



School of Geography, Archeology and Environmental Studies

University of the Witwatersrand, Johannesburg

**AN ASSESSMENT OF SPATIAL AND TEMPORAL
VARIATIONS OF NITROGEN DIOXIDE OVER
MPUMALANGA HIGHVELD**

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DECLARATION

I Lucky, Samuel Malaza, declare that this mini-dissertation is a product of my own effort. It is submitted to the School of Geography, Archeology and Environmental Studies at the University of the Witwatersrand, Johannesburg. This mini-dissertation has never been submitted to any University.

(Lucky Malaza)

Submitted on the 31st day of March 2017

ABSTRACT

High concentrations of nitrogen containing compounds are a growing concern in the Mpumalanga Highveld with satellite measurements confirming high NO_2 in different hotspots around the globe including Mpumalanga Highveld. Nitrogen oxides are produced from the eight coal fired power stations in Mpumalanga Highveld, a petrochemical industry in Secunda, steel processing plants in Middelburg and Emalahleni and tail emissions from traffic in the Mpumalanga Highveld. Monitoring of these trace gases is important to estimate an impact that they cause to human health and the environment and also to implement air quality emission standards by government Authorities. A 2008 data from Elandsfontein monitoring station and seven other monitoring stations in the Mpumalanga Highveld have been compared with the 2008 satellite data taken from Ozone Monitoring Instrument (OMI) overpass over the Mpumalanga Highveld. Elandsfontein monitoring station is situated on the highly industrialized Mpumalanga Highveld and its purpose is to monitor impacts of stack emissions on air quality. The study focuses on a 2008 nitrogen dioxide dataset which was taken from Elandsfontein monitoring station. An analysis of data from other monitoring stations located in Ermelo, Bulfour, Hendrina, two stations in Middelburg, Emalahleni, Standerton and Secunda have been undertaken to indicate temporal variation and spatial distribution of nitrogen dioxide in the Mpumalanga Highveld. Temporal variability and spatial distribution of nitrogen dioxide in the Mpumalanga Highveld were estimated by analyzing the ground based measurements and satellite data sets. Smoke stacks emit NO into the atmosphere where it reacts with atmospheric oxygen to form NO_2 . Subsequent reactions of NO_2 result in the formation of ozone. The satellite derived data has been modelled and compared with the ground measured data. Meteorological factors including diurnal and temporal variations of the NO_2 concentrations have been analyzed to establish differences and similarities between the two data sets. Vertical column densities of nitrogen oxides from satellite measurements with high resolution are presented in $\text{mole} \times (10^{15})/\text{cm}^2$ and together with ground measured data from other eight air quality monitoring stations have been converted into $\mu\text{g}/\text{m}^3$. Analysis of both data sets have been done on the same units, $\mu\text{g}/\text{m}^3$. Seasonal and diurnal variations between the two data sets seem to form the same graphical trends by showing high concentrations during winter than in summer. Ground measured and satellite born datasets do not agree because clouds, air mass factor, aerosols and surface albedo create retrieval errors on the satellite data.

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ABBREVIATIONS

AMF	Air mass factor
DEBITS	Deposition of Biogeochemically Important Trace Species
DEAT	Department of Environmental Affairs and Tourism
IGAC	International Global Atmospheric Chemistry
µg/m ³	micrograms per cubic meter
mole/cm ²	Mole per square centimeters

NO _x	nitrogen oxides
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO ₃	Nitrate
NH ₄	Ammonia
O ₂	Oxygen
OMI	Ozone Monitoring Instrument
Ra	Aerodynamic resistance
Rb	boundary layer
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Cartography
TEMIS	Tropospheric Emission Monitoring Internet Service
VCD	Vertical column density
VOC	Volatile organic compounds
V _d	Deposition velocity

CHAPTER 1: INTRODUCTION

1.1 Background

Nitrogen oxides are formed by the combination of nitric oxide and nitrogen dioxide. Nitrogen oxides are abundant in the atmosphere of the Mpumalanga Highveld (Figure 1) as they are generated from the fossil fuel combustion at eight coal fired power stations, metallurgical and petrochemical industries. Atmospheric nitrogen (N_2) is a stable chemical; however, burning fuel at a high temperature like in car engines promotes a reaction between N_2 and atmospheric O_2 . It is this reaction that results in the formation of NO_x . The Mpumalanga Highveld lies at an elevation exceeding 1500m and in a subtropical high pressure belt (Zunckel *et al.*, 1996). Transportation sources also contribute to the ambient levels of these trace gases in the atmosphere through tail pipe emissions. Use of coal for domestic energy by low income households in the Mpumalanga Highveld contributes to the ground level concentrations of nitrogen oxides. Nitrogen occurs in rainwater in the form of NH_4^+ . The NH_4^+ part of precipitation is generated from the incorporation of gaseous NH_3 and NH_4^+ particles which are present in clouds and rainwater (Mphepya, 2005). Nitrogen oxides are mainly produced by fossil fuel combustion from tail pipe emissions and in coal fired power stations. Ammonia is a nitrogen containing compound which is produced from manure when applied to agricultural activities. Nitric oxide is a form of nitrogen which is produced through stack emissions, once in the atmosphere it becomes oxidized to form nitrogen dioxide. The formation of nitrogen species in the atmosphere creates disturbance of natural nitrogen cycle. Analysis of nitrogen dioxide from the eight air quality monitoring stations including Elandsfontein air quality monitoring station has been done and compared with the satellite borne data over the Mpumalanga Highveld.

Concentrations of priority gases including nitrogen oxides increase in the atmosphere of the Mpumalanga Highveld. Heavy industries, including the coal fired power stations and informal settlements are the main source of atmospheric pollutants in the area. Priority pollutants are a health and environmental concern because of their pollution effect on the ambient air quality and human health. Eskom has put Elandsfontein air quality monitoring station in the highest point near Secunda to monitor ground concentrations of trace gases including nitrogen dioxide. This

monitoring station is able to capture pollutants in the ambient atmosphere of the Mpumalanga Highveld. Other monitoring stations have been put in strategic areas in Balfour, Ermelo, Middelburg, Hendrina, Standerton, Secunda and Witbank. Their positions in respect of wind directions enable them to capture pollutants from point sources. NO₂ satellite data in the Mpumalanga Highveld is available through an overpass snap shot taken by the Ozone Monitoring Instrument (OMI) which passes over the area between 11:00 to 12:00. The satellite borne and ground measured data of nitrogen dioxide have been converted to $\mu\text{g}/\text{m}^3$ in order to assess its spatial and temporal variation over the Mpumalanga Highveld.

1.2 Rationale

Mpumalanga Highveld is a heavily industrialised area of the Mpumalanga province. The petrochemical industry in Secunda, steel processing plant in Middelburg and eight coal fired power stations make the area a measure emitter of trace gases including nitrogen oxides. Oxidation of nitrogen oxides results into nitrogen dioxide which is a focus of this research work. Informal settlements in the Mpumalanga Highveld use coal fired stoves for cooking and providing heat inside houses, the resulting emissions from household's chimneys contribute to air pollution in the area. In 2007, the Minister of Environmental Affairs declared Mpumalanga Highveld a priority area in terms of the National Environmental Management: Air Quality Act, 2004 (Act No 36 of 2004). Ground monitoring is done through air quality monitoring stations in different locations of the Mpumalanga Highveld and has been assessed with satellite measurements over the Mpumalanga Highveld. Temporal variation and spatial distribution of nitrogen dioxide must be determined to establish its significance over the Mpumalanga Highveld.

1.3 Aim of the research

The main aim of this study is to establish the spatio-temporal variations of nitrogen dioxide over the Mpumalanga Highveld and attempt to assess whether the relationship between *in-situ* measurements and satellite estimated concentrations of nitrogen dioxide can be modelled.

1.4 Objectives of the research

- To determine temporal variability of Nitrogen dioxide in the Mpumalanga Highveld;
- To establish the spatial distribution of Nitrogen dioxide in the Mpumalanga Highveld; and:
- To model the relationship of *in situ* measurements with satellite estimated concentrations of Nitrogen dioxide

1.5 Structure of the report

This mini dissertation is divided into six chapters. **Chapter one** gives an introduction, background, rationale, aim of the research, objectives and structure of the report. **Chapter two:** provides a literature review, temperature systems and disturbances, nitrogen oxides chemistry in the atmosphere, remote sensing application to nitrogen compounds assessment Sources of nitrogen dioxide, natural sources: lightning, soil, anthropogenic sources: fossil fuel combustion, fertilizers, biomass burning, other sources, nitrogen oxides in the Mpumalanga Highveld, weather systems over Southern Africa, anticyclones, transportation of nitrogen oxides, Deposition of nitrogen oxides over the Mpumalanga Highveld, wet deposition of nitrogen oxides, dry deposition of nitrogen oxides, impacts of nitrogen oxides on the environment. **Chapter three:** provides a description of materials and methods of the study, Elandsfontein monitoring station, data collection at Elandsfontein monitoring station, Elandsfontein data analysis, monthly variation, seasonal variation, diurnal variation, other monitoring stations in the Mpumalanga Highveld: Balfour monitoring station, Ermelo monitoring station, Hendrina monitoring station, Middelburg 1 monitoring station, Middelburg 2 monitoring station, Standerton monitoring station, Secunda monitoring station and Witbank monitoring station, Ozone monitoring instrument, satellite data collection, satellite data retrieval, and satellite data analysis. **Chapter four:** provides results and discussions, temporal variability of nitrogen dioxide in the Mpumalanga Highveld, other monitoring stations in the Mpumalanga Highveld, nitrogen dioxide at Elandsfontein monitoring station, monthly variations of nitrogen dioxide, seasonal variations of nitrogen dioxide, diurnal variations of nitrogen dioxide, the spatial

distribution of nitrogen dioxide in the Mpumalanga Highveld, modelling satellite data for ground measurement, influence of diurnal variation, summary of satellite data over the Mpumalanga Highveld, monthly variation of nitrogen dioxide, seasonal variations of nitrogen dioxide and diurnal variations nitrogen dioxide, retrieval uncertainties related to surface albedo, retrieval uncertainties related to clouds and retrieval uncertainties related to aerosols and weather influence on nitrogen dioxide distribution over the Mpumalanga Highveld are described.

Chapter five: provides a conclusion and recommendation of the study and responses to spatial and temporal variability of nitrogen dioxide over Mpumalanga Highveld, spatial distribution of nitrogen dioxide from satellite measurement and whether the satellite data can be used to estimate surface concentration of nitrogen oxides. **Chapter six:** provides references.

CHAPTER 2: LITERATURE REVIEW

2.1 Temperature systems and disturbances

Tropical circulation transfers excessive heat that accumulates in the low altitudes to other parts of the atmosphere with low heat. Westerly waves converge at the surface level and diverge at the upper level of the atmosphere. This atmospheric condition results to adiabatic cooling of less dense air as it is uplifted. The surface convergence and divergence of westerly waves as air is uplifted result in the formation of clouds and ultimately rainfall. The maximum rainfall often occurs just north and south of the equator (Sitnikov, 2010). Cold fronts occur when there are westerly waves and cut-off lows. Cold fronts indicate the northward movement of cold air from the south and south-west and create sharp snaps. The air flow before the cold front has a northerly component with clear skies and is stable as a result of near surface subsidence and convergence of the uplifted air. The cold front creates, distinct clouds with a variation in wind direction, wind speed, temperature, humidity and surface pressure occur. This is followed by a drop in temperature.

2.2 Nitrogen oxides chemistry in the atmosphere

Nitrogen oxides (NO_x) are formed from the chemical reaction between nitrogen and oxygen in the atmosphere. They include other gaseous compounds and they are: (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrogen sesquioxide (N_2O_3), nitrogen tetroxide (N_2O_4), and nitrogen pentoxide (N_2O_5). Oxides of nitrogen which are emitted from combustion processes comprise primarily of nitric oxide (NO) and nitrogen dioxide (NO_2) occurring as NO (Webb & Hunter 1998) and these are the main forms of nitrogen oxides which are of primary concern in air pollution because they are emitted in significant quantities to the atmosphere from biogenic and anthropogenic sources. In the troposphere, NO is involved in the chemical production processes of different environmental pollutants, such as ozone and nitric acid (Weitz *et al.*, 1998). NO and NO_2 (the NO_x radicals) interconvert rapidly in the troposphere, with reactions timescales on the order of minutes. Conversion of NO_x to nitric acid (HNO_3) and subsequent wet and dry deposition occur on longer timescales, hours to days (Horri *et al.*, 2006). This indicates that these trace gases undergo conversion processes and reach the surface through dry or wet depositions.

The atmospheric chemistry of nitrogen oxides partially controls the oxidizing capacity of the troposphere, oxidation of nitrogen dioxide (NO_2) in the atmosphere results in the formation of ozone (O_3), the abundance of ozone and its lifetime is relatively short, on the order of hours on the boundary layer and few days in the upper troposphere and is usually considered to occur particularly in polluted areas (Ordonez *et al.*, 2006). The difference in diurnal variations of secondary aerosols between the more polluted and the less polluted periods depends not only on the concentrations of acidic gases and ammonia, but also depends heavily on the chemical composition of particulates, the boundary layer height and weather conditions (Kai *et al.*, 2006). This suggests that rainy and cloudy days may disturb the data capturing for trace gases by both satellite and ground monitoring.

The position of the Mpumalanga Highveld and the presence of precursor gases favor the formation of ozone. In the regions of low NO_x concentrations, O_3 is destroyed catalytically (Roberto *et al.*, 1998). Photolysis of NO_2 during day time is the major source of ozone (O_3) in the troposphere and photolysis of O_3 in turn initializes the production of the hydroxyl radical (OH) (Zyrichidou *et al.*, 2004), the main cleansing agent of the atmosphere. This confirms the presence of ozone in the Mpumalanga Highveld where nitrogen oxides are emitted in high concentrations from stack emissions of power stations and its reduction further away from this area. There are five air quality stations that are used by Eskom within the Deposition of Biogeochemically Important Trace Species (DEBITS) program of the International Global Atmospheric Chemistry (IGA) in the southern Africa to monitor monthly average background concentration of key pollutants including ozone (Zunckel *et al.*, 2004). The Elandsfontein air monitoring station is one of them and located in the remote area to prevent direct anthropogenic influence. Monitoring is done through passive sampling of priority pollutants including the three species of nitrogen oxides on which this work is focused. NO_2 data from Elandsfontein air quality monitoring station an eight other air quality monitoring stations in Mpumalanga Highveld is assessed with the satellite NO_2 data from the satellite instrument. (NO_2) is heavier than air and readily soluble in water. When reacting with water it forms nitrous acid and its nitrate radical (NO_3) forms nitric acid and nitric oxide as indicated in the following equations:



NO_2 can react with O_3 and the product becomes a nitrate radical (NO_3), which is a strong oxidant that participates in the night time chemistry and the main reactions which determine the concentration of nitrogen dioxide (NO_2) in the lower atmosphere (Webb *et al.*, 1998). Nitric acid is formed through from either a homogenous reaction of NO_2 and the OH radical, reaction of NO_3 with aldehydes or hydrocarbons or hydrolysis of N_2O_5 in the atmosphere (Russel *et al.*, 2010). Concentrations of nitrogen oxides are influenced by relative humidity, ambient temperature and ammonia concentrations where NH_4NO_3 is formed (Dale *et al.*, 1989). NH_4NO_3 is unstable under normal atmospheric conditions that exist in the reversible phase equilibria with gaseous precursors (Matsumo and Tanaka, 1986). During the day nitric oxide is oxidized by O_2 , O_3 or alkyl group, while O_3 is a highly abundant oxidant in the atmosphere. The resulting nitrogen dioxide subsequently produces ozone and hydroxyl radicals. Oxidation of nitric oxide by ozone occurs as follows:



Equations (3) and (4) lead to the formation of NO_3 , which breaks down rapidly during day light and remains in low concentrations. Equation (4) represents an important reaction because of high concentrations of NO_2 in the atmosphere and the data confirms continuous production of nitrates in the atmosphere. The following equations show photolysis of NO_3



O₃ is a reactant in the formation of nitrate during the day and is also formed from NO₂. In areas where O₃ is available, the interconversion between NO and NO₂ is rapid as indicated in equation 7.



