box directly affects the production of the surface ozone. Our diagram shows a chain of processes from which it becomes clear how the surface ozone at the Highveld may be significantly linearly dependent on the variability of ENSO.
Chapter 2
DATA AND METHODS

This chapter is dedicated to the information about the data that we use in our study as well as the multiple linear regression model that we apply to this data.

2.1 ESKOM Surface Air Quality Monitoring

Long term measurements of \( \text{O}_3 \), NO, \( \text{NO}_2 \), \( \text{NO}_x \), \( \text{SO}_2 \) along with the ambient temperature, wind speed, and wind direction are available from the five ESKOM air quality monitoring stations: Elandsfontein, Makalu, Palmer, Kendal 2, and Verkykkop. ESKOM is South African Power Company that is responsible for the supply of electricity to the country as well as for the funding and the maintenance of the mentioned monitoring sites. The stations were set up in the strategic locations in order to monitor the influence of the major power plants. All of the stations are located in the close proximity to at least one power plant; however, in addition to the coal power plants, petrochemical industries and traffic may significantly affect \( \text{NO}_x \) concentrations of each specific area.
Figure 2-1. Close up of the Highveld showing the locations of the 5 air quality ESKOM monitoring stations along with Irene weather station (near Pretoria).

**Elandsfontein** is located 25 km east of Kriel and Matla Power Stations and 50 km south-south-east of Witbank in central Mpumalanga. The site is surrounded by coal mining and other industry, non-electrified townships and motor vehicle emission sources (Rorich and Galpin, 1998). **Kendal 2** is located 2 km south of Kendal Power Station. The station is close to the direct pollution sources and can at times exhibit chaotic diurnal or weekly behavior depending on the pollution plumes; nevertheless, it is still may be sensitive to the meteorology on the longer seasonal scales (Thomas and Scorgie, 2006). **Verkykkop** is positioned 10 km north of town Volksrust and 35 km away from the nearest power plant (Mokgathle, 2006; Rorich and Galpin,
1998). Palmer is within an approximately 20 km radius of 3 towns; the major power plants are to the southwest (Rorich and Galpin, 1998). Finally Makalu is situated in the agricultural farmlands and is considered a generally rural station; however, it is 5 km east of the Sasolburg industrial area and 12 km south-south-west of Lethabo Power Station which makes it exposed to the corresponding emissions (Rorich and Galpin, 1998). We note that this location is rather different from others as it is principally rural. Table 2-1 summarizes some technical aspects of the mentioned air quality monitoring stations.

Table 2-1. Contains technical details regarding ESKOM air quality monitoring.

<table>
<thead>
<tr>
<th></th>
<th>Elandsfontein</th>
<th>Kendal 2</th>
<th>Verkykkop</th>
<th>Palmer</th>
<th>Makalu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altitude (meters)</td>
<td>~1600</td>
<td>~1550</td>
<td>~1700</td>
<td>~1800</td>
<td>~1450</td>
</tr>
<tr>
<td>Calibration Procedure</td>
<td>Eskom calibration procedures for ambient air quality monitoring analyzers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calibration Frequency</td>
<td>Quarterly</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Calibration Standards</td>
<td>Eskom Calibration Laboratory (SANAS Lab No 1503)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Analyzers</td>
<td>Monitor Labs, Thermo Electron Company, and Dasibi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Meteorological Data

Meteorological data for this study is provided by South African Weather Service from the Irene weather station located near Pretoria (figure 2-1). Parameters obtained are near-surface values of temperature in Celsius, relative humidity in percent, precipitation in millimeters, and cloud cover in total cloud octas where octas observations are taken three times a day: 8:00 am, 2:00 pm, and
8:00 pm local time. For our study we average all three octas observations to constitute an average cloud cover for a single day. The weather data is not complete at Irene. From the four weather elements that we use only temperature and cloud cover data are available for 18 years, relative humidity begins at 1992 and precipitation measurements only start in 1993.

### 2.3 Multiple Linear Regression Model

#### 2.3.1 Model Overview

One way to identify an ENSO signal in the surface ozone data or for that matter in the any other parameter it might affect is to use the generalized multiple linear regression model similar to the one described in Ziemke et al. (1997). Similar models have been used extensively in the atmospheric science (Bloomfield et al., 1996; Ghude et al., 2008; Randel and Cobb, 1994; Stolarski et al., 1991). Such a model assumes a linear relationship between the parameter in question and the chosen predictors, which is an appropriate method as a first approximation of the problem. In our case the predictors are time and ENSO leading to the following equation modeling the time series $T(t)$ in the consideration:

$$
\hat{T}(t) = \alpha + \beta \cdot t + \gamma \cdot ENSO(t) + R(t)
$$

(2.1)

where $\alpha$ is the seasonal fit, $\beta$ is the trend coefficient, $t$ is the time, $\gamma$ is the regression coefficient for the time series $ENSO(t)$ given by Oceanic Niño Index (ONI) as the three-month running average with 12 values per year starting from DJF and continuing as JFM, FMA, etc., and finally $R(t)$ is the residual series that is calculated by subtracting modeled time series from the actual observed time series $T(t)$. Because the parameters of interest exhibit a strong seasonal variability
the model implements cosine and sine harmonic series to determine the regression coefficients. Let us look at this procedure in more detail.