N₂O₅ is formed from the reaction of NO₂ and NO₃ in the reverse action. N₂O₅ concentration is reduced in the atmosphere through wet and dry deposition and uptake by aerosols in the atmosphere. A photolytic decomposition of nitrogen dioxide during the day occurs as follows with the subsequent rapid reaction.



NO_x is the precursor of NO₂⁻ and NO₃⁻ formation, and an increase of its concentration can lead to an increase of NO₂ and NO₃. This indicates that in the tropospheric NO₂ is continually decreased by an increase in ozone formation and that nitrogen oxides are major precursors for the formation of ozone in the lower troposphere. Ozone results from the reaction between NO and NO₂ in the presence of sunlight. O₃ is also transported from the stratosphere into the troposphere by eddy diffusion which adds to the concentration that further breaks down into NO₂ and O₂. After its formation in the presence of sunlight, O₃ reacts with NO in the atmosphere to form NO₂ which is then replaced in the troposphere, (equation 3). High concentration of NO due to anthropogenic production in the atmosphere of the Mpumalanga Highveld may create frequent production of NO₂ after reacting with O₃. The reaction between ozone and volatile organic compounds results in the formation of smog that reduces visibility. The absence of NO in the less polluted areas may result in low concentrations of ozone and subsequently reduce impact on visibility impairment. Atmospheric visibility impairment is a particular noticeable form of air quality degradation that can generate much emotive response (Held *et al.*, 1996). Variation of ozone may be observed during different seasons and over twenty-four hours in the Mpumalanga Highveld. This follows temporal variations of nitrogen oxides as precursor species for its formation.

Nitrogen oxides in the troposphere are generated from biogenic and anthropogenic processes. They are deposited on the ground in the form of wet and dry deposition which increases over the Mpumalanga Highveld. Eutrophication in the water bodies is created by acid rainfall as wet deposition on the water surface. Generally, nitric acid, the key intermediary in nitrate formation, can be produced in the atmosphere through the following reactions



Or



Nitrogen oxides in the troposphere are used up by the gas formation of HNO_3 during day in the presence of sunlight and hydrolysis of N_2O_5 during the night. During winter and night times the height of a boundary layer is reduced and it is during these times when dispersion is poor and pollutants are kept beneath inversion. However, there are certain specific reactions or areas of uncertainty that impact on the ability to qualitatively understand the formation, cycling and losses of O_3 and NO_x in the troposphere (in some cases specifically in the boundary layer) (Atkon, 1998) except that it is formed from photolytic reaction of NO_x with carbon monoxide and hydrocarbons during the day.

The nitrogen from NH_4^+ occurs in rain water and contributes to the level of NO_x in the atmosphere. NO_3^- and NH_4^+ concentrations of 25.0 and $22.3 \mu\text{eq.l}^{-1}$ respectively in the precipitation at Amersfoort were found to be relatively high compared to 8.0 and $9.7 \mu\text{eq.l}^{-1}$ respectively (Mphepya *et al.*, 2004). High nitrogen oxides concentration in the precipitations found in Amersfoort, as a southern part of the Mpumalanga Highveld may be ascribed to

industrial activities which take place upwind of the area. This confirms the contribution of the NO_x and other traces gases emitted in the Mpumalanga Highveld to acid rainfall formation in the region.

A primary source of NO_x in the troposphere is NO which reacts rapidly with ozone to form NO₂ and reaches a photo stationary equilibrium governed by the following reactions (Pertritoli *et al.*, 2004):



The formation of NO_x in the reaction between NO₂ and OH radicals to form nitric acid reduces the concentration of OH in the troposphere. Nitric acid reaches the ground in the form of wet or dry deposition.

2.3 Remote sensing application to nitrogen compounds assessment

Remote sensing refers to the use of electromagnetic radiation to acquire information without being in physical contact with the object, and in this case the atmosphere (Martin, 2008). NO₂ data from the satellite instrument for this research has been collected in this manner. Daily recording of data through remote sensing forms basis for analysis of air quality and levels of impact of pollutants on the atmosphere. Data from OMI is presented in total vertical columns and the unit for the measurement is 10¹⁵ mol/cm². For remote sensing the backscattered signal is measured by a light detecting instrument called a lidar. However, the lidar only yields results when the laser beam is fully in the field of view of the telescope which occurs beyond a distance of 300 m (Volten *et al.*, 2009). Different instruments are used in remote sensing and for this research a satellite data for NO₂ has been measured by the OMI. Measurement of trace gases in

the troposphere is influenced by their presence in the boundary layer. Seasonal changes in the level of the boundary layer may influence data taken through remote sensing, for instance when the top of the boundary layer is lower, especially during the early mornings of winter months, the atmosphere is not well mixed. Well mixing of the atmosphere occurs when the top of the boundary layer has risen which makes satellite instruments to do better measurements of trace gases within this region. The spatial resolution of the satellite instruments however, has significant effect on the observed NO₂ levels in the troposphere. The larger the pixel size the more inhomogeneous are the actual NO₂ levels in the troposphere within the area covered by one measurement (Hilboll *et al.*, 2013). OMI resolutions taken from Mpumalanga Highveld are approximately 200 square kilometers which may cause inhomogeneity in the data values if more than one satellite instrument may be used over a similar area.

2.4 Sources of nitrogen dioxide

2.4.1 Natural sources

2.4.1.1 Lightning

Lightning occurs mainly over land, with an average land to ocean ratio of 6 to 10 derived from the lightning Imaging Sensor (LIS) satellite data over 1997-2002 and the Optical Transient Detector (OTD) satellite data over 1995- 200 (Hui and Hong, 2013). Lightning produces NO which provides an important source of NO_x in the atmosphere, nitrogen dioxides is produced from oxidation of NO. Lightning NO_x occurs mostly in the upper troposphere and has a longer life time in this region than in the boundary layer. Therefore, mid and upper –tropospheric ozone concentrations are substantially enhanced by lightning NO emissions (Allen *et al.*, 2010). Climate change may influence production of NO_x from lightning. The abundance of lightning during the summertime suggests that ozone concentration in the free troposphere increases than during winter where no thunderstorms occur. The Mpumalanga Highveld occurs in the plateau of the Highveld and is liked by thunderstorms which generate flushes that contain nitrogen oxides. These nitrogen species contribute to air quality of the atmosphere in the region.

2.4.1.2 Soil

The production of NO from soils is the result of microbial denitrification, nitrification and chemodenitrification (Bouman, 1990). Nitrogen oxides are produced in soils by biotic and abiotic processes, but soil microbial activity is the most important source and sink for NO and N₂O (Weitz *et al.*, 1998). This also includes NO from the natural fires and in situ generation from lightning. These latter regions do not contribute to the soil NO emissions in the Mpumalanga Highveld because of its location in the grassland. Emissions of nitrogen (N) from the grassland soils can, depending on the intensity of management, be substantial with opportunities for major environmental impact on the atmospheric and water quality (Jarvis *et al.*, 1997). This suggests that biogenic sources contribute to ground measurements of nitrogen oxides at Elandsfontein data where ground measured data has been taken.

2.5 Anthropogenic sources of nitrogen dioxide

2.5.1 Fossil fuel combustion

Eskom manufactures electricity by burning coal in the eight power plants located in the Mpumalanga Highveld. Coal is burnt at high temperature and NO is produced and emitted through the emission stacks of the power stations. This NO is oxidized to produce NO₂ in the atmosphere. Nitrogen oxides are a bi-product of fuel combustion from both point and mobile sources. Power stations are point sources of nitrogen oxides while vehicles and trucks are mobile sources. At sites, which are mainly impacted by industrial and power station emissions, (Elandsfontein, Kendal, and Verkykkop), NO_x concentrations are highest during the day reflecting the influence of the tall stack source (Ross *et al.*, 2007). The petrochemical industry in Secunda and Steel smelters at Emalahleni and Middelburg are also responsible for nitrogen oxides in the Mpumalanga Highveld. Measurements of emissions including NO₂ is done by air quality monitoring stations in these areas.

2.5.2 Fertilizers

Nitrogen may result from the fertilizers which are applied on the soil for agricultural purposes. However, among agricultural chemicals, nitrogen based chemicals are the most important materials for growing crops and are also the most concerning nutrient element for maintaining a clean environment (Maleki *et al.*, 2012). Nitrogen undergoes chemical reactions in the soil and emitted to the atmosphere due to solar radiation. Contributions of soil NO_x emissions to the total tropospheric NO₂ column can be overshadowed by the strong signals from other sources (e.g. anthropogenic, biomass burning, or lightning) (Vinken *et al.*, 2014). Nitrogen is added directly to the soil to help plants to grow. Soil bacteria use the same nitrogen in the soil to build up their energy to grow. The processes of nitrification and denitrification result in production of nitrogen oxides in the soil which evaporates and add to the nitrogen budget in the atmosphere. The use of manure as a fertilizer may also cause emissions to the atmosphere. Nitrogen oxides may be created by adding reactive N₂ in the warm and moist soil. The created nitrogen oxides evaporate to the atmosphere.

2.5.3 Biomass burning

Natural processes produce nitrogen oxides that add to the atmospheric emissions. The burning of biomass produces major concentrations of trace gases and particulates (Fleming and Van Der Merwe, 2002). The Mpumalanga Highveld occurs in the grassland biome with few scattered indigenous trees. This vegetation is susceptible to veld fires during dry seasons which generate emissions to the atmosphere. The burning of biomass is always an incomplete combustion process; therefore, production of nitrogen dioxide can be ascribed to incomplete biomass combustion. Biomass burning result in the emissions of CO, CH₄ and NO_x and the latter is the precursor of ozone formation. Stable layers of the atmosphere allow an accumulation of trace gases including NO_x in the troposphere. Nitrogen dioxide is one of the major ingredients for the formation of Tropospheric ozone and 30% of such production on global scale can be attributed to biomass burning (Helas *et al.*, 1992). Biomass burning creates high NO_x concentrations because nitrogen has a high content in the biomass. Concentrations of NO_x and secondary species that result from photolytic processes increase in the atmosphere during winter, i.e. during July and

August. This peak in NO_x during this time may be ascribed to the atmospheric accumulation below the thermal layer during stable conditions and no rainfall. Concentration of NO_2 which result from the oxidation of NO would also be high during this period.

2.5.4 Other sources

Human waste is treated in wastewater treatment plants. The plants culture bacteria which produce nitrogen oxides when breaking down the suspended solids in the plant. Other nitrogen oxides come from the atmospheric deposition. NO_2 is also found in the stratosphere. Low costs houses use coal for cooking and provide warmth for households. The amount of smokes from chimneys of households in the Mpumalanga Highveld produce nitrogen oxides which remain at the ground concentration and therefore picked by the ground monitoring at the Elandsfontein monitoring station, and other air quality monitoring stations in the Mpumalanga Highveld.

2.6 Nitrogen oxides in the Mpumalanga Highveld

Nitrogen oxides are generated anthropogenically from human activities and biogenically through natural processes. A total of 90% of the industrial NO_x emissions in South Africa originates from the Highveld Hotspot. In recent assessment of global emissions, South African emissions amounted to 420kt/year on nitrogen, which constituted 1.6% of the global anthropogenic NO_2 emissions (Alexandra *et al.*, 2012). Mpumalanga Highveld is part of the highly industrialized area of South African Highveld which contains coal reserves. Coal is burnt for the generation of electricity in the eight power stations which occur in this region. Activities in the coal fired power stations are responsible for the disturbance of nitrogen budget in the atmosphere. Highveld SO_2 and NO_x emissions have grown significantly over the past eighty years from <100 ktpa to over 900ktpa for NO_x and 1.9 ktpa for SO_2 . By 2020, SO_2 and NO_x emissions are estimated to reach 2.26 Mtpa and 1.23 Mtpa respectively (Scorgia and Kornelius, 2009). Anthropogenic sources of these trace gases include fossil fuel burning for electricity generation in the eight power stations located in the Mpumalanga Highveld. Other sources of trace gases are tail pipe emissions and aircrafts, the latter being responsible for stratospheric NO_2 .

A power plant plume contains large quantities of NO_x, little CO and virtually no VOCs, hence O₃ production from NO_x in power plant plume is highly limited by the availability of VOCs in the surrounding environment as it dilutes (Dinise *et al.*, 2004). In the presence of sunlight, reactions between NO_x and hydrocarbons, volatile organic compounds which include methane and other hydrocarbons result in the formation of O₃ and is a pollutant in the lower troposphere. Mean average ozone concentrations over a month at DEBITS sites on the Highveld of South Africa take place over a range between minimum values of 14ppb near the main industrial source area at Elandsfontein and Palmer air quality stations which occurs more or less 100 km north of the main industrial source region (Zunkel *et al.*, 2006). Diurnal cycle in surface ozone occurs at Elandsfontein in the Mpumalanga Highveld region. It reflects the relationship between the buildup of ozone precursor gases in the early morning and the subsequent photochemical formation of ozone (Combrink *et al.*, 1994). Being formed from NO₂, ozone concentration may be trapped near the surface during winter and reduce visibility. Concentration of NO₃ is higher during winter because of stable atmospheric conditions and prevailing westerly and north westerly air flow. NO₂ oxides vary with time of the day and peak during midday. This results from the oxidation of NO from emission stacks of the power stations in the Mpumalanga Highveld. The same process occurs with the NO resulting from biomass burning during August when veld fires takes place.

2.7 Weather systems over Southern Africa

2.7.1 Anticyclones

Anticyclones over South Africa occur when there is convergence in the high altitude troposphere and divergence in the wind near the surface. The troposphere is, in turn often subdivided into vertical zones. The lowest 1-2 km is termed the boundary layer, a region of strong horizontal and vertical mixing (Beer *et al.*, 2001). A free troposphere occurs above the lower troposphere and is the region where photochemistry occurs. Anticyclonic circulation creates inversions, stable conditions with no rainfall and light variable winds. The development of stable layers depends on the prevalence of persistent circulation fields that occur primarily on no-rain days (Cosijn and Tyson, 1996). The Mpumalanga Highveld experiences anticyclones during winter months, while

low level of anticyclones occur during December. Winter inversions and stable atmospheric conditions keep pollutants near the surface while little wind variation prevents horizontal transport of pollutants. Strong anticyclones are associated with heat waves and occurrence of Berg winds along the coast. Berg winds are associated with high pressure systems over the interior while depressions along the coast are responsible for sharp increases in temperature in these areas.

2.8 Transportation of Nitrogen dioxide

Horizontal transport of air occurs mostly in the lower troposphere. Atmospheric stability at this level of the atmosphere which occurs during winter determines an extent of transport. The troposphere is characterized by generally decreasing temperature with increasing altitude, from average of 289K at the ground level of 210 – 215K at the tropopause (Atkinson, 1998). The lowest 1-2 km is termed the boundary layer, a region of strong horizontal and vertical mixing (Beer *et al*, 2001). Before the Southern African Fire-Atmosphere Research Initiative in 1992 (SAFARI-92), a common assumption was that material emitted from the industrial source region of South Africa was transported and deposited relatively close to the source, or was quickly advected eastward toward the Indian Ocean (Piketh *et al.*, 2002). Both anticyclonic circulations and westerly disturbances will bring conditions that are conducive for the transportation of aerosols and other trace gases away from the continent to the east over the Indian Ocean (Garstang *et al.*, 1996). The ability of the atmosphere to disperse pollution depends on the upward movement of the air. This vertical movement of air determines the stability of the atmosphere. The horizontal movement is dependent on wind speed and direction (Tyson *et al.*, 1998). Southern Africa is dominated by the subsistence limb of the southern Hadley cell of the general circulation of the atmosphere, particularly in winter (Tyson *et al.*, 2001). An absolutely stable layer is defined as, having a lapse rate which is less than the saturated adiabatic lapse rate (Freidman *et al.*, 2000).

Absolute stability occurs during inversions in winter and during the night. When this condition prevails free upward movement is inhibited and pollutants are trapped below inversion. This occur during atmospheric stability in winter. An inversion which forms during winter nights is

cleared during the day and allows upward mixing. Upward movement of pollutants may occur due to deep convections. The synoptic scale meteorology in the south and central parts of southern Africa is largely influenced by the semi-permanent and mid-latitude high pressure systems during anticyclonic and subsistence circulation. (Zunckel *et al.*, 2005). The warm air conveyor belt (WCB) – a strongly ascending airstreams ahead of the cyclone's cold air front is an important mechanism to lift the air pollutants emitted at the surface into the upper troposphere, where the faster winds facilitate their intercontinental transport (ICT) (Stoch and Trichl, 1999).

The semi-permanent south Atlantic anticyclone, continental anticyclone over southern African, and Indian anticyclone have a dominating effect on the transportation of aerosol and other trace gases in the troposphere over southern Africa (Zunckel, *et al* 1999). The wind direction and speed determines the extent of horizontal transport of pollutants in the Mpumalanga Highveld. Pollutants are transported by the northeasterly wind from the power electricity generating stations that include, (Arnot, Hendrina, Komati, and Duvha power station) to Elandsfontein monitoring station. South easterly wind transport pollutants from Kriel power station, Matla power station and Sasol to Elandsfontein monitoring station and this is in accordance to the position of this pollution sources to the monitoring station. Due to unique meteorological condition, the industrial emissions could leave the South African continent and be transported by wind towards Australia (Wenig *et al.*, 2003).

In the Mpumalanga Highveld the diurnal variation cycle may be attributed to the oscillation between daytime convection and the strong thermal stratification near the surface during the night. During the day, the high level plumes can mix with down to ground level, while at night this mixing is prevented as pollutants are released above the surface temperature inversions (Zunckel *et al.*, 1998). This suggests that the day time deposition of NO₂ is associated with the mixing down of plumes emitted from tall power plant emission stacks with the day time convective layer. During the day, NO₂ and undergo photolytic reaction with the atmospheric oxygen to produce ozone. Diurnal cycle of NO₂ and ozone formation in the Mpumalanga Highveld follows a uniform pattern over a large spatial resolution because of the location of power stations and other industrial pollution sources in a plateau. The presence of ozone may be

identified by the presence of smog that affect visibility in the roads. Ozone may also show diurnal cycle because of its dependence on NO_2 as a precursor gas.

2.9 Deposition of Nitrogen Oxides in the Mpumalanga Highveld

Deposition of trace gases occurs from the high altitude to the surface in the form of dry and wet depositions. This implies that pollutants from anthropogenic and natural sources are deposited on the earth surface in the form of wet and dry deposition. NH_3 reacts, initially with acidic species to form ammonium nitrate or ammonium chloride, or it may reach the surface through either dry or wet deposition processes (Aneja *et al.*, 2001). A dry deposition is the process by which trace chemicals from the atmosphere are transported to the surface by air motion.

2.9.1 Wet deposition of Nitrogen Oxides

NO_x species undergo chemical reactions in the atmosphere with ammonia, moisture and other compounds in the atmosphere to form nitric acid, the latter falls on the surface with rain. Wet deposition of nitrogen oxides occurs when soluble nitrogen compounds are mixed and dissolve in the clouds and rain. Biomass burning produces pollutants which mix with clouds and reach the ground as rainfall. This ultimately determines acidity of rain in the South Africa. However, the effects of fossil fuel emissions from the power stations and other industrial sources are clearly dominating the industrial part of the Mpumalanga Highveld and subsequently downward areas. This suggests that acid rainfall in Mpumalanga Highveld which is driven by availability of biomass fuel combustion may remain constant from year to year in the region or increase with the addition of pollution sources. Nitrogen oxides in the acid rainfall contributes to the eutrophication of rivers and other surface water bodies in the Mpumalanga Highveld.

2.9.2 Dry deposition of Nitrogen Oxides

Dry removal process includes: sedimentation, impaction, diffusion and gravitational settling (Jacob *et al.*, 1996). Dry deposition processes are clearly observed in the Highveld plateau, the

reason being that summer rainfall occurs mostly on average only for 60 days (Kirsten *et al.*, 2010). The annual dry deposition on the Highveld ranged between 0.18 kg N/ha per year and 6.6kg N/ha per year for the period of April 2005 to March 2006 (Stuart *et al.*, 2010). Part of this deposition occurred in the Mpumalanga Highveld. Dry deposition of nitrogen oxides occurs mostly as NO₂ throughout the year but occurs in the form of NO₃⁻ during spring. Dry deposition rates of NO₂ varies throughout the year, with a general peak during winter (Collet *et al.*, 2012). Winter deposition of the NO, NO₂ and NO₃⁻ occur predominantly during winter because of the increased atmospheric stability. The rate of dry deposition, F is determined as follows:

$$F = -V_d \times C \quad (19)$$

Equation 19 implies that spatial variation, variation in ambient air, concentrations and deposition rates influence dry deposition of pollutants. Hot spots in deposition and fluxes are associated with the grassland where veld fires occur during August and source emissions in the Mpumalanga Highveld industrial area. The stable atmospheric condition during the night influences the variability of dry deposition on the surface. Seasonal changes also influence the rate of deposition. The stable boundary layer traps pollutants below inversions and facilitates horizontal transport which result into minimum deposition near emissions points. Reactive nitrogen which becomes excessive in the atmosphere due to industrial emissions falls to the ground as dry deposition.

2.10 Impacts of Nitrogen Oxides on the environment

In order to control emissions of pollutants including nitrogen oxides from coal fired power stations mitigation equipment must be installed to reduce their emission levels. Equipment like bag filters are used once, then disposed. Costs of disposal and constructing suitable landfill sites create higher economic impact for Eskom. Elevated N concentration is associated with the acidification of both terrestrial and aquatic ecosystems and create negative impact on biodiversity in many natural and semi-natural terrestrial ecosystems. High nutrient levels may also promote eutrophication of surface waters and elevated N concentrations may be toxic to some aquatic fauna and terrestrial flora (Marner and Harrison, 2004). Changes in the composition and function of an ecosystem may therefore occur as deposition continues. Water

quality of water bodies in the Mpumalanga Highveld may deteriorate because of an increased nitrogen load in water bodies. The level of exceedance of emissions from the acceptable standards may be compared with the level of acidic deposition exceedance in the Mpumalanga Highveld. This occurs in the form of HNO_3 depositions on the surface water and result into water quality degradation leading to disturbances of aquatic habitat for animal and plant species. Acidification can be caused directly by acid deposition (N and S), but also indirectly through leaching of cations, soil microbial processes and plant uptake (Steven *et al.*, 2011).

NO_x are precursors of ozone which poses negative impacts on visibility and vegetation. Ozone is produced in the troposphere when carbon monoxide and hydrocarbons are oxidized photochemically in the presence of nitrogen oxides (NO_x) and water vapor (Beer *et al.*, 2001). Volatile organic compounds are not emitted from the stack emissions of the power plants but must be present in the environment for the production of O_3 . NO_x has an indirect climate impact via its effect on ozone and hydroxyl radical (OH) concentrations (Jourdain, *et al.*, 2010). Burning of fossil fuel is a primary source of NO_x in the troposphere. Toxicity of ozone may affect humans and vegetation and is a component of smog. Ozone is the greenhouse gas which contributes to the global warming of the atmosphere. NO_x contributes to environmental impacts including the formation of acid rain (via the formation of nitric acid), PM 2.5 (via the formation of secondary particulates such as ammonium nitrate) with the resulting health impacts and contribution to regional haze, eutrophication of aquatic systems (via addition of excess nitrogen), and elevated O_3 concentration (via the reaction with hydrocarbons and carbon monoxides) with the resulting impact on health and agriculture (Denise *et al.*, 2005). Eutrophication which is generated from excessive addition of nitrogen into water bodies creates oxygen depletion in the water bodies. The ultimate impact is the reduction of aquatic population in such water bodies. Ground level Ozone results from the reaction of NO_x and volatile organic compounds when there is heat and sunlight. Atmospheric N deposition poses a wide range of effects on the semi-natural ecosystems. Amongst the effects would be direct toxicity, increased sensitivity to secondary stress, acidification and eutrophication. Ozone may create a health impact to people with lung disease such as asthma, people who work or exercise outside may have lung tissues damaged and reduction in lung functioning.

Biomass burning in the tropics will result in faster distribution in the troposphere over other surface sources as vertical mixing is very strong in this region and the plumes have a thermal buoyancy of their own (Lee *et al.*, 1997). Nitrogen dioxide is a reactive form of nitrogen oxides, forms from biomass burning and becomes oxidized when there is sunlight to form ozone and nitrogen dioxide. Formation of haze would reduce visibility that negatively impact road users in the affected areas. Acidification may affect ecosystems in the natural environment because of the toxicity it may cause on plant and animal diversity. It may also affect grassland for grazing and maize which is planted for commercial farming in the Mpumalanga Highveld. An increased acidity of the soil may affect the availability of plant nutrients with the resulting decline of the plant yield.

Air pollution is formed by an accumulation of trace gases including nitrogen oxides in the atmosphere particularly in the boundary layer. These gases are generated naturally and from human activities. Nitrogen oxides are produced from fossil fuel burning in the power generating plants in the Mpumalanga Highveld. Different species of NO_x occur in the atmosphere and each impact on the environment in a different way. Nitrogen dioxide forms as a result of the oxidation of nitrogen oxides which is mostly emitted through smoke stacks of Eskom's power stations and tail pipe emissions from traffic.

CHAPTER 3: MATERIALS AND METHODS

This study is focused on the Mpumalanga Highveld for the fact that there are eight coal fired power stations, mining and metallurgical industries which are major sources of nitrogen oxides and other trace gases. A data on the three species of nitrogen oxides, namely, NO, NO₂ and N₂O has been presented and the study is focused on an analysis of NO₂ from the Eskom's 2008 data taken from its Elandsfontein monitoring station, Mpumalanga Highveld. Its central and elevated location in relation to point sources makes Elandsfontein a representative monitoring station for trace gases in the Mpumalanga Highveld. The station measures trace gases within the radius of 200 kilometers from its position. Humidity, temperature, wind driven rain, wind speed and wind direction are included in the data. The study includes an analysis of nitrogen dioxide data taken from other eight monitoring stations for 2008. They are located in Hendrina, Balfour, Middelburg, Witbank, Secunda and Ermelo. These monitoring stations form a Provincial Ambient Air Quality Monitoring Network of the Mpumalanga Highveld. Ground measurement of NO₂ from Elandsfontein monitoring station will be assessed with the OMI retrieved NO₂. Data. Corresponding satellite NO₂ data from the satellite measurement for 2008 has been retrieved and was taken from overpass pixels in the Mpumalanga Highveld including the area where Elandsfontein monitoring station is located. The OMI data contains geolocated and integrated concentrations of NO₂ presented in ($10^{15} \times \text{mol/cm}^2$). Monthly NO₂ averages from the satellite measurement have been calculated in order to be compared with ground measured data. Monthly DOMINO data from the satellite instrument is a Level 2 product, i.e. it provides geophysical information for each ground pixel that is observed by the satellite instrument without additional binning, averaging or gridding which is applied for level 3 data (Boesrma *et al.*, 2008). The OMI data has been taken between 11 and 12 hours of each day. This would probably allow the characterization of the well mixed day time atmospheric boundary layer and may also avoid complexities of night time chemistry.

Nitrogen oxide data for January to December 2008 has been retrieved from Eskom's Elandsfontein monitoring station for analysis and compared with satellite data of NO₂ of the same period. Data from other monitoring stations in Mpumalanga Highveld have been analyzed

with satellite data from OMI. OMI is a satellite instrument that has been used for satellite data collection. The Ozone Monitoring Instrument (OMI) is an Ultraviolet/Visible spectrograph with wavelength ranging between 270 to 500nm and employs arrays of CCD detectors to simultaneously register numerous spectra of the ground pixels in the swath that is perpendicular to the direction of the flight (Laan *et al.*, 2003). For the Earth's measurements the OMI has a wide instantaneous field of view which is perpendicular to the direction of the flight (Dobber *et al.*, 2008). The wavelength calibration may be done by fitting the Fraunhofer absorption lines in both the irradiance and radiance spectra. A good on- ground calibration that delivers a reliable calibration key data for 0 to 1 data processing is done for OMI, and a continuous in-flight calibration is essential to meet the required accuracies of the target scientific data products (Dobber *et al.*, 2006). This is important for the data comparison purpose that becomes part of a long term trend for ozone records.

Eskom is the power utility in South Africa with a core business of supplying electricity to the country, as well as funding and maintaining air quality monitoring stations that were set up in strategic locations in the 1980s and 1990s. The satellite data which has been used for this study has been retrieved from OMI. The OMI data indicates a number of pixels with different sizes, a size of one pixel is approximately 117km X 69.79km as measured in the satellite image of the Mpumalanga Highveld. The instrument properties depend on orbit position, season and accumulated time in flight and should therefore, in principle be calibrated in space (Laan *et al.*, 2004). The study has been focused on the vertical column densities of tropospheric NO₂ from the satellite measurement and ground measurement from Elandsfontein monitoring station including other air quality monitoring stations in the region.

3.1 Elandsfontein monitoring station

Eskom's ground measurement has been done at Elandsfontein monitoring station, Mpumalanga Highveld. The data for this analysis was taken from 1 January 2008 to 31 December 2008. The August data has been used for comparison because other stations which have been analyzed have only August data for analysis. Elandsfontein monitoring station is situated in the highest point of

the Mpumalanga Highveld plateau in the altitude of 1752 m above sea level which enhances data capturing from the Mpumalanga Highveld trace gases emitters (Figure 1). The monitoring site occurs in the central position of various nitrogen oxides emission sources including eight coal fired power stations, a petrochemical industry, iron, steel, manganese and vanadium smelters (Figure 1). The Highveld is covered by grassland and used for agricultural activities, residential settlements and industrial activities. The station measures concentrations of NO₂, nitric oxide (NO), nitrate (NO₃), Sulphur dioxide, hydrogen sulphide (H₂S) and black carbon. Arnot power station and Hendrina power station occur on the north east of Elandsfontein, Camden power station which is south east of Elandsfontein, Majuba power station also on the south east of the monitoring station, Kriel and Matla power station on the west of Elandsfontein. Besides Elandsfontein monitoring station, there are other monitoring stations that measure trace gases in the Mpumalanga Highveld. They have been established to enhance regulating emitting companies in the region as it was declared a priority area in terms of the National Environmental Management: Air Quality Act, 2004 (Act 56 of 2004). Sasol is a petrochemical industry which is situated south west of Elandsfontein power station. The station also receives pollutants from low costs houses and tail pipe emissions from traffic.