A time series \( T(t) \) with an apparent annual cycle or cycles can be modeled using cosine function (figure 2-2) such as

\[
\hat{T}(t) = \bar{T} + C \cos[2\pi(ft - \varphi)]
\]  

(2.2)

where \( \hat{T}(t) \) denotes modeled time series, \( \bar{T} \) is a constant vertically translating the function toward the appropriate magnitude, \( f = \frac{1}{n} \) is a frequency, \( t \) is time units, \( C \) is a constant responsible for adjusting amplitude of the wave, and phase angle \( \varphi \) shifts harmonic function horizontally to match the peaks and troughs of the series. Our initial goal is to effectively fit the function given by the equation (2.2) to the time series \( T(t) \). The common method to do this is by minimizing the sum of the squared residuals

\[
\sum R(t)^2 = \sum [T(t) - \hat{T}(t)]^2 = \sum [T(t) - \bar{T} - C \cos[2\pi(ft - \varphi)]]^2.
\]  

(2.3)

To simplify the least squares problem it is wise to modify the equation (2.2) so it becomes linear. Using the trigonometric identity

\[
\cos(\theta - \varphi) = \cos(\varphi)\cos(\theta) + \sin(\varphi)\sin(\theta)
\]  

(2.4)

we can write

\[
\hat{T}(t) = \bar{T} + C \cos(\varphi)\cos(2\pi ft) + C \sin(\varphi)\sin(2\pi ft)
\]

\[
= \bar{T} + A \cos(2\pi ft) + B \sin(2\pi ft).
\]  

(2.5)

Now using least-squares regression it is possible to find the values for \( A \) and \( B \). A more in depth explanation of this method can be found in the chapter 2 of Bloomfield (2000). In our case we add more cosine waves or overtones to improve the fit to \( T(t) \).
Figure 2-2. An example of how a cosine function can be modified by changing various constants. The three major adjustments are varying amplitude and translating function vertically and horizontally.

Extra cosine waves are known as harmonics and they can be added by introducing a variable $k$ inside the cosine function. The general frequency expression can be written as $f_k = \frac{k}{n}$ with $k = 1$ being a fundamental frequency $f_0 = \frac{1}{n}$ signifying one full cycle for the given $n$ time units. When $k = 2$ there are two full cycles for the designated $n$ value. The series of $\frac{n}{2}$ higher harmonics can now be implemented in our model:

$$T(t) = T + \sum_{k=1}^{n/2} [A_k \cos \left(\frac{2\pi kt}{n}\right) + B_k \sin \left(\frac{2\pi kt}{n}\right)]. \quad (2.6)$$

Whether we use all of $\frac{n}{2}$ harmonics or not depends on the context of the problem and discussed in more detail in Wilks (2011) on page 436. Equation (2.6) provides a seasonal cycle of the parameter in question; however, we are interested in more than the seasonal cycle so we apply the equation (2.6) to the equation (2.1). Because there are more constants in our regression equation (2.1) we adapt the new constant notation, $\bar{T} = \alpha_0$, $A_k = \alpha_{1k}$, $B_k = \alpha_{2k}$ and similarly for $\beta$ and $y$, to improve the cosmetic aspects of the resulting equation:
\[
\hat{T}(t) = \alpha_0 + \sum_{k=1}^{n/2} \left[ \alpha_{1k} \cos \left( \frac{2\pi k t}{n} \right) + \alpha_{2k} \sin \left( \frac{2\pi k t}{n} \right) \right] + \\
\beta_0 \cdot t + \sum_{k=1}^{n/2} \left[ (\beta_{1k} \cdot t) \cos \left( \frac{2\pi k t}{n} \right) + (\beta_{2k} \cdot t) \sin \left( \frac{2\pi k t}{n} \right) \right] + \\
\gamma \cdot ENSO(t) + \sum_{k=1}^{n/2} \left[ (\gamma_{1k} \cdot ENSO(t)) \cos \left( \frac{2\pi k t}{n} \right) + (\gamma_{2k} \cdot ENSO(t)) \sin \left( \frac{2\pi k t}{n} \right) \right] \\
+ R(t).
\] (2.7)

An important aspect of this model is an uncertainty involved in calculating the regression coefficients. This uncertainty depends on variance of \( T(t)_i \) and can be expressed as \( \sigma^2 = \frac{\Sigma(T(t)_i - \bar{T}(t))^2}{N - M} \), where \( N \) is the total number of observation points and \( M \) is the total number of coefficients. The reason we have \( N - M \) degrees of freedom is because every coefficient may be thought of as a new sample and since we assume it is a sample and not a population we must account for that by decreasing our numerator by 1 with every coefficient we add. When we calculate a regression coefficient, say \( \alpha \), using the least squares method we can rewrite it as \( \alpha = \Sigma c_i T(t)_i \) with \( c_i = k_i + d_i \) and its variance is

\[
\sigma^2(\alpha) = \sigma^2 \left( \Sigma c_i T(t)_i \right) \\
= \Sigma c_i^2 \sigma^2 T(t)_i \\
= \sigma^2 \Sigma c_i^2 \\
= \sigma^2 \left( \Sigma k_i^2 + \Sigma d_i^2 + 2 \Sigma k_id_i \right) 
\] (2.8)

where \( \Sigma k_id_i = 0 \) by Gauss-Markov Theorem [for further information, see pages 39 and 64 of Neter et al. (1985)] and \( \sigma^2 \Sigma k_i^2 = \sigma^2(\alpha_0) \). This leads us to the subsequent equation:
\[ \sigma^2(\alpha) = \sigma^2(\alpha_0) + \sigma^2 \sum d_i^2. \]  

(2.9)