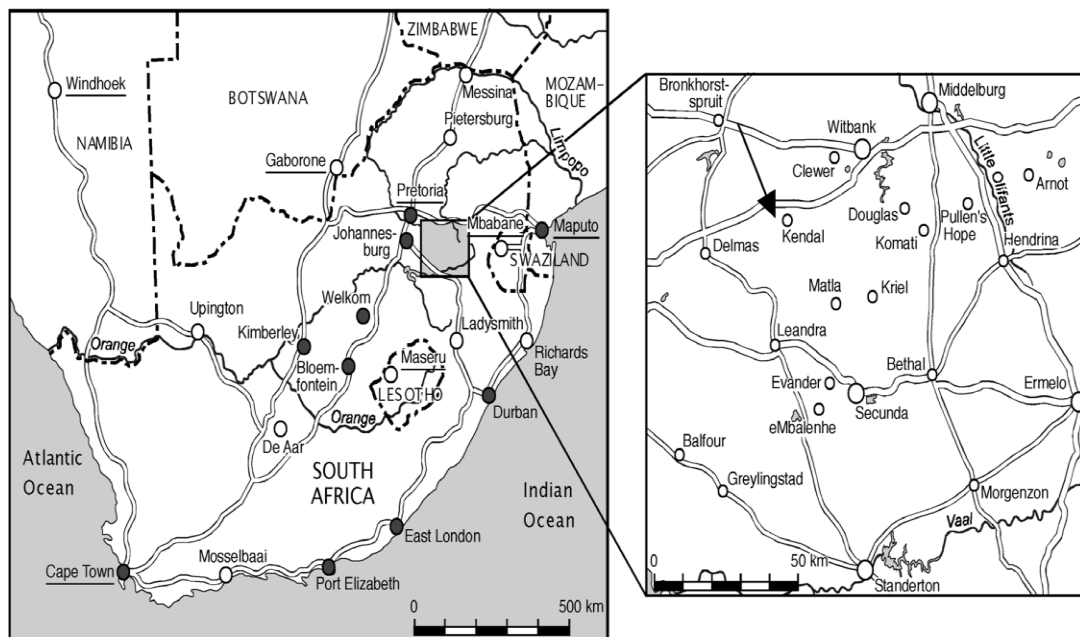


Figure 1: Location of the study area: The Mpumalanga Highveld (After Piketh *et al.*, 2010)

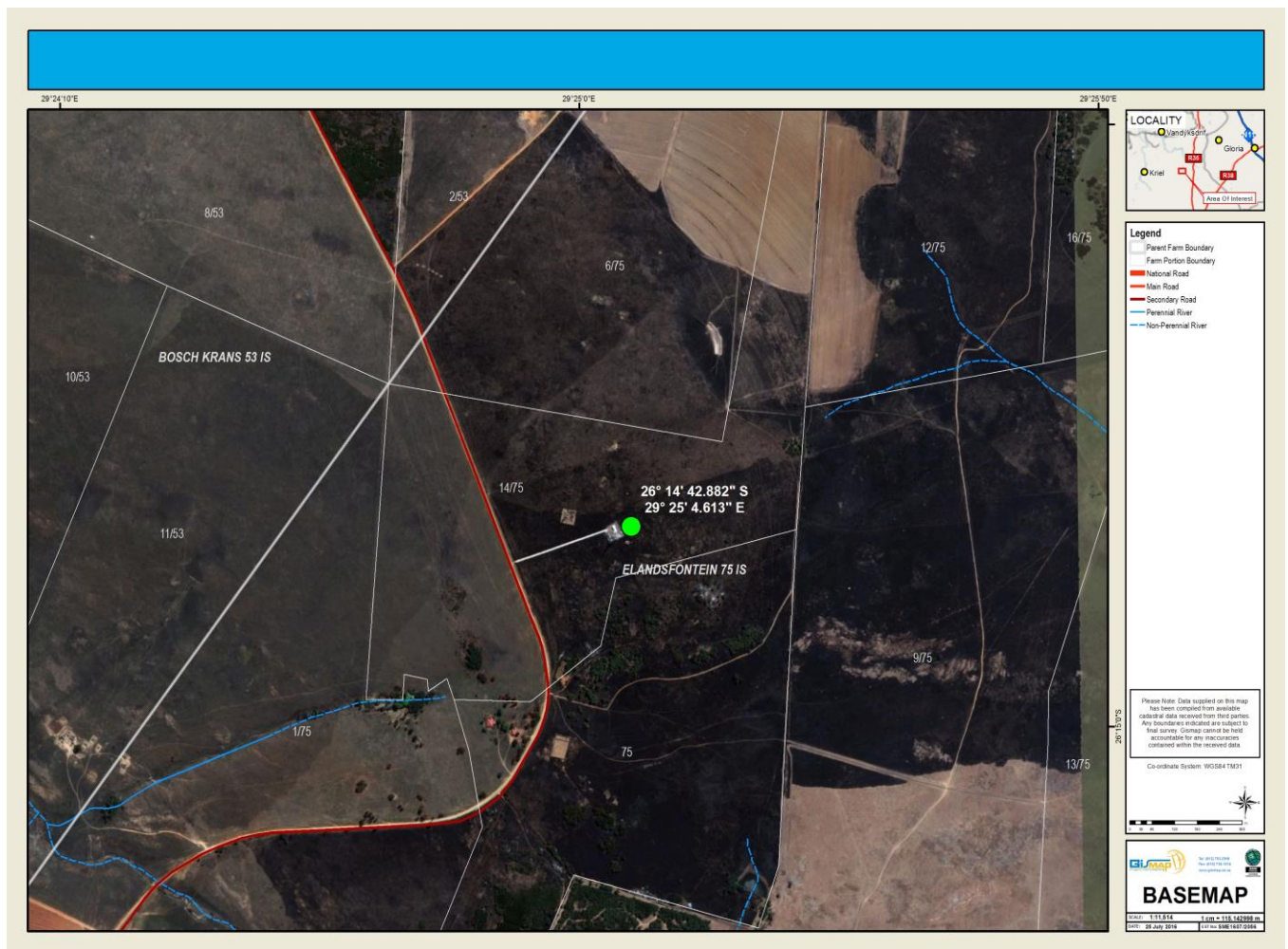


Figure 2: Locality map of Elandsfontein monitoring station

3.2 Data collection at Elandsfontein monitoring station

Elandsfontein monitoring station is located at S26° 14' 43.44" and E 29° 25' 02.87" (Figure 2) and is 1752 meters above sea level, at a higher position from the surrounding areas to receive pollutants from power stations and other pollution sources from all directions (Figure 1 and figure 2). Pollutants including NO₂ are captured through the pipe which is elevated three meters from the roof of the monitoring station (Figure 3, Figure 4). Emission stacks of power generating plants are 200 meters high to allow the dilution of emissions in the atmosphere. The Elandsfontein monitoring station provides a representative data for the Mpumalanga Highveld because of its elevated position from measure emission point sources. It is able to capture

nitrogen oxides which are generated from Arnot, Hendrina, Komati, Duvha, Kriel and Matla power stations (Figure 2 and Figure 4). It also captures nitrogen oxides from the metallurgical industries at Emalahleni and Sasol in Secunda. The air sample is sucked through a glass tube which is elevated 3 meters above the roof of the monitoring station (figure 4). From the glass tube, it is channeled through the inlet pipe to the molycon where NO is converted to NO₂. A direct tube from the molycon is connected to the reactor cell (Chemiluminescence) and an unconverted NO is passed through this tube to the reactor cell. The NO₂ is also channeled to the reactor cell. From the reactor cell NO and NO₂ are displayed in the screen on hourly basis. Other sources of nitrogen oxides which are measured in the monitoring station come from vehicle traffic of the neighboring roads and biomass burning during dry seasons. The sum of NO₂ and NO is equal to NO_x. Elandsfontein monitoring station measures humidity, wind speed and direction. These parameters show how the data is influenced during different times of the day and season. Calibration of the instrument is done in the monitoring station. Data for the pollutants is recorded hourly in ppb. The three species of nitrogen oxides, NO, NO₂ and NO_x for 2008 were recorded in the station and NO₂ data has been assessed with the satellite borne data of NO₂.



Figure 3: Photo of Elandsfontein monitoring station



Figure 4: Photo of Elandsfontein monitoring station showing the surrounding grassland

3.3 Elandsfontein data analysis

3.3.1. *Monthly variation*

Data from Elandsfontein and other air quality monitoring stations is presented in parts per billion, but for this study it has to be converted to microgram per cubic meters in order to compare with the satellite data which has also been converted into this unit. The following equation has been used under an average temperature of 15° C

$$\mu g/m^3 = \frac{ppb \times 12.187 \times M}{273.15 + 15^{\circ}C}$$

Where M= 46, molecular weight of NO₂,

$$\mu\text{g}/\text{m}^3 = \frac{\text{ppb} \times 12.187 \times 46}{273.15 + 15^\circ\text{C}} = 1.95 \times \text{ppb} \quad (20)$$

Ambiguous figures in the data have been taken as outliers and omitted to avoid calculation mistakes. The data from Elandsfontein for NO, NO₂ and NO_x was averaged in terms of months starting from December to January 2008. The monthly averages were plotted in a column chart in order to represent concentrations of nitrogen oxides during the time of the data. Monthly averages of NO₂ from Elandsfontein monitoring station were calculated using equation 20 in excel and plotted in the column charts and compared with the monthly averages of NO₂ from satellite measurements.

3.3.2 Seasonal variation

Data from Elandsfontein monitoring station has been grouped into four seasons of the year starting from summer, autumn, winter and spring. Monthly averages for each season were calculated. Seasonal data was then plotted in the bar chart to establish the variation of concentrations in different months of the seasons and concentrations of NO₂ to compare with seasonal concentrations of NO₂ from the satellite data.

3.3.3 Diurnal variation

A twenty-four hours' data for one month of each season was chosen from the Elandsfontein data. This was preceded by choosing a twenty-four hours' data that shows the relationships between the three species of nitrogen oxides i.e. NO, NO₂ and NO_x which presents the sum of the two. A twenty-four hours' data sets for the first days of January, April, July, and October 2008 were chosen and a column chart for each was plotted for the analysis of the diurnal concentrations of NO₂ and to establish diurnal variations of nitrogen dioxide amongst different chosen days of each season. August data for other ground monitoring stations have been compared with the August data taken from OMI. Diurnal comparison of data has been done for the period between 11:00 and 12:45 because of the satellite overpass time over the Mpumalanga Highveld.

3.4 Other Air quality monitoring stations in the Mpumalanga Highveld

3.4.1 Balfour air quality monitoring station

Balfour monitoring station is located in the area which is medium dense with informal houses. As occurring in the Highveld, coal and wood is used for domestic fuel by households. Being in the Highveld, South of Secunda, a heavy petroleum industry and high traffic volume, northeasterly winds transport pollutants south of SASOL where they are captured by the Balfour air quality monitoring station. The monitoring station occurs in the following coordinate: S 25° 39,464' E28° 35.510' west of Siyathemba Township. Spatial distribution of pollutants including nitrogen oxides is limited to source areas because of poor dispersions when the atmosphere is stable.

3.4.2 Ermelo Air Quality Monitoring Station

Ermelo air quality monitoring station is located in Wesselton Township, at S26° 29.576' E29°58.111' where coal combustion takes place to provide household fuel. Measure sources of pollution are the mine operations on the north eastern side of Wesselton, and vehicle traffic in the Township. A sewage treatment plant occurs on the northwest border on the Township and nitrogen oxides emissions from this plant may also be captured by the monitoring station. The Township is bordered by N11 National Road on the east and N17 National road on the West. Both National roads carry heavy traffic with the resulting tail pipe emissions that may captured by the monitoring station.

3.4.3 Hendrina Air Quality Monitoring station

The station captures pollutants from the Township and other sources in the area. Arnot and Hendrina Power stations are the two main sources of pollutants that are captured by Hendrina air quality monitoring station. The station is located at Kwazamokuhle Township in the following coordinates: S25° 09,084'E29°42.975'. Concentrations of pollutants from tail pipe emissions and households coal combustion are also recorded by Hendrina air quality monitoring station.

3.4.4 Middelburg 1. Air Quality Monitoring Station

The first Middelburg air quality monitoring station is located at Aerorand, next to the residential area in the position well suited to capture emissions from Columbus Steel manufacturing company. The station is located on the following coordinates: S 25° 47,760' E29° 27,840'. Like other stations already indicated, Middelburg 1 air quality monitoring station also captures pollutants from traffic generated from the road networks inside Middelburg and N4 National road on the North of the station. Mine operations occur on the west of Middelburg air quality monitoring station.

3.4.5 Middelburg 2 Air Quality Monitoring Station

The second Middelburg air quality monitoring station is located at Mhluzi Township in the following coordinates: S 25° 46,232' E29° 26,190'. Most tail pipe emissions and mining activities along the Middelburg -Witbank road are captured by this monitoring station. The open cast mining and plant occur along this road. Pollutants from the N4 National road are also captured by the monitoring station.

3.4.6 Standerton Air Quality monitoring station

Standerton air quality monitoring station occurs adjacent to the Township in the following coordinates: S 25° 57,507' E29° 13,245'. Pollutants including nitrogen oxides which are captured by the monitoring station come from traffic, power generation at Thuthuka Power Station and mining activities. The cold climate of areas around Standerton makes residents to prefer burning coal for energy and household heat during winter with the resulting near ground emissions of nitrogen oxides and associated pollutants.

3.4.7 Secunda Air Quality Monitoring Station

Secunda air quality monitoring station is located at Embhalenhle Township in the following coordinates: S 26° 33.039' E29° 04.747'. Embhalenhle Township is a residential area on the South of Secunda with high traffic volume and there are informal settlements which still depend on coal energy for cooking and related domestic purposes. The station captures pollutants including nitrogen oxides from SASOL and mines. Secunda lies adjacent to the N17 National road which carries high volume traffic with the resulting tail pipe emissions which are also captured by Secunda air quality monitoring station.

3.4.8 Witbank Air Quality Monitoring Station

Witbank air quality monitoring station occurs at Kwaguqa Township on the following coordinates: S25° 52.655' and E29° 11.246'. Emalahleni Township occurs in the Mpumalanga Highveld Priority area which is surrounded by heavy industries. Highveld Steel and Vanadium occurs on South of the Township and a measure source of nitrogen oxides emissions. Ferrobank steel smelter plant occurs almost at the western border of Kwaguqa Township and also emit nitrogen oxides to the atmosphere. Emalahleni is a receptor of high pollutants concentration because of the mine dumps and smelters around it including tail pipe emission from both N12 and N4 National roads.

3.5. Ozone Monitoring Instrument

The satellite data which has been used for this study has been taken from the overpass of an Ozone Monitoring Instrument (OMI) over the Mpumalanga Highveld. The OMI is a nadir-viewing imaging spectrometer that takes measurement of the solar radiation backscattered by the Earth's atmosphere and surface over a wavelength that ranges from 270-500nm, with spectral resolution of about 0.5 nm/pixel, depending on the wavelength (Pieternel *et al.*, 2006). It is an Ultraviolet/Visible spectrometer that measures trace gases, including nitrogen oxides. The NASA EOS Aura platform, launched on July 15 2004, carries the Ozone Monitoring Instrument (OMI), a visible hyper spectral Ultraviolet/Visible spectrometer which rotates around the earth and

measures trace gases in the atmosphere. OMI has a 2600 km swath for daily, global contiguous mapping that was provided by the Netherlands Agency for Aerospace Programm (NIVR) in collaboration with the Finnish Meteorological Institute (FMI) to the NASA EOS Aura mission for continued monitoring of ozone and other trace gases (Nickolay *et al.*, 2006). The primary objective of the OMI instrument is to obtain daily global measurements of ozone and nitrogen dioxide in both the troposphere and stratosphere (Dobber *et al.*, 2006). Satellite measurements through OMI includes data for the total Ozone column, total nitrogen dioxide column, aerosol optical thickness and cloud parameters. Such data together with atmospheric parameters is used in the chemistry of NO_x, air quality and climate. The instrument is able to pick and retrieve data that falls within sixty kilometers from the surface ultraviolet radiance.

The instrument consists of two parts called an optical assembly and an electronic assembly. The optical design is further divided into OMI VIS channel (Figure 5) and OMI UV channel (Figure 6). The optical bench of the optical assembly is an aluminum structure on which the two detector modules are attached. OMI uses the scrambler to depolarize radiation. Because OMI uses a polarization scrambler, to depolarize the measurement signal, and the instrumental slit function only exhibit small spectral variation, OMI radiances over 307 – 325nm are much easier to model than GOME radiances (Liu *et al.*, 2010). An ability of OMI to perform measurement with daily global coverage is enhanced by the 114° viewing angle of the telescope which is perpendicular to the flight direction that corresponds to a 2600km wide swath on the earth surface. OMI pixel is about 13km x 12km at nadir. The pixel size increases in the swath direction for the increasing distances from the satellite ground track (Di Noia *et al.*, 2013). OMI has two on board devices, and they are White Light Source (WLS) labeled 007 (figure 5) and Light Emitting Diodes (LED). The while light source is a halogen lamp and its function is the calibration of the detector pixel to pixel gain variations. This function is important because data products from OMI rely on the instrument calibration. An inflight calibration of the instrument is necessary for the observation of the sun. The light source is solar radiation which is back scattered from the surface reflectance and cloud, aerosol and Rayleigh scattering (Chance, 2005). The strong absorption lines of the NO₂ molecule which occurs in the visible wavelength of the spectrum facilitate the use of the optical spectroscopy for measuring NO₂ abundance (Hilboll *et al.*, 2012).