This is not the final variance value that we use in our results. Each value of \( n \), where \( n \) denotes time units per cycle, has its own variability or if \( n \) stands for the number of months in a cycle then each month has a unique variability. To account for this individual variability we will add seasonal weights to the already existing variance of the regression coefficients. Let \( P \) be a specific time period such as the same month of every year in the dataset or the same 3-month period such as DJF of every year in the dataset. Consequently \( l \) is the counter of \( P \) representing how many of a specific time unit there are in the dataset (how many Januaries are in the dataset or how many DJFs in the dataset) and \( m \) denotes a specific time unit of each cycle (DJF, JFM, etc.). \( S(m) \) can be used to signify the individual \( P \) variability (variances across DJFs, JFMs, etc.) determined by finding the sums of squares of corresponding residuals or errors \( E(l) \) (for example observed January 1990 – modeled January 1990, then observed January 1991 – modeled January 1991, etc.) in the following way:

\[ S(m) = \frac{\sum_{l=1}^{P} E(l)^2}{P}, \]  

(2.10)

then it is possible to find the mean of all monthly variances,

\[ \bar{S} = \frac{\sum_{m=1}^{n} S(m)}{n}, \]  

(2.11)

and finally get the seasonal modulation factor for each \( n \) value (specified with \( m \)) by

\[ \text{Seasonal Modulation Factor (m)} = \frac{S(m)}{\bar{S}}. \]  

(2.12)

If \( \delta(m) = \text{Seasonal Modulation Factor (m)} \) it follows that our final variance of the regression coefficient such as \( \alpha \) is

\[ \sigma^2(\alpha)_f = \delta(m) \left[ \sigma^2(\alpha_0) + \sigma^2 \sum d_i^2 \right] = \delta(m)\sigma^2(\alpha). \]  

(2.13)

The approximation of 95% confidence interval for the regression coefficient is estimated as
\[ \alpha \pm 2\sqrt{\sigma^2(\alpha)_f}. \]  

(2.14)

For further information on this topic in statistics please go to the pages 60-66 in Neter et al. (1985) and see Randel and Cobb (1994).

### 2.3.2 Application of the Regression Model

We are interested in quantifying the effects of ENSO on the surface ozone and chemistry-affecting meteorology over the Highveld during **1990-2007 period**; therefore, we first apply the regression equation (2.1) to the temperature, relative humidity, cloud cover, and precipitation and then to the five ozone data sets described in the section 2.1 using **the time \( t \) as the first predictor** and **the time series \( ENSO(t) \) as the second predictor**. The typical way to present \( t \) is in months; however, for the consistency with our ENSO proxy we indicate time by 3-month running periods. It is common to use Oceanic Niño Index (ONI) to study direct impacts of ENSO on the meteorology over eastern South Africa such as precipitation and air transport anomalies (Kanyanga, 2008; Landman et al., 2012). ONI is an ENSO operational index used by National Oceanic and Atmospheric Administration (NOAA) that is defined as a three-month running average of the SST anomalies from 1971-2000 climatology in the 3.4 Nino region located in the equatorial Pacific Ocean (figure 2-3). An event is classified as El Niño if the 3-month SST anomaly mean exceeds +0.5 °C for five consecutive months, while La Niña conditions require 3-month SST anomaly mean to persist below -0.5 °C for five consecutive months (ONI; [http://www.cgd.ucar.edu/cas/ENSO/enso.html](http://www.cgd.ucar.edu/cas/ENSO/enso.html)). Since a single ONI value represents a 3-month running average of Pacific Ocean temperature state it seems appropriate to smooth our time series of interest in the similar 3-month running mean fashion. As an example we will examine a regression analysis of the Irene ambient temperature time series.
Figure 2-3. Nino 3.4 region in the equatorial Pacific Ocean (Taken from http://www.ncdc.noaa.gov/teleconnections/enso/indicators/sst.php).

First we define $T(t)$ which consists of 18 years of data from 1990 to 2007 where each year entails 12 3-month temperature averages starting from the December. The time in series can be written as

$$t_y = [D\bar{J}F_y, F\bar{M}A_y, M\bar{A}M_y, A\bar{M}J_y, M\bar{J}J_y, J\bar{A}A_y, J\bar{A}S_y, A\bar{S}O_y, S\bar{O}N_y, O\bar{N}D_y, N\bar{D}J_y].$$

Next we state the temperature series (figure 2-4a):

$$T(t_y) = [\bar{T}_{D\bar{J}F_y}, \bar{T}_{F\bar{M}A_y}, \bar{T}_{M\bar{A}M_y}, \bar{T}_{A\bar{M}J_y}, \bar{T}_{M\bar{J}J_y}, \bar{T}_{J\bar{A}A_y}, \bar{T}_{J\bar{A}S_y}, \bar{T}_{A\bar{S}O_y}, \bar{T}_{S\bar{O}N_y}, \bar{T}_{O\bar{N}D_y}, \bar{T}_{N\bar{D}J_y}].$$

In the similar fashion we express ONI time series that were described in the previous paragraph (figure 2-4b):

$$ENSO(t_y) = \left[\bar{SST}^{*}_{D\bar{J}F_y}, \bar{SST}^{*}_{F\bar{M}A_y}, \bar{SST}^{*}_{M\bar{A}M_y}, \bar{SST}^{*}_{A\bar{M}J_y}, \bar{SST}^{*}_{M\bar{J}J_y}, \bar{SST}^{*}_{J\bar{A}A_y}, \bar{SST}^{*}_{J\bar{A}S_y}, \bar{SST}^{*}_{A\bar{S}O_y}, \bar{SST}^{*}_{S\bar{O}N_y}, \bar{SST}^{*}_{O\bar{N}D_y}, \bar{SST}^{*}_{N\bar{D}J_y}\right],$$

where $\bar{SST}^{*}$ is the sea surface temperature anomaly for the 3.4 Nino region based on 1971-2000 climatology.
To demonstrate how the regression model works, we will present three different model fits: no predictors, time as a predictor, and time combined with ENSO time series as 2 predictors. Figure (2-5) shows temperature climatology derived from the model by changing number of predictors. We can see that red and green lines are similar and blue line is slightly warmer. The blue line only uses an $\alpha$ term with the total of 9 coefficients (3 harmonics) from the equation (2.7) and there is no way for it to describe the change in the temperature data set; all it can do is to attribute the existing temperature variability to the seasonal cycle. From the red line, which uses $\alpha$ and $\beta$ terms in the equation (2.7), we can tell that the change in temperature over the given time is positive because the line now is below the blue line due to the fact that the warming in the data set can be described by the trend term slightly decreasing the seasonal cycle. Finally the green line uses full equation (2.7) that employs ENSO time series in addition to the trend term helping it to describe the temperature variability even more than in the second case particularly in the
summer months where ENSO seem to have a noticeable influence. Additionally our model is able to calculate temperature trend along with model fits.

Figure 2-5. Modeled temperature climatology for Irene from the 1990-2007 temperature time series without predictors (blue), with trend (red) and with trend and ENSO (green).

Figure 2-6 compares trends with and without ENSO influences. Over the green line, where ENSO regime is accounted for, several error bars are smaller and consequently significant specifically during the wet season because more of the temperature variability can now be explained through the oscillations of the Pacific Ocean temperature anomalies (figure 2-7). This is consistent with what has been discussed in the section 1.1.3. These results can be visualized by breaking down the model into the specific fits. In the figure 2-8 it is possible to discern how and when both predictors are contributing to the variability in the temperature. First plot from the top shows the seasonal fit, which always repeats the change over one cycle. The second plot down describes the temperature trend over 18 years that is derived from the trend seasonal coefficients
displayed green in the figure 2-6. Because each 3-month period has a different warming rate
seasons did not warm uniformly by the year 2007. In the third screen we can see the specific
effects model attributed to ENSO. Most striking are the temperature amplifications during the
wet seasons of 1991-1992 and 1997-1998 as well as the evident cooling in the wet seasons of
observed time series versus modeled time series. Finally the last plot presents residuals from the
three different runs of the model where purple corresponds to no predictors, brown to the one
predictor, and cyan to the two predictors. It is possible to find out how well the model explains
the temperature variability by using the coefficient of determination (Page 241 in Neter et al.,
1985):

\[ R^2 = \frac{\sum (\bar{f}_t - \bar{t})^2}{\sum (\bar{T}_t - \bar{T})^2}. \]  

(2.15)

By using the equation (2.15) we find that the purple line has \( R^2 = 0.93 \), the brown line has
\( R^2 = 0.94 \), and the cyan line has \( R^2 = 0.95 \) [typically to compare coefficients of determination
one is required to find an adjusted coefficient of determination, but because this is not a central
result of our study and our sample population is above 100 it is plausible to estimate the
coefficient of determination with equation (2.15)]. We see that the model slightly improves by
adding the predictors, but because seasonal temperature cycle already explains 93% of the
Highveld temperature variability it is difficult to improve by much. Despite having the highest
coefficient of determination the model fit with two predictors (cyan curve in the residuals screen)
may introduce a local error such as in this case, where early summer of 1999 is too cool in the
model because of strong La Niña. Errors of this type are unavoidable in our model because the
relationship between ENSO and meteorology to be precise is non-linear and only is approximated
to be linear in our model. With this model it is now possible to analyze the connection, if it
exists, between the surface ozone at the Highveld and ENSO.
Figure 2-6. Seasonal trends in °C per year (β coefficients) derived from the Irene temperature data without ENSO influence (red) and with ENSO influence (green).

Figure 2-7. ENSO coefficient γ in °C per 1 °C of the Pacific Ocean temperature anomaly (ONI) that shows significant ENSO influence on the temperature for the summer and the early spring.
Figure 2-8. Model separated contributions to describe the temperature series, combined contributions vs. observations, and residuals where a) extracted temperature seasonality b) extracted temperature trend c) extracted ENSO influence on the temperature series d) temperature according to model vs. temperature observations e) residuals for three different regressions: just temperature seasonality (purple), seasonality with trend (brown), and finally seasonality with trend and ENSO (cyan).
Chapter 3

RESULTS AND DISCUSSION

This section is broken into the three parts: small case study, ENSO and Meteorology, and ENSO and ozone. Before we show the results of our linear regression model applied to the Highveld ozone, we demonstrate an actual observation example where it is possible to see how clouds, temperature and other relevant parameters may affect the ozone over the Highveld on a day to day basis.