OMI has been built from the predecessor satellite instruments, like TOMS and SCIAMACHY, with its high resolution and global coverage, it is a powerful monitoring tool for trace gas emissions. A high spatial resolution of the instrument is responsible for an increase of incidences for cloud free scenes, which result into better coverage. The satellite instrument shows to have a potential to detect global point sources including the Mpumalanga Highveld. Satellite based instruments offer a better geographical distribution but continuous validation with the ground based measurements are required to assess the accuracy of the satellite data (Ialongo *et al.*, 2008). The instrument measures earth radiance and only obtain slant column density measurements. The integrated abundance of NO₂ is represented by the slant column along the average photon path from the sun, through the atmosphere to the satellite (Lamsal *et al.* 2010). Vertical columns may be obtained from the slant columns with consideration of the air mass factor. Like a ground measurement of trace gases, a satellite instrument shows seasonal and diurnal variations of the data. The OMI satellite image shows global pollution hotspots which also differ following seasonal and diurnal variations.

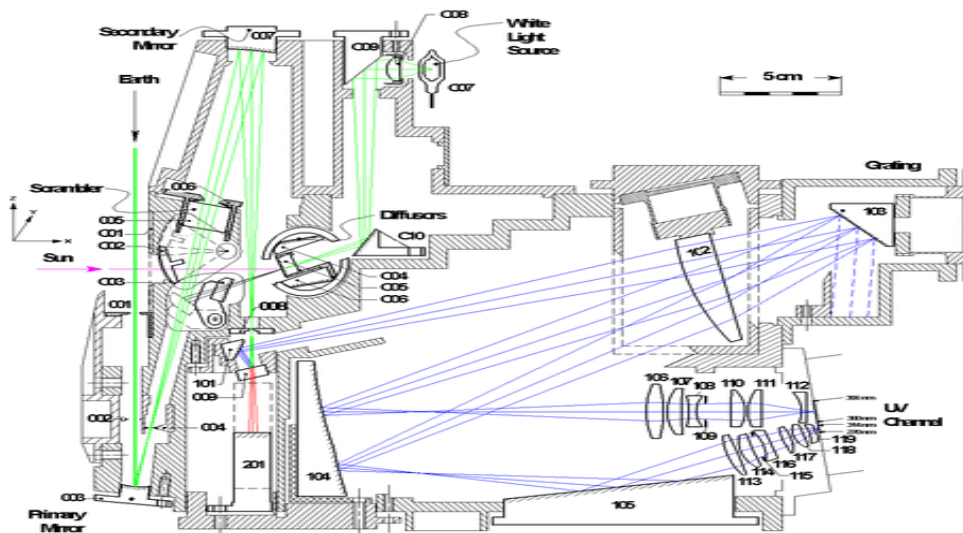


Figure 5: Optical design UV channel of OMI: After (Lamsal *et al.*, 2010)

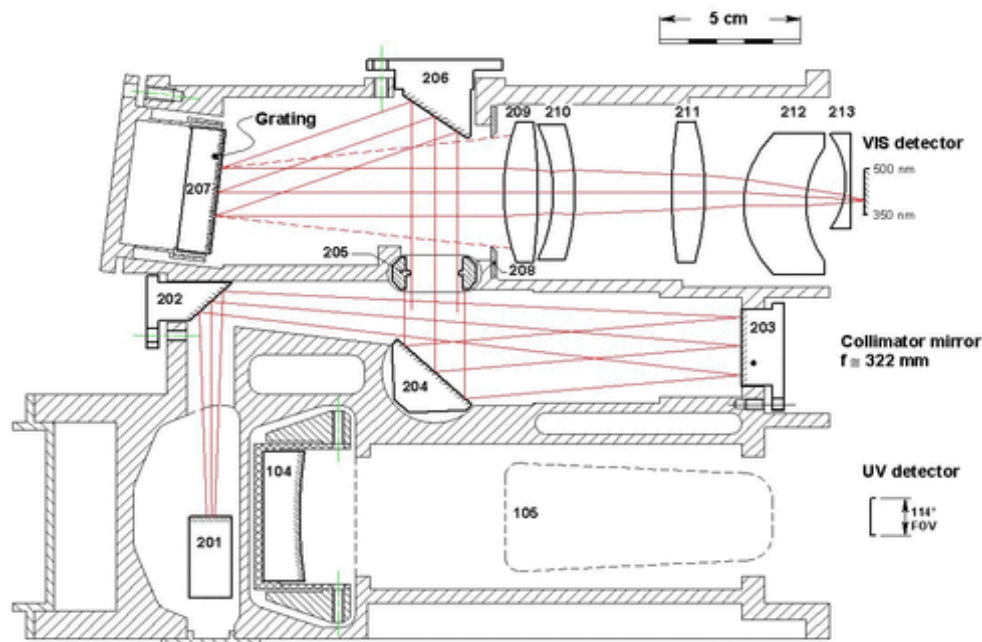


Figure 6: Optical design VIS channel of OMI: After (Lamsal *et al.*, 2010)

3.5.1 Satellite data collection

OMI data for this study is a DOMINO product version 1.0.2 collection 3 which has been taken from Tropospheric Emission Monitoring Internet Services (TEMIS). The OMI data set contains more wavelengths in the ultraviolet region, and has a higher spatial resolution, that allows more precise retrievals of trace gases in the wavelength range of 328 – 500nm (Kleipool *et al.*, 2008). The satellite data reflects vertical columns of NO₂ in the Mpumalanga Highveld around Elandsfontein monitoring station. Data from this area is also picked by the Elandsfontein monitoring station. The vertical columns for the satellite measurement covers spatial resolution of 200 square kilometers on the ground and indicated by coordinates in the satellite data. The pixels which were taken are indicated by decimal coordinates in the satellite data. The areas include Secunda, Standerton, Emalahleni and west of Secunda along the N17 National road. Global estimates of trace gases and aerosols from satellite observations is done by the Differential Optical spectroscopy (DOAS). DOAS is used to measure the in situ concentration of ozone, BrO, NO₂ and SO₂ in the atmosphere. The satellite instrument is able to detect pollution hotspots and provide global information on the distribution of NO_x sources. Satellite data is

obtained through measurements of the radiation which is backscattered from the Earth's surface and atmosphere as well as daily measurements of the sun. The instrument is therefore able to measure the stratospheric NO₂. The slant column density which is obtained by the instrument is modified by making use of the Air Mass Factor to vertical column density which is required for this study. The Air Mass Factor is ratio between the observed column density (slant column) and the vertically integrated column through the troposphere (Heland *et al.*, 2002).

OMI measures earth shine radiances and the solar irradiance to calculate the slant column density of NO₂. For NO₂, which is a weak absorber and not widely distributed in the troposphere, an AMF in the stratosphere can be used to obtain a first order approximation of the VCD (Eric *et al.* 2006), such AMF is obtained by taking a 24hrs measurements of NO₂ in the stratosphere and make it a global estimate. The vertical column density is obtained by dividing the slant column by the AMF. It is therefore clear that the tropospheric air mass factors (AMFs) must have been used to convert the tropospheric slant columns into vertical columns.

The slant column (Ns) calculated with the DOAS method can be converted to the vertical column (x) by applying the air mass factor (Van Der A *et al.*, 2010).

$$\text{Vertical column} = \frac{\text{Slant column}}{\text{Air Mass Factor}}$$

$$VCD = \frac{SCD}{AMF} \quad (21)$$

3.5.2 OMI data retrieval

Satellite retrievals provide a spatial coverage that is better than in situ measurements, which can provide constraints on estimates of surface emissions (Miyakazi *et al.*, 2012). This suggests that a better data can be measured in a vertical column starting from the ground concentration of a trace gas, including nitrogen oxides species may be measured to the height of the pixel. The Ozone profiles from the surface to a height of about 60 km are retrieved from the Ozone Monitoring Instrument (OMI) ultraviolet radiance by using the optical estimation technique (Liu *et al.*, 2009). OMI must be first calibrated for measurements of trace elements in space. A

Differential Optical Absorption Spectroscopy (DOAS) algorithm is applied to derive slant column densities of NO₂ from the radiance measurements (Russel *et al.*, 2012). The other OMI product is the standard product (SP, version 1.0.5, collection). DOAS is a spectral fitting technique which is applicable in a window from 405 nm to 465nm. The spectral fit retrieves NO₂ in the form of a slant column density for each OMI pixel. Larger columns are observed during winter than summer because of the reduced sunlight in winter which result in longer life time of NO_x than in summer. As a trace gas, NO₂ leaves its absorption fingerprints in the spectra thereby allowing determination of the concentration by the DOAS.

The AMF calculation must be done with a knowledge of the viewing geometry, surface albedo, clouds and aerosols. In a given partial atmospheric region, (stratosphere or troposphere), the air mass factor is calculated as the ratio of the sum of layers of the slant sub column S_i , to the sum of vertical sub-column V_i (Buscela *et al.*, 2013). For the cloud- free pixels, the OMI measured reflectance at the top of the atmosphere (TOA) at these wavelengths is fitted for the total 50 aerosol models (Curier *et al.*, 2006. During the cloudy period retrieval of trace gases including NO₂ may be disturbed because of the possible complications in the calculations of the AMF. The Mpumalanga Highveld experiences high rainfall during summer. Rainfall occurs after cloud formation which suggests that there may be difficulties in the retrieval of satellite data during this season.

OMI surface NO₂ [Sep/2005]

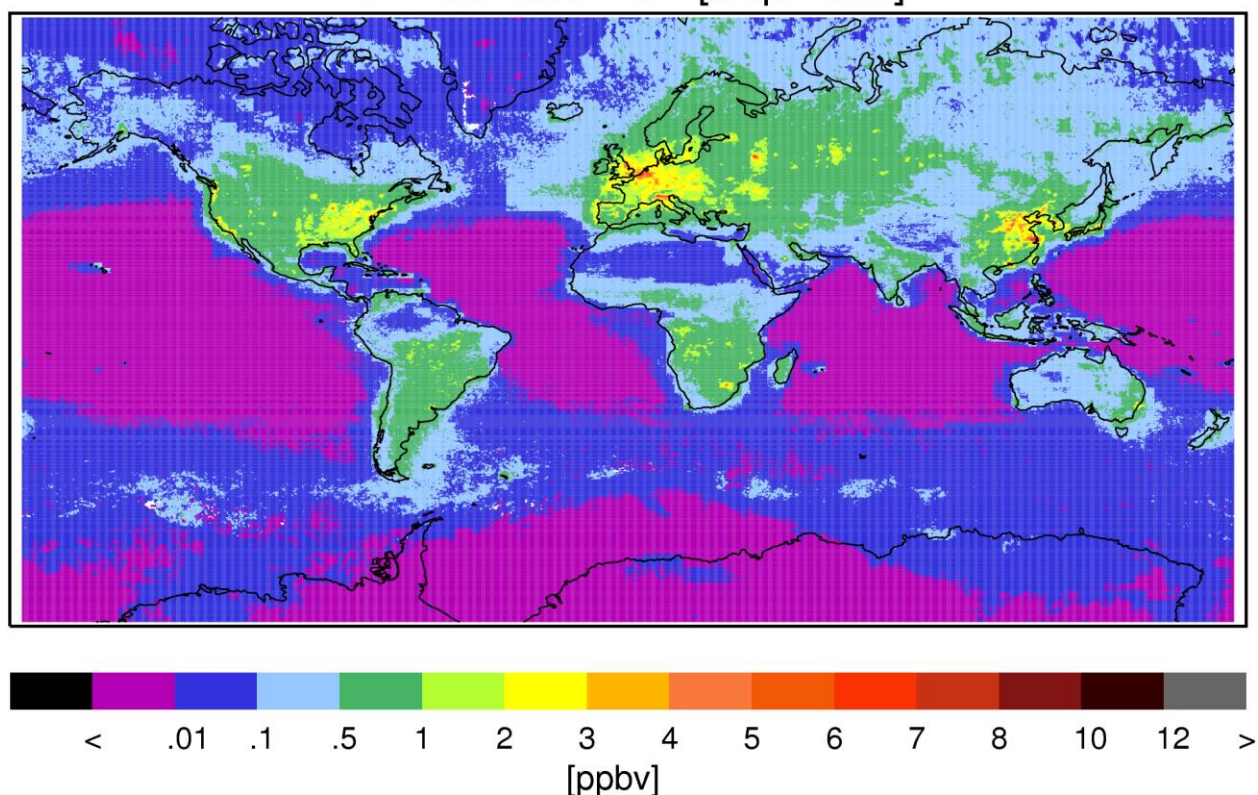


Figure 7: Tropospheric NO₂ column during summer (Nov 2008), Regional NO₂ of 6 November 2008

Source: Temis, OMI data

3.5.3 Satellite data analysis

A satellite data has been analyzed following the same principles which have been applied for the ground data analysis. The purpose of the analysis is the compare the two data sets. Only NO₂ from the satellite data has been compared with the ground data in the analysis. As in the ground analysis, monthly averages of NO₂ have been calculated for twelve months to determine annual variation on NO₂ in the atmosphere. The data has been divided into four seasons of the year and monthly averages of each season has been calculated. This is to establish seasonal variation of NO₂ in the atmosphere. Furthermore, hourly averages for one month of each season have been calculated for diurnal variation of NO₂. Seasonal and diurnal averages have been presented in the plots for analysis.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Temporal variability of nitrogen dioxides over the Mpumalanga Highveld

4.1.1 Other monitoring stations in the Mpumalanga Highveld

Data from Balfour, Ermelo, Hendrina, Middelburg 1, Middelburg 2, Secunda, Standerton and Witbank monitoring stations have been evaluated for the spatial distribution of nitrogen oxides in the Mpumalanga Highveld. An evaluation of the formation of NO_2 from the oxidation of NO has been done for each station and graphs have been plotted which show the resulting NO_x . Diurnal variation of NO_2 has been evaluated for each station. An assessment of nitrogen oxides may not necessarily belong to similar months of 2008 because data collection has started in different months of 2008. A twelve-month analysis has been made for the Ermelo monitoring station because of the availability of a data for the period between January to December 2008. NO_2 has been analyzed for hourly and daily variations over 24 hours.

Nitrogen oxide is generated from the burning process in the power plants smelters and petrochemical industry in the Mpumalanga Highveld. Nitrogen oxide may be captured by the nearby air quality monitoring stations and recorded as such. When exposed to the atmosphere, it reacts with atmospheric oxygen to form nitrogen dioxide and the two together make up nitrogen oxides. NO occurs as a lower curve, followed by NO_2 and NO_x forms the most higher curve (Figure 10), (Figure 11), (Figure 16) and (Figure 19). The 24 hours' diurnal variation of NO_2 during August to December 2008 shows a peak during October than in November and December in all stations (Figure 8), (Figure 9), (Figure 13), (Figure 17), (Figure 18), (Figure 22), (Figure 28) and (Figure 29). The high peak of NO_2 during October, a month of the summer is caused by unstable atmospheric conditions which allows upward mixing of pollutants. For the Ermelo monitoring station, January showed minimum concentration of $19.5\mu\text{g}/\text{m}^3$ with a peak of $43\mu\text{g}/\text{m}^3$ to $45\mu\text{g}/\text{m}^3$ during February to April 2008, October and November are the highest reaching $49\mu\text{g}/\text{m}^3$ whilst July and August stayed at $40\mu\text{g}/\text{m}^3$ (Figure 12). The Middelburg 1 monitoring station shows almost less hourly variations of NO_2 during August, September and October 2008. This station occurs close to a pollution source which allows a short period for

species evolution (Figure 19). Secunda monitoring station shows almost similar results because of its proximity to SASOL, the main pollution source (Figure 23). Significant diurnal variation occurs for Middelburg 2, monitoring station (Figure 21) as it occurs further away from the pollution source. This station shows less than $0.5\mu\text{g}/\text{m}^3$ of nitrogen oxides between the 9th and 15th hour for the periods October to December 2008. During this time wind direction blows pollutants including NO_2 away from this monitoring station. Standerton monitoring station shows significant variability of NO_2 with the peak reaching $30\mu\text{g}/\text{m}^3$ during November and the minimum of $0.35\mu\text{g}/\text{m}^3$ during December 2008 (Figure 25). Although Elandsfontein monitoring station occurs on the elevated position, the trends of its data are similar to those of other air quality monitoring stations with regard to temporal variability of NO_2 in the Mpumalanga Highveld.

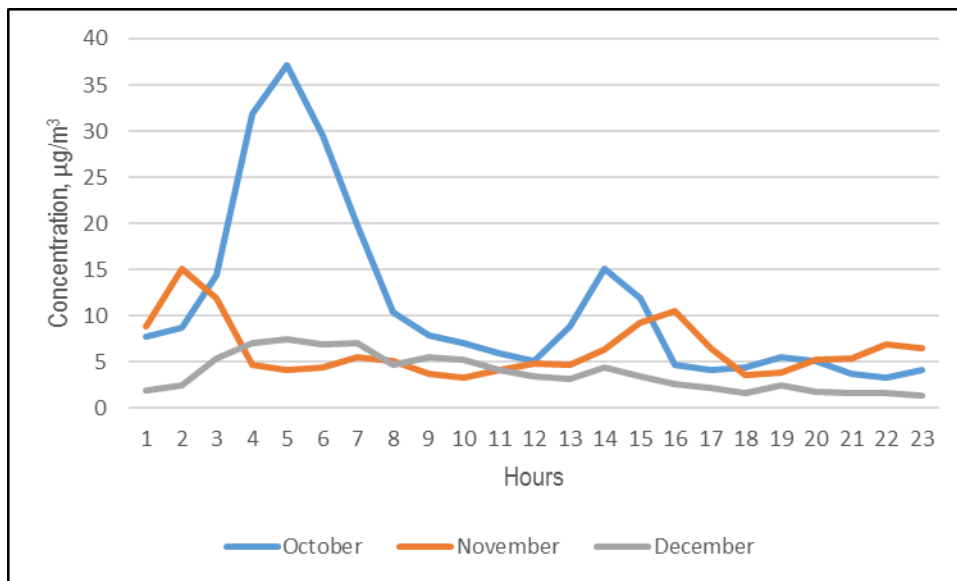


Figure 8: Balfour monitoring station showing hourly NO_2 concentrations over three months

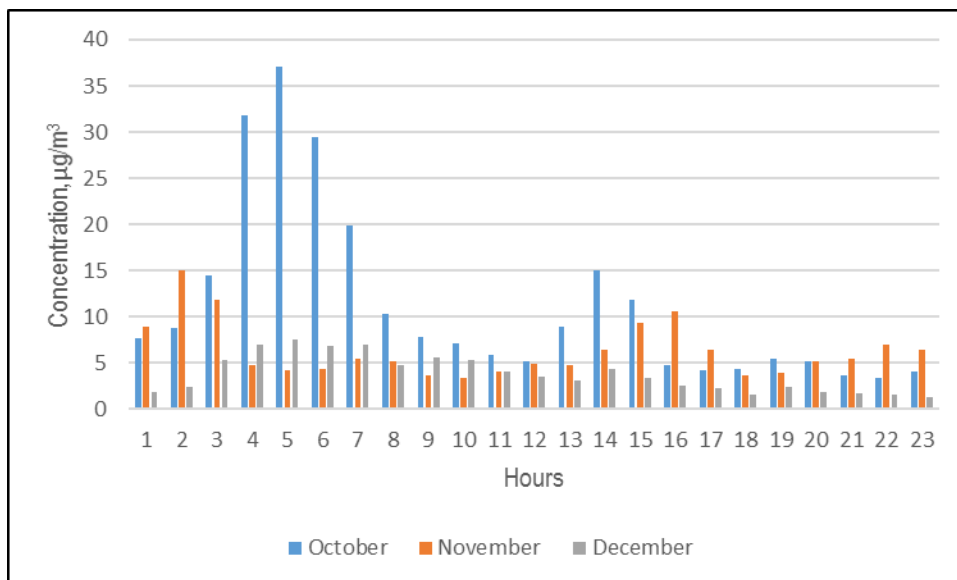


Figure 9: Balfour monitoring station showing hourly variation of nitrogen oxides

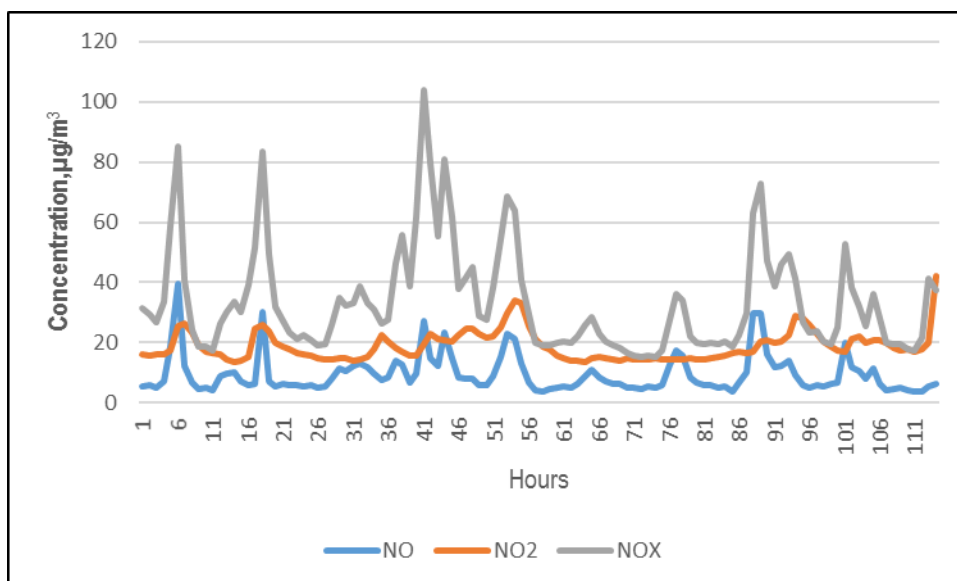


Figure 10: Ermelo monitoring station showing evolution of nitrogen oxides

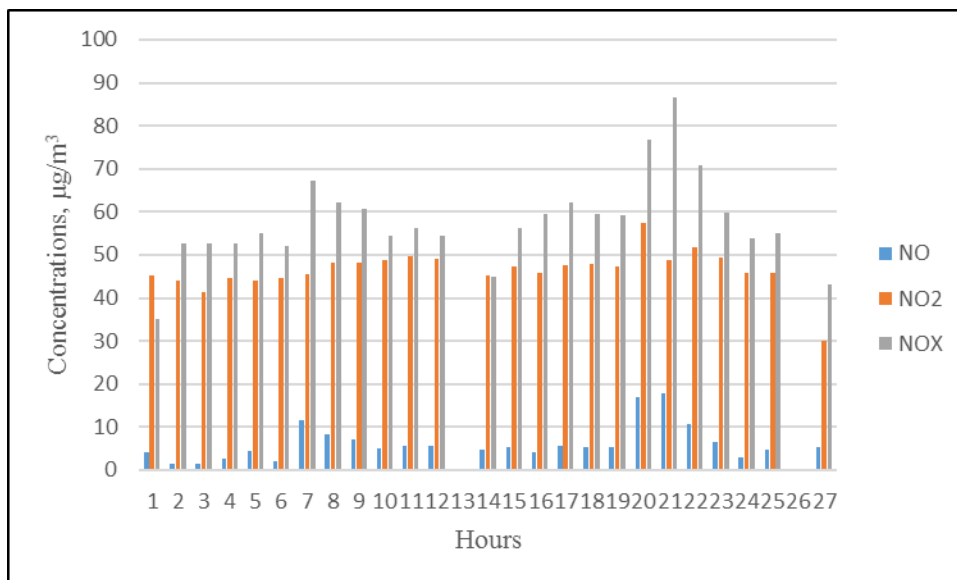


Figure 11: Ermelo monitoring station showing hourly nitrogen oxides

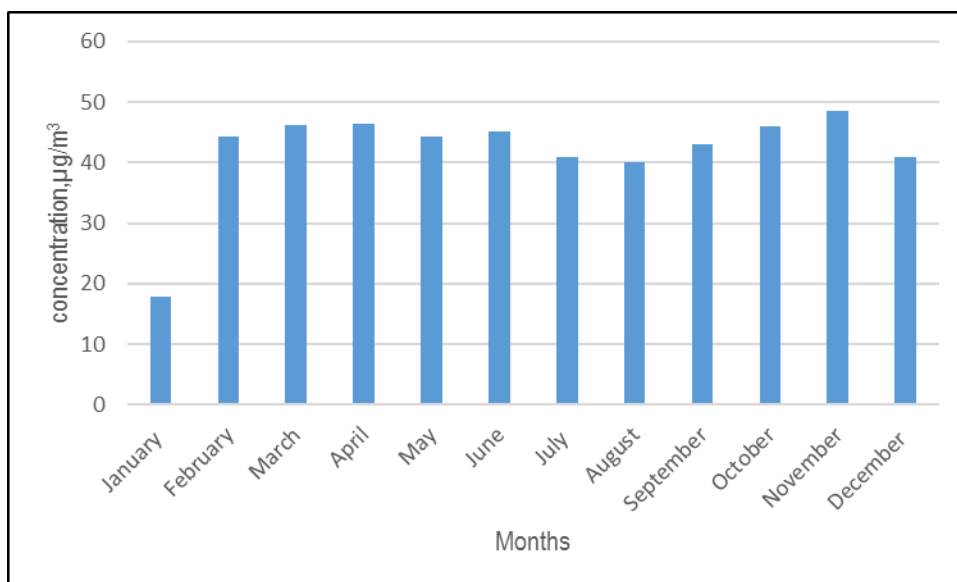


Figure 12: Ermelo monitoring station showing NO₂ monthly averages

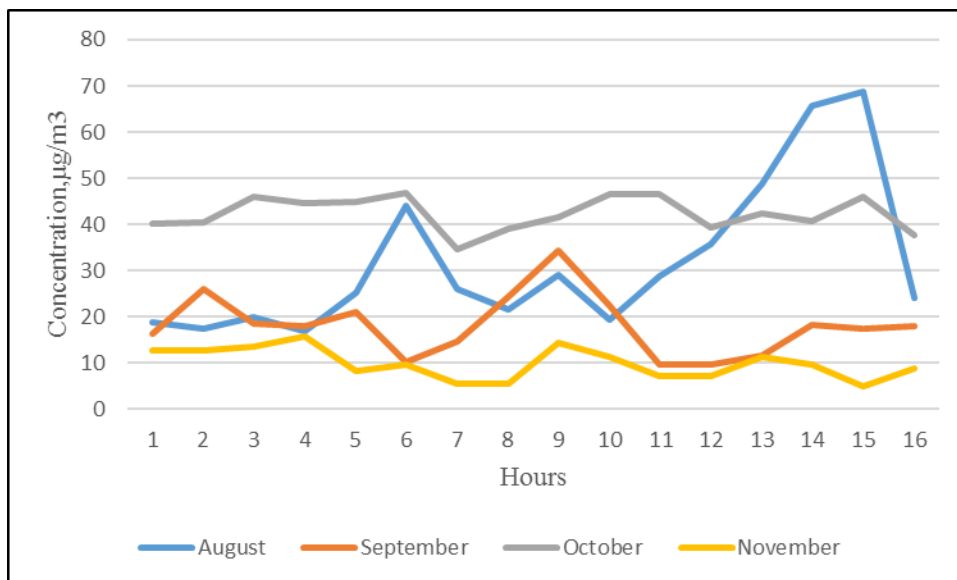


Figure 13 :Ermelo monitoring station showing 24 Hours concentration of NO₂ over three months

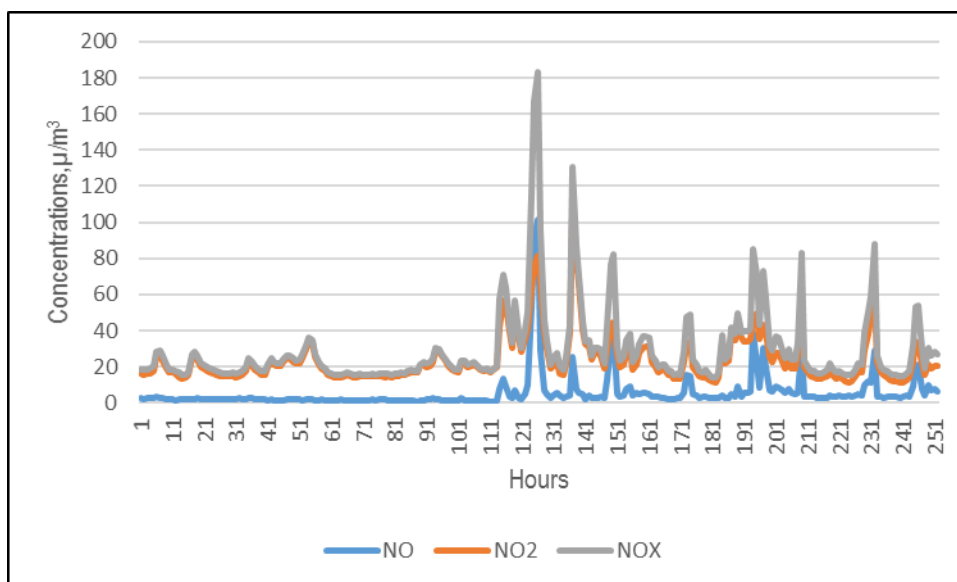


Figure 14: Hendrina monitoring station showing the evolution of nitrogen oxides

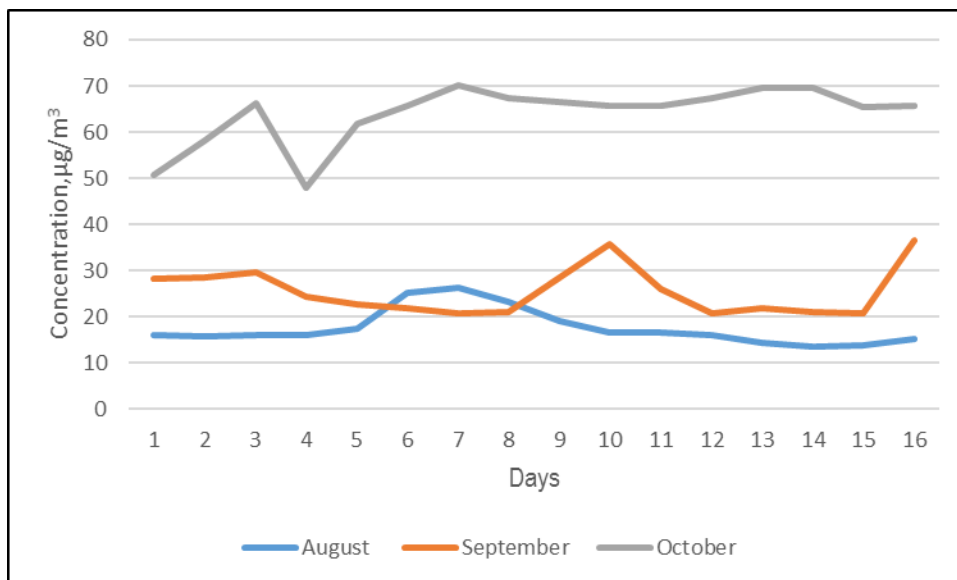


Figure 15: Hendrina monitoring station showing 24 hours concentration of NO₂ over three months

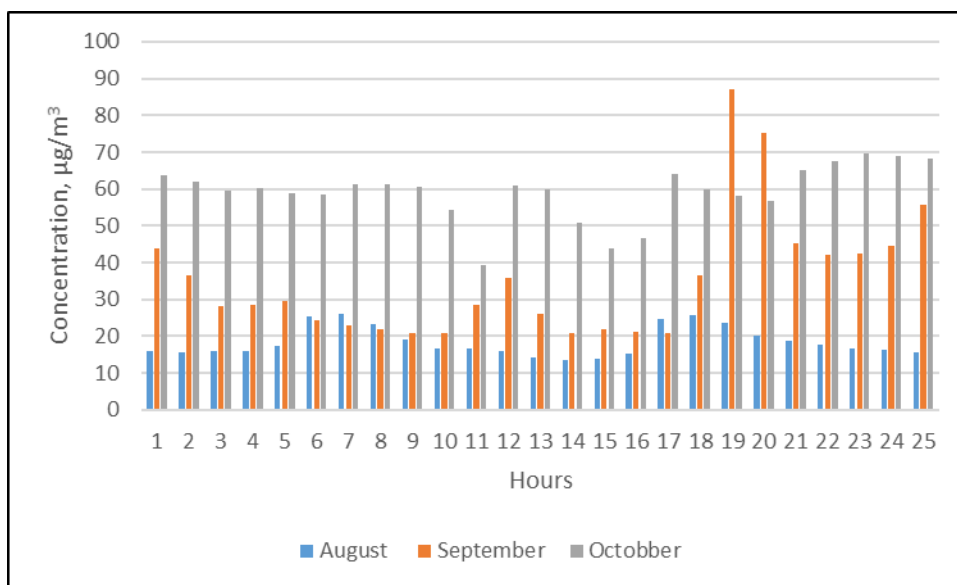


Figure 16: Hendrina monitoring station showing 24 hours variation of nitrogen oxides