3.1 Case Study

In this case study we explain how meteorological parameters may affect the surface ozone concentrations over the Highveld on a day to day basis. A quick look at the data from the 4 of the Highveld air quality monitoring stations (see section 2.1; also Makalu is not included because it is a slightly different site in comparison from others) reveals that the ozone responds to its environment mainly in the expected fashion (figure 3-1). The first three days exhibit cloudy and relatively cool conditions, which prevent needed photochemistry to occur. Day four seem to be warmer and less cloudy, but low morning NO, with erratic wind speed probably tend to prohibit accumulation of ozone. Days 5, 6, 8, and 9 experience higher ozone amounts as temperatures are relatively high, clouds are limited, and the needed NO is available. Also day 9 presents an example where the higher wind speed may encourage ozone formation, given the right direction, as a huge plume of NO is advected in during the morning (since the data is an average of the four stations the plume may not have been present at all of the stations). Day 7 sees lower air
temperatures as well as cloudy conditions so the ozone is relatively low. Warm and clear conditions seem to occur on the 10th of January 1998, but the low NOx environment inhibits any high ozone concentrations.

**Figure 3-1.** 10 days of ozone, NOx, temperature and wind speed observations averaged from the four of the Highveld stations: Elandsfontein, Kendal 2, Verkykopp, and Palmer. 10 days of averaged cloud cover is from Irene. Note: NOx is rescaled as ppbv*3 and cloud cover is rescaled as octas*3 for easier comprehension of the data.

### 3.2 ENSO and Meteorology at the Highveld

In section 1.1.3 we talked about the teleconnection of the eastern South African meteorology with ENSO and in section 2.3.2 we saw that the Irene temperature correlates significantly with ENSO
in the summer and the spring given our regression model parameters. Here we apply the regression model to relative humidity, clouds and precipitation at Irene. First we present our results by looking at the ENSO coefficients for each of the variables in order to assess the significance of the ENSO influence and then we show a quantitative impact of ENSO on the mentioned meteorology derived from the corresponding coefficients.

![3-month Running Average of Nino 3.4 SST Anomalies](image)

**Figure 3-2.** Positive and negative anomalies of Pacific Ocean region Nino 3.4.

The figure 3-2 indicates warm and cold periods of the equatorial Pacific 3.4 Nino region (figure 2-3), but according to the definition given in section 2.3.2 not all warm and cold episodes could be classified as El Niño and La Niña. Table 3-1 specifies which years are categorized as El Niño events and which years are categorized as La Niña events according to Oceanic Niño Index. El Niño events of 1991-1992 and 1997-1998 are the strongest in the time series, while the episode of 1998-2000 is the strongest La Niña event over the 18 years investigated. Now we can take a look at how these events are reflected in the meteorological parameters measured at Irene.
Table 3-1. El Niño and La Niña events as classified by ONI during the 1990-2007 period. Strongest episodes are marked in bold.

<table>
<thead>
<tr>
<th></th>
<th>Event Periods</th>
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</table>

ENSO coefficients for the weather elements indicate the calculated seasonal ENSO effect on each of the elements (figure 3-3). The temperature coefficient (briefly mentioned in section 2.3.2) is grouped into 12 3-month running average periods or 12 smoothed monthly averages ($DFJ = \bar{f}, JFM = \bar{F}$, etc.) such that each smoothed month has its own sensitivity toward the ENSO time series. A coefficient tells us how many units of a variable are changed by the one unit of ONI (1 ºC SST anomaly of the Pacific Ocean region Nino 3.4). In order for the coefficient to be significant at the 0.05 $\alpha$ level it is necessary for the error bar not to touch or cross the zero line, in other words be significantly different from zero. Smoothed January or DJF (from now on we will just use January or whatever the corresponding month is appropriate) has an ENSO coefficient of approximately 0.5 ºC per one unit of ONI. The coefficient is largest for March and April where we see 1 ºC per 1 ONI. Effect is significant from November until April. In June through October the consequence of ENSO is insignificant. So even though October value is positive we cannot ascertain for certain its plausibility because of the uncertainty in calculating the regression coefficient. Moving on to the relative humidity we notice an opposite effect of El Niño on this parameter in the similar smoothed months: December-March. The maximum drop occurs in April where about 7 % of the relative humidity is reduced per ONI. In August, however, relative humidity changes to about 2 % for 1 ONI. The cloud cover ENSO coefficient
generally follows the relative humidity sensitivity towards ENSO, but with a few minor differences. April still exhibits a minimum with 0.7 octas reduced per 1 ONI; however, the effect is still statistically significant in June and no significant increases in cloud cover for positive change in ONI are evident. Precipitation decreases with the largest rate of 30 mm per ONI in February and March. Smaller but significant reduction in precipitation is evident in October and November. From these ENSO coefficients it is possible to calculate, using the ONI time series, the specific impact of ENSO on each of the parameters.

Figure 3-3. ENSO coefficients derived by the model for the four Irene meteorological parameters a) temperature ENSO coefficient b) relative humidity ENSO coefficient c) cloud cover ENSO coefficient d) precipitation ENSO coefficient. Zero line is indicated in black.
Figure 3-4 displays ENSO impact on the meteorological variables according to the ENSO coefficients calculated by the regression model. We looked at the temperature in section 2.3.2 where we remarked that the model attributed significant warming to ENSO in the wet seasons. Especially notable are the strong El Niño and La Niña episodes (table 3-1) where the temperature during the El Niño events of 1991-1992 and 1997-1998 is approximately amplified by +1.2 °C and consequently during the strong La Niña of 1998-2000 the decrease is by about -1 °C. The most reduction in relative humidity is by about 10 % in April 1992 and March 1998, while February-April of both 1999 and 2000 exhibit increase of 5-6 %. Irene cloud cover experiences similar tendencies as the relative humidity. In strong El Niño cloud cover decreases by 1 octa and in strong La Niña cloud cover increases by 0.5 octas. The model attributes a precipitation decrease of about 50 mm in early 1998 due to the potent El Niño episode and close to 40 mm increase of precipitation due to La Niña occurrences in 1999 and 2000. We observe a statistically significant relationship between all of the four meteorological variables and ENSO.