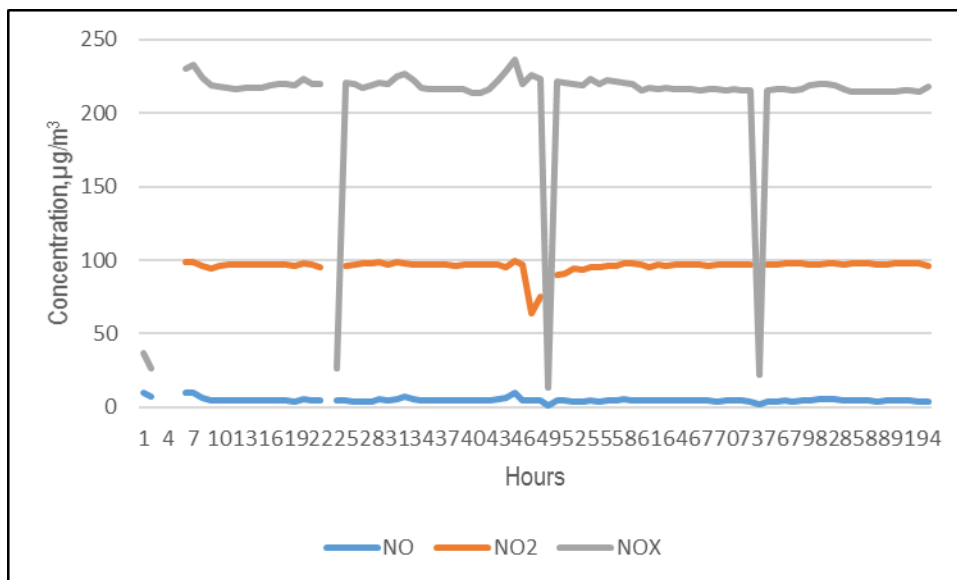


Figure 17: Middelburg1 monitoring station showing evolution of nitrogen oxides

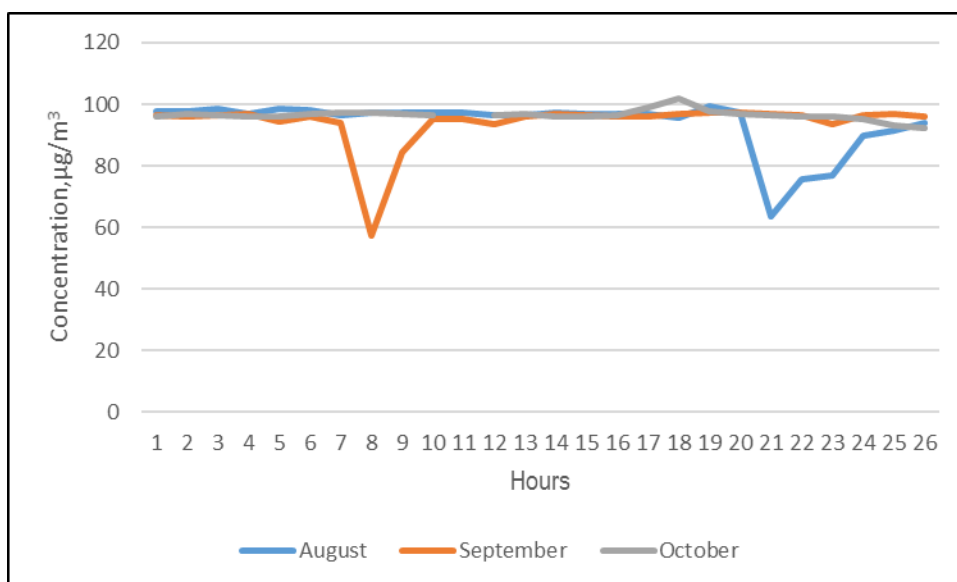


Figure 18 : Middelburg 1 monitoring station showing 24 hours concentration of NO₂ over three months

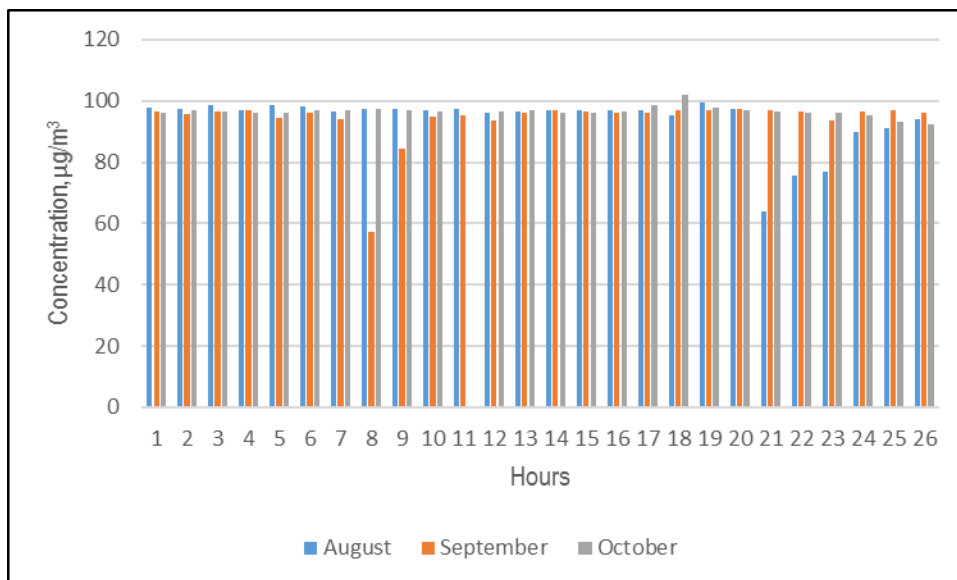


Figure 19: Middelburg 1 monitoring station showing 24 hours variation of nitrogen oxides

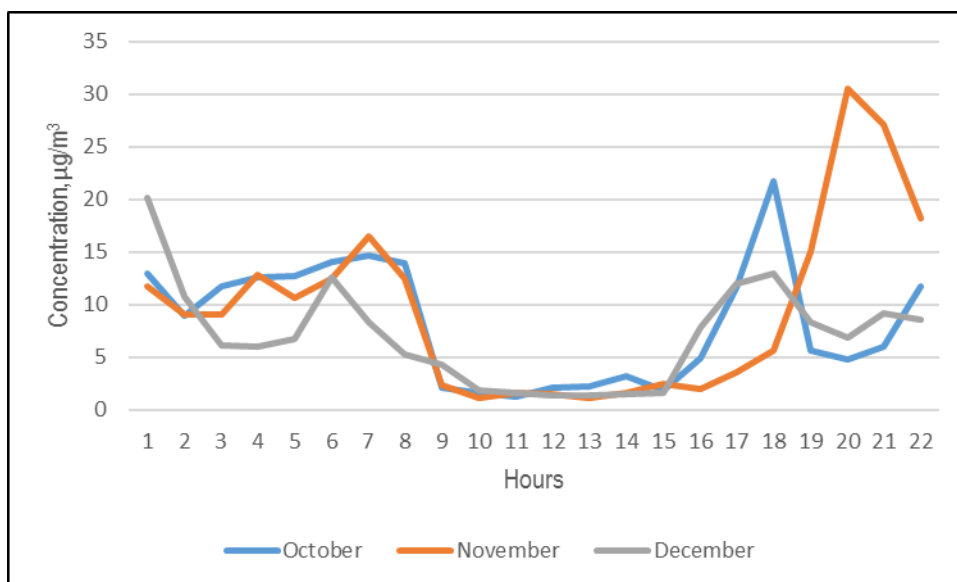


Figure 20: Middelburg 2 monitoring station concentration of NO_2 over three months

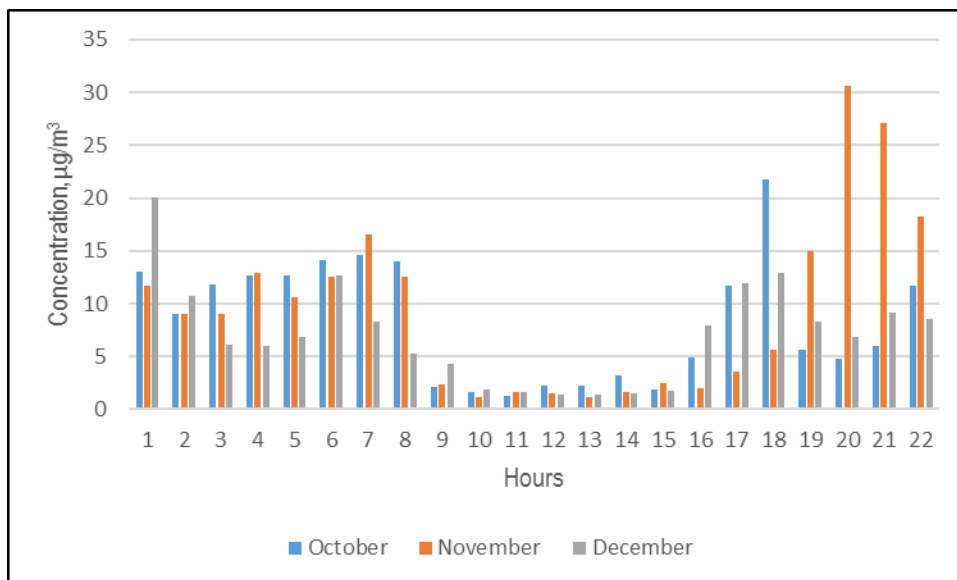


Figure 21: Middelburg 2 monitoring station showing 24 hours variation of nitrogen oxides

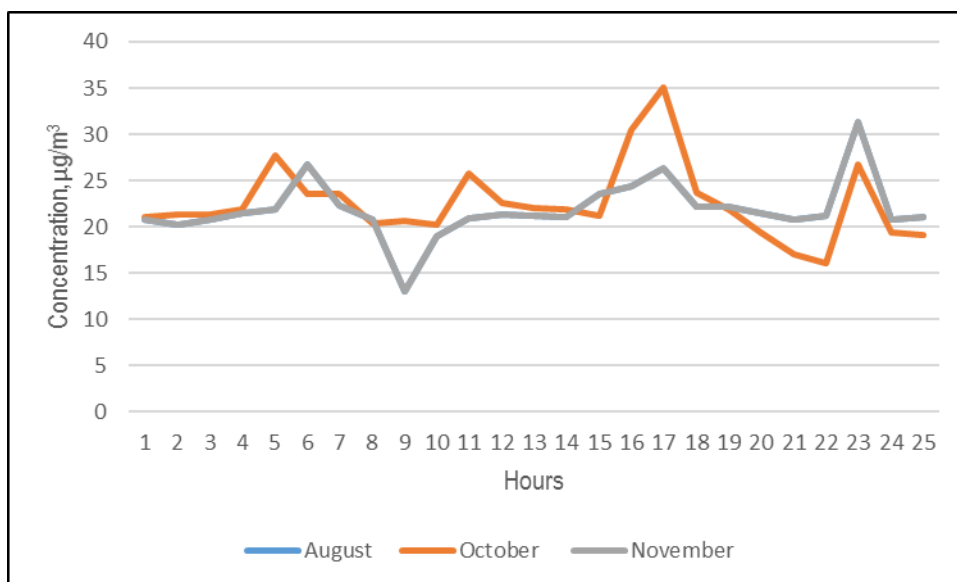


Figure 22: Secunda monitoring station showing 24 hours NO_2 concentration over three months

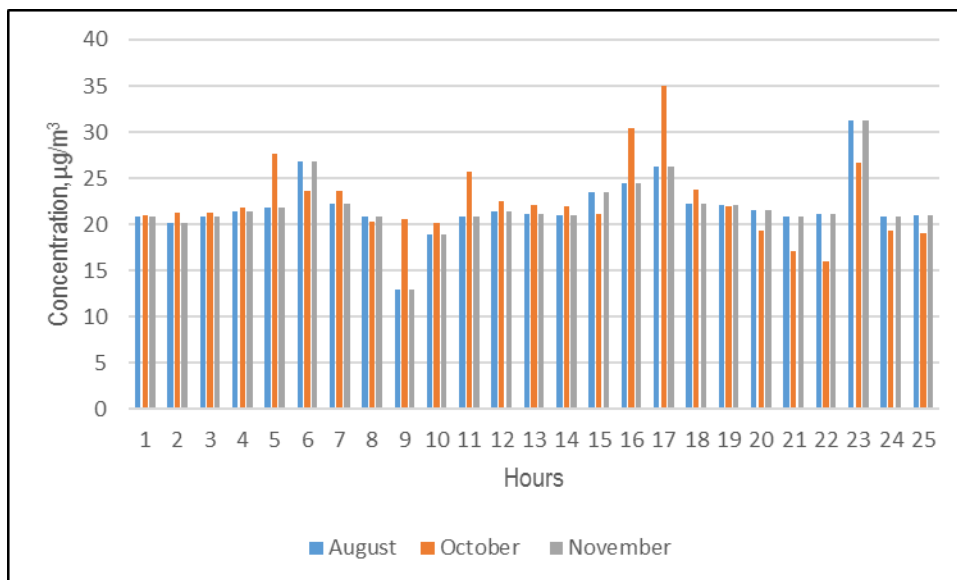


Figure 23: Secunda monitoring station showing 24 hours' variation of nitrogen oxides over three months

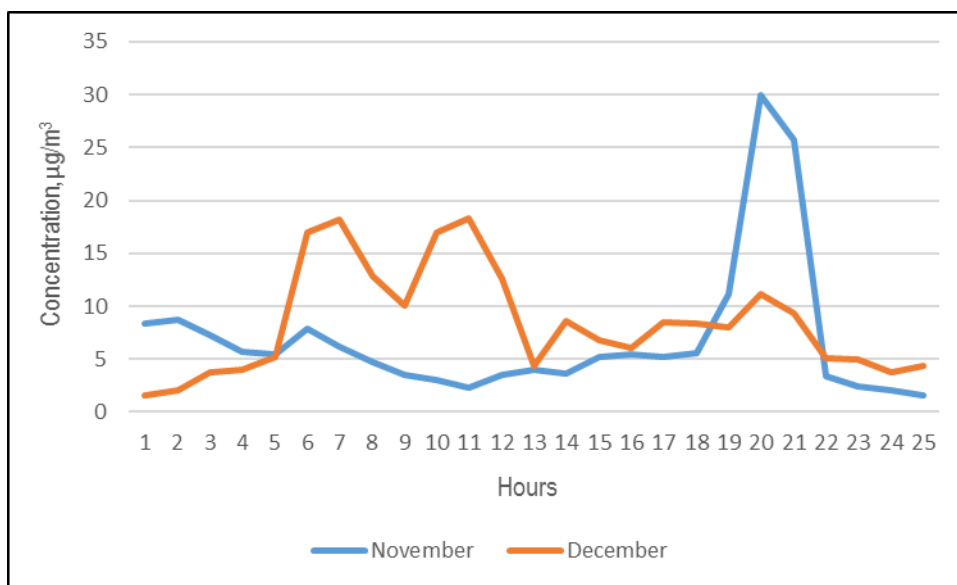


Figure 24: Standerton monitoring station showing 24 hours NO_2 concentration over two months