Our analysis supports several of the points mentioned in section 1.1.3 about the prominent teleconnection between Pacific Ocean SSTs and South African synoptic patterns. Although our data is limited to a single site we gather an important result regarding our period of study. The meteorology, at least the four parameters studied, is sensitive toward the ENSO events primarily in the wet season starting in November until about April. Temperature, humidity, and cloud cover appear to vary with Pacific Ocean temperature more smoothly than precipitation, with cloud cover extending its significance response to as far as June. This is an important point as it presents a significant consequence regarding surface ozone variability during the autumn. In the next section we will discuss our results regarding the connection between the surface ozone over the Highveld and ENSO including the influence of the weather variables on this connection.
3.3 ENSO and Ozone at the Highveld

3.3.1 ENSO Signal in the Ozone Data

The 3-month running average ozone from the five Highveld air quality monitoring stations (see section 2.1) is summarized in the figure 3-5 over the 18 years from 1990 until 2007. Only Elandsfontein and Verkykkop have measurements that actually span for 18 years. Three other
stations – Kendal 2, Palmer, and Makalu miss either 4 or 3 years. Specifically Kendal 2 goes from 1994 to 2007, Palmer goes from 1990 to 2003, and Makalu goes from 1990 to 2004. Strong variability of the surface ozone is evident after examination of the figure 3-5. In addition there is quite a bit of difference in the ozone concentrations from one site to another. Most of the years at every station tend to exhibit ozone cycles, but at times the amplitude of these cycles varies to a large extent compromising the apparent consistency of the data. At a closer examination of the figure it is possible to note that the cycles do not always overlap in fact the station Makalu is peculiar in this regard. The middle of year 1994 stands out as Makalu experiences a minimum while all other stations show an increase or even a local maximum. Another curious aspect about this figure is the early 2000 minimum that is unmistakable almost in all of the stations. Similarly the increase of the ozone local minima from 1996 until about mid-1998 is discernible. It is of course rather perplexing to analyze these time series just by an eye examination. In order to explain some of this curious variability in the Highveld ozone data we shall use the model described in section 2.1. As already mentioned we suspect that the natural variability evoked by ENSO can be discerned in the ozone data through the seasonal analysis.
Figure 3-5. 18 years of 3-month running averaged ozone over the Highveld from Elandsfontein (blue), Kendal 2 (red), Verkykkop (green), Palmer (black), and Makalu (cyan).

It is useful to examine the seasonal cycle of each station in more detail. Figure 3-6 displays observed and modeled ozone climatologies for every site. The observed climatology is calculated by the equation (2.6), while the modeled climatology is given by $\alpha$ term with harmonic expansion from the equation (2.7) accounting for the trend and ENSO influences in the time series. If a station exhibits a significant trend then the model may noticeably alter its climatology. When we look at the observed ozone seasonality (red curve, figure 3-6) it is possible to notice that all of the stations besides Makalu exhibit a minimum in February and maximum in the September-October period. Makalu represents somewhat different case. The minimum is observed in July and maximum is observed in December. This pattern is remarkably different from the other stations. In section 1.1.2 we write that it is typical to experience the lowest
seasonal ozone in March-April and the highest seasonal ozone in September-October. This information comes from the Irene ozonesonde dataset (Clain et al., 2009; Diab, 2004), which seems to match the ozone climatologies observed at Elandsfontein, Kendal 2, Verkykkop, and Palmer at least in terms of minimum and maximum contour. It is then unclear what is going at Makalu that offsets observed climatology by about couple of months. It is specifically an agricultural monitoring location, which is relatively rural in comparison with other sites. Perhaps an array of dissimilar to other stations sources contribute a variety of different chemical species that alter the ozone cycle.

**Figure 3-6.** Observed ozone climatologies (in red) and modeled climatology (in blue) for the five Highveld air quality monitoring stations a) Elandsfontein b) Kendal 2 c) Verkykkop d) Palmer e) Makalu.
The modeled ozone climatologies, with effects of trend and ENSO, are different from the observed climatologies (blue curve in figure 3-6). All of the stations exhibit similar maxima that are still approximately in the September-October range, but minima position shifts to March except for Kendal 2 which keeps its February minimum. If seasonal trend is able to horizontally offset climatology (meaning change minimum and maximum) there must be no completely stable climatology for the ozone at Highveld. This change can be seen for all of the stations, but the most dramatic example is Makalu. Makalu has no consistent minimum and no consistent maximum. To show this in more detail we investigate Makalu site a bit further and in the figure 3-7 plot the mean observed ozone climatologies for the four different periods. Maximum and minimum ozone concentrations change with time during 1990-2005. For some reason the September-October ozone maximum that occurs in 1990-1993 period is not seen in any of the other periods. We believe this implies that the ozone at Makalu environment is sensitive to precursors to such extent that the anthropogenic activities are able to modify its annual cycle. Now that we have looked at the ozone climatologies of each station it is finally the time to determine to what extent an ENSO may affect the ozone concentrations over the Highveld.
Figure 3-7. Observed ozone climatologies at Makalu for four different periods.

To estimate the ENSO impact on the surface ozone over the Highveld, we calculate ENSO coefficient for each of the 5 stations (figure 3-8). At Elandsfontein ENSO effects are significant from January to June (smoothed months, see section 3.2) with maximum in May of about 6 ppb per ONI. Kendal 2 sees similar significant influence from January to June as well as comparable maximum in April-May of about 4-5 ppb per ONI. A somewhat different case occurs at Verkykkop where we still see an analogous peak in May-June of approximately 6 ppb per ONI; however, ENSO impact is statistically significant through all of the months except October. Palmer reflects the Verkykkop situation and reveals statistically significant ENSO coefficients for all of the months except October with maximum in May of 6-7 ppb per ONI. Finally Makalu does not show any significant influence from ENSO. We have discussed the complexities of Makalu ozone climatology and therefore suspect that the environment at this station is dissimilar.
to the environment of the other sites possibly disrupting or altering the regular meteorological influence on the ozone production. This requires further investigation.

![Figure 3-8. ENSO coefficients in ppbv per ONI derived from the model for the surface ozone at 5 Highveld stations a) Elandsfontein b) Kendal 2 c) Verkykkop d) Palmer e) Makalu.](image)

It is important to note that in the 4 out of 5 sites we observe significant effects of ENSO on the ozone especially in the months of *January, February, March, April, May, and June*. In figure 3-3 (see section 3.2) we looked at the ENSO coefficients for the four weather elements and concluded that ENSO significantly influences temperature during November-April, relative
humidity during November-May, cloud cover during December-June, and finally precipitation during October-November and February-March. We think that at least for the first six months of the year (January-June) meteorology plays an important role in enhancing or inhibiting the Highveld surface ozone through the connection to ENSO where the cloud cover is likely to be the single most important parameter that inhibits ozone production (see section 1.3). More difficult is to understand the statically significant effects of ENSO on the July-September ozone at Verkykkop and Palmer. There is some evidence that the transport patterns over southern Africa are influenced by ENSO throughout the lifetime of an episode (Kanyanga, 2008), but the study is limited to the El Niño of 1991-1992 and the La Niña of 1999-2000. To understand how the transport patterns may impact the surface ozone over the Highveld with relation to ENSO is beyond the scope of this work and would require the use of coupled weather-chemistry models. We believe that October has no sensitivity to ENSO in all of the stations because of the burning season at this time in the southern Africa and much of the ozone may be transported into the region with the strong dependence on the wind patterns that may not be connected to ENSO.

Now we move on to address the quantitative monthly impact of ENSO on the Highveld surface ozone.

in January-March 1998 with reductions of -6 ppb in May 1999 and April 2000. Makalu shows no significant events.

The values at Verkykkop and Palmer are especially prominent with as much as +11 ppb in July 1997 at Palmer. July falls into the dry season and the significant ENSO influence can only come from the air transport or the temperature but we did not find the temperature variability significant for July using the Irene weather data and analysis on the air transport was not performed. Another explanation for the above-mentioned results is the limitations of our regression model. Because July 1997 ONI value is +1.7 °C it has a high weight and adds significance to any variable that happens to be above its typical seasonal cycle in that month. It is therefore possible that the ozone at Palmer is higher than normal in July 1997 due to the increased NOx emissions for instance but our model has no knowledge of that and attributes everything to either trend or ONI. Since this is the first approximation study we do not address this problem; however, we acknowledge the limitations of the regression model we use. At this point we move on to the discussion of ozone trends to evaluate the air pollution at the Highveld over the 18 years of the study.
3.3.2 Ozone Trends?

Ozone trends are important for the regional assessment of the air pollution. For example, Clain et al. (2009) used Irene ozonesondes to calculate the ozone trends in the lower troposphere from 1990-2007 (with 1994-1998 data missing). There is evidence that this study has a flaw due to inconsistent ozonesonde balloon launches (Thompson and Balashov, *paper in progress*). The
mentioned study has found significant positive trends for the Irene ozone. We therefore take advantage of our long term, and generally consistent, data to take a look at the ozone trends over the Highveld with the regression model and determine whether or not ENSO has any influence on these trends.

Figure 3-10 demonstrates ozone trends for every smoothed month in ppbv per year with and without effects of ENSO at the Highveld. Starting with Elandsfontein we observe only few slight differences between two of the model outputs. The trend is either marginally negative or not significant. At Kendal 2 no ENSO influence is apparent and the trend is only barely significant in August. Verkykkop shows no signs of significant trend and no signs of any notable difference between the two model runs. Palmer has a significant negative trend from September to March without ENSO influences; however, when the ENSO influences are accounted for we see a slight change as the negative trend becomes significant for August but no longer for March. Additionally a barely significant positive trend appears in May. Finally at Makalu we immediately notice the striking negative ozone trend from July through October with September decreasing at a dramatic rate of 1 ppb per year. No ENSO influence is evident at Makalu. After analyzing these trends we are able to conclude that according to the data of these five sites there are practically no statistically significant positive trends of the surface ozone at the Highveld but on the contrary statistically significant negative trends are observed at Palmer, Makalu, and to the lesser degree at Elandsfontein. It is likely that NO\textsubscript{x} plays an important part in controlling the surface ozone trends. In the figure 3-11 we use the same linear regression model to determine NO\textsubscript{x} (no ENSO term in this case just seasonal coefficient and trend). The figure shows complex result that we are not able to comprehend here without deeper analysis; nevertheless, it is likely that negative NO\textsubscript{x} trends at Elandsfontein and Palmer have some effect on the negative ozone trends. Makalu once again exhibits a strange behavior with NO\textsubscript{x} decreasing significantly in February through July period, while ozone reduces significantly from July
through October period. Even with trend and ENSO we are not able to explain a lot of surface ozone variability at the Highveld. In the last section of the results we will discuss these uncertainties in more detail.

Figure 3-10. Modeled seasonal surface ozone trends in ppb per year without (red) and with (blue) effects of ENSO at the 5 Highveld air quality monitoring stations a) Elandsfontein b) Kendal 2 c) Verkykkop d) Palmer e) Makalu.
3.3.3 Uncertainties in Ozone over the Highveld

Even after the analysis of the surface ozone time series over the Highveld with trends and ENSO influence much of the uncertainty and unattributed ozone remains (figure 3-11). Some of the residuals that are shown in figure 3-11 may be accounted for with NO\textsubscript{x} (not completed in this study), but others may relate to much more complex processes. For example we have not considered at all the interactions of VOCs and CO during the burning season. Variability in the fire numbers in the neighboring regions of the Highveld may significantly affect the ozone at any

Figure 3-11. Modeled seasonal NO\textsubscript{x} trends in ppb per year at the 5 Highveld air quality monitoring stations a) Elandsfontein b) Kendal 2 c) Verkykkop d) Palmer e) Makalu.
of the mentioned stations. Ozone transport is another issue that could be different from station to station. Natural VOCs such as isoprene play a vital role in the ozone formation, but only very scarce data is available on the biogenic emissions. Additional issues for unexplained ozone come from the limitations of the regression model we use. In the figure 3-12 it is possible to notice that 1997-1998 along with 1999-2000 still contain significant portions of unexplained ozone. It is likely that some of these residuals may be correctly attributed to ENSO, but because the relationship between the surface ozone over the Highveld and ENSO is not entirely linear the model is unable to determine the true impact of each particular ENSO event estimating the overall effect of ENSO on the ozone over the 18 years of study. Table 3-2 displays coefficients of the determination for the model fit with ENSO and without ENSO (R² values have not been adjusted). We do not try here to explain the residuals, but rather leave them to an open interpretation of the reader because in order to truly understand these uncertainties much more thorough investigation is required with lots of additional measurements.

Table 3-2. Coefficients of determination corresponding to the residuals shown in the figure 3-12.

<table>
<thead>
<tr>
<th></th>
<th>Elandsfontein</th>
<th>Kendal 2</th>
<th>Verkykkop</th>
<th>Palmer</th>
<th>Makalu</th>
</tr>
</thead>
<tbody>
<tr>
<td>R² without ENSO (red)</td>
<td>0.21</td>
<td>0.46</td>
<td>0.31</td>
<td>0.50</td>
<td>0.51</td>
</tr>
<tr>
<td>R² with ENSO (blue)</td>
<td>0.28</td>
<td>0.54</td>
<td>0.49</td>
<td>0.70</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Figure 3-12. Modeled ozone residuals without (red) and with (blue) ENSO effects at the 5 Highveld air quality monitoring stations a) Elandsfontein b) Kendal 2 c) Verkykop d) Palmer e) Makalu.
Chapter 4

CONCLUSIONS

In our study we attempt to identify El-Nino Southern Oscillation (ENSO) effects on the surface ozone at the five ESKOM air quality monitoring stations located in the South African Highveld. We use the generalized multiple regression model to first fit the meteorological data – temperature, relative humidity, cloud cover, and precipitation that is available from the local weather station Irene and then the model is also applied to surface ozone time series to determine seasonal, trend, and ENSO coefficients. Our results show that South African wet season that lasts from October to March is mostly sensitive to ENSO for the aforementioned meteorological variables, whereas the dry season that extends from April to September is only partially sensitive to ENSO. In terms of ozone, Elandsfontein and Kendal 2 exhibit ENSO effects from smoothed January to smoothed June. Verkykkop and Palmer show the statistically significant ENSO influences in all the months of the year except October. The fifth site, Makalu, does not appear to have any response to ENSO. This may be in part attributed to the ozone observed climatology of Makalu that appears to change its maximum and minimum values throughout 4 or 3-year periods. The reason for this is unknown, but this site appears to be exposed to a different environment relative to the other air quality monitoring Highveld sites. Our study also looks at the surface ozone trends at each of the monitoring stations. Palmer, Makalu, and to the lesser degree Elandsfontein, exhibits statistically significant negative trends in the surface ozone. Verkykkop and Kendal 2 generally show no statistically significant change in the surface ozone. Ozone trends are in part attributed to the trends in NOx. Overall our study reveals a lot of uncertainty and unexplained ozone data even in the strong ENSO events. Considering our regression model such errors are expected because the model is greatly simplified based on only linear dependence.
between variables. For example, the model does not account for the non-linear processes which may include complex changes in ozone chemical sources or feedbacks between sources and perturbed meteorological conditions.

This study shows statistically significant results that ENSO has an effect on the surface ozone over the South African Highveld through the meteorological variables that directly affect the ozone formation process at least during the most of the summer and most of the autumn where El Niño amplifies ozone and La Niña reduces ozone. We also may conclude that in the wet season the Highveld ozone depends significantly on the natural variability that ENSO partially explains while in the late dry season ozone seems to be driven mainly by the biomass burning and ozone advection. The results of this work invite us to think about the other places in the world that may experience similar ENSO teleconnection. How has the surface ozone in those places responded in the past 20 years?
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