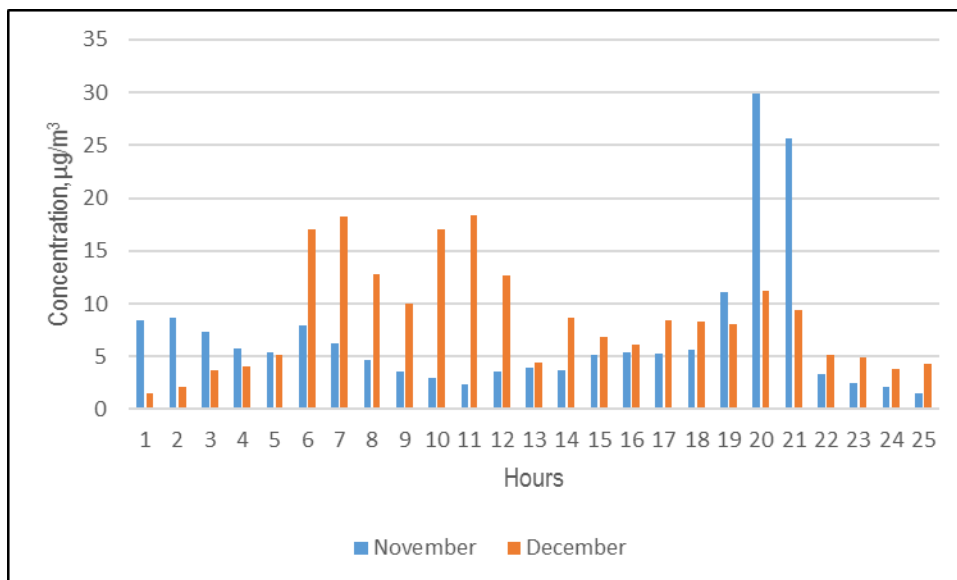


Figure 25: Standerton monitoring station showing 24 hours' variation of nitrogen oxides

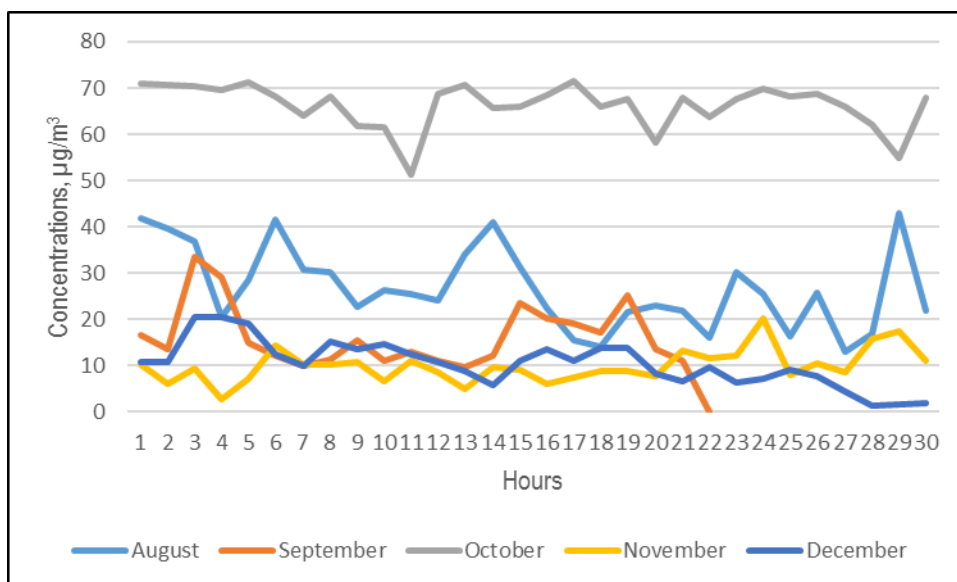


Figure 26: Witbank monitoring station showing NO_2 concentration over five months (August to December, 2008)

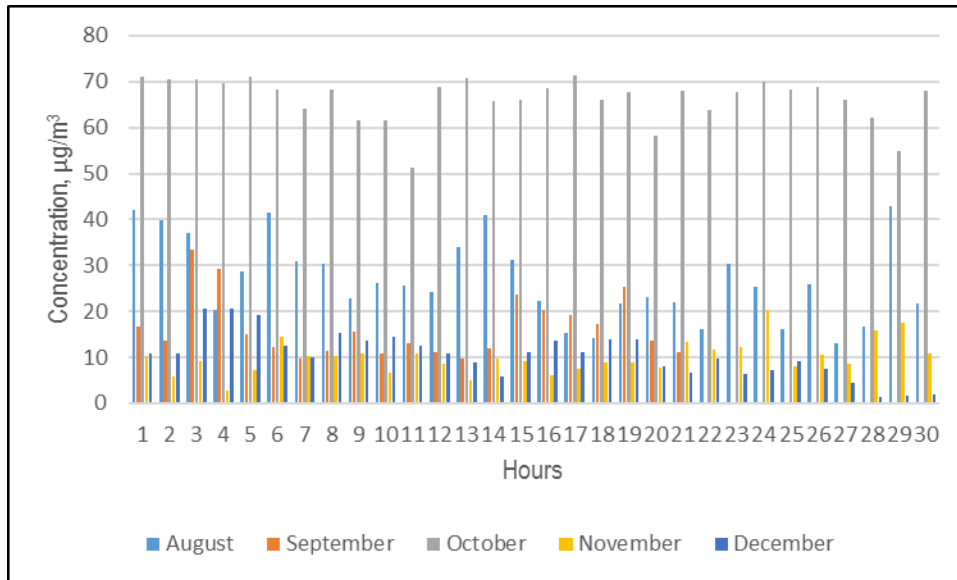


Figure 27: Witbank monitoring station showing hourly variation of nitrogen oxides over three months

4.1.2 Nitrogen dioxide at Elandsfontein air quality monitoring station

Temporary variation of surface concentrations of nitrogen oxides occurs in the Mpumalanga Highveld in the form of seasonal and diurnal variations. Nitrogen oxides are emitted at the top of the stack in the form of NO. This species combines with atmospheric O₃ in the lower atmosphere to form NO₂ and O₂, (Equation 3). The combination of NO₂ and NO gives NO_x and such formation is proportional for the four seasons (Figure 9, Figure10, Figure 11 and Figure 14). The ground measured data from Elandsfontein Monitoring station shows the variation in concentrations throughout the year. Variation in NO₂ have been divided into monthly, seasonal and diurnal variations and each trend is discussed

4.1.2.1 Monthly variation of nitrogen dioxide

Nitrogen dioxide concentrations varied from month to month and showed a peak during the winter months. Concentrations were 5.2 µg/m³ in June, 4.7 µg/m³ in July and 4.5 µg/m³ in August (Figure 12). The presence of inversion and stable atmospheric condition prevents the

upward movements of pollutants and away from the source area and may result in their accumulation in the surface concentration. The presence of westerly and northwesterly air flow transports NO from the nearby industrial sources to the Elandsfontein monitoring station. The subsequent conversion of NO to NO₂ result in the accumulation of NO₂ in the lower atmosphere during winter. The lowest concentrations were 4.5 µg/m³ in January, 4.0 µg/m³ in April and 3.0 µg/m³ in September (Figure 28). Lower concentration of pollutants occurs as a result of the presence of atmospheric turbulences during summer in the atmosphere. The presence of this unstable atmospheric condition forces pollutants including NO₂ away from the pollution source area.

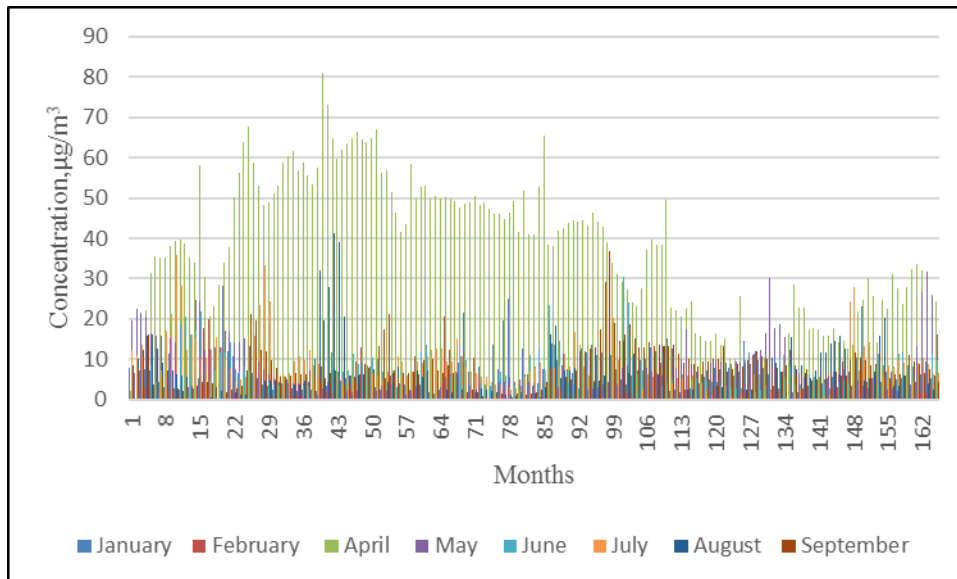


Figure 28 :2008 monthly variations of NO₂ concentrations taken from Elandsfontein monitoring station

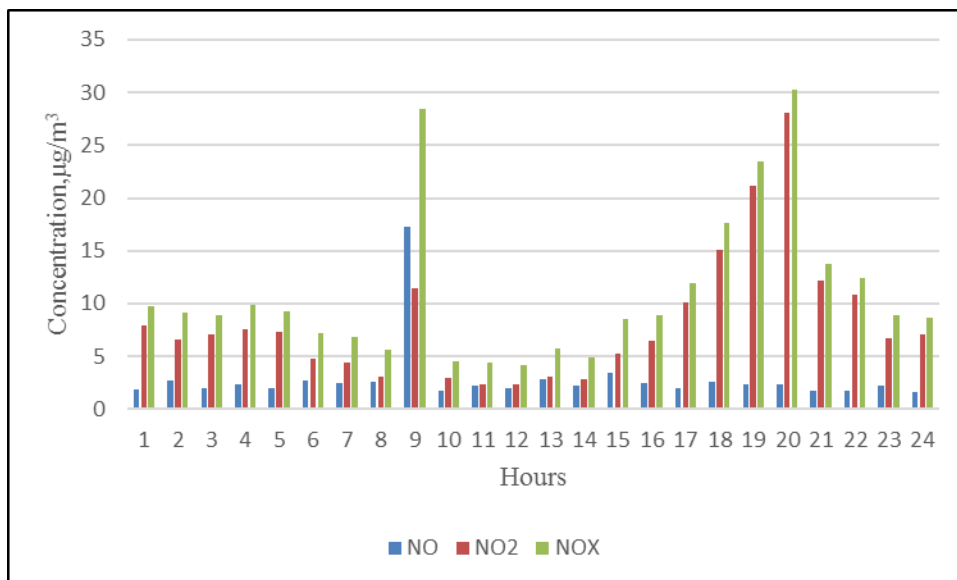


Figure 29: 24 hours' concentrations of nitrogen oxides, January 2008 Elandsfontein monitoring station

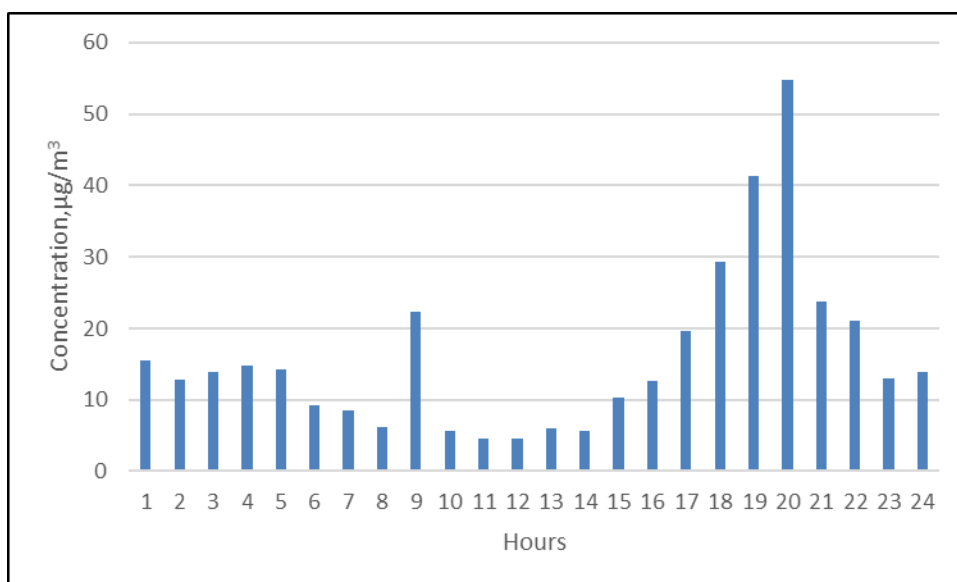


Figure 30: 24 hours' concentrations of NO₂, January 2008, Elandsfontein monitoring station

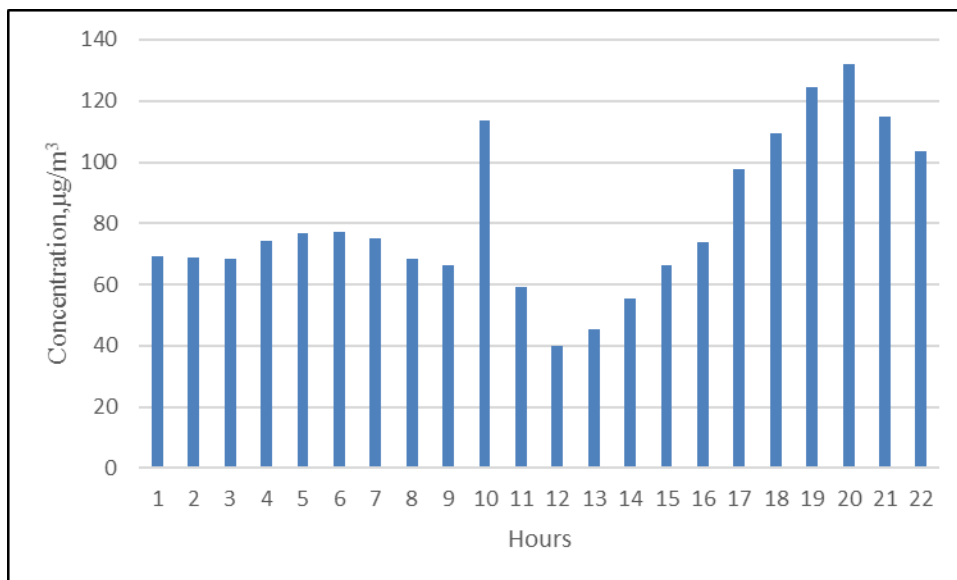


Figure 31: 24 hours' concentrations of NO₂, April 2008, Elandsfontein monitoring station

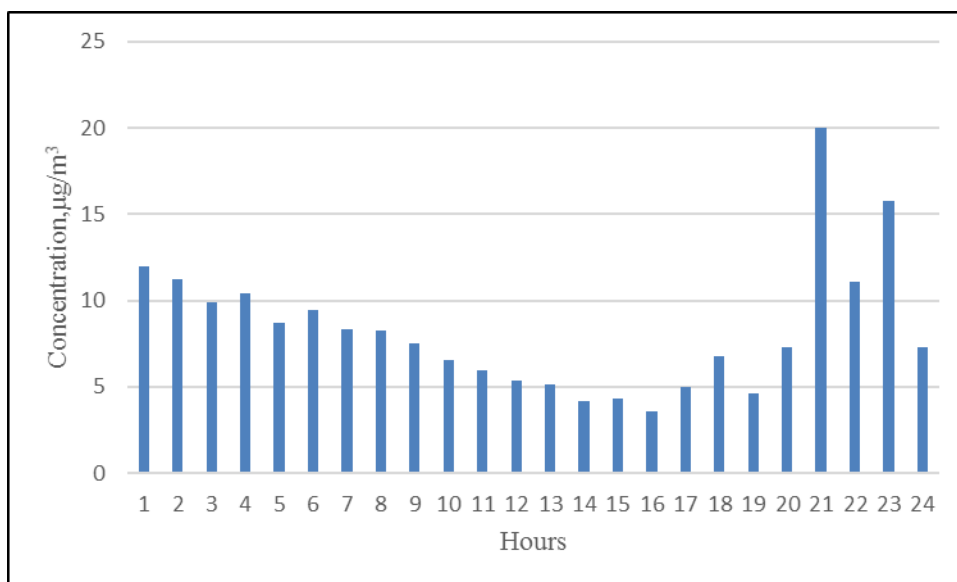


Figure 32: 24 hours' concentrations of NO₂, June 2008, Elandsfontein monitoring station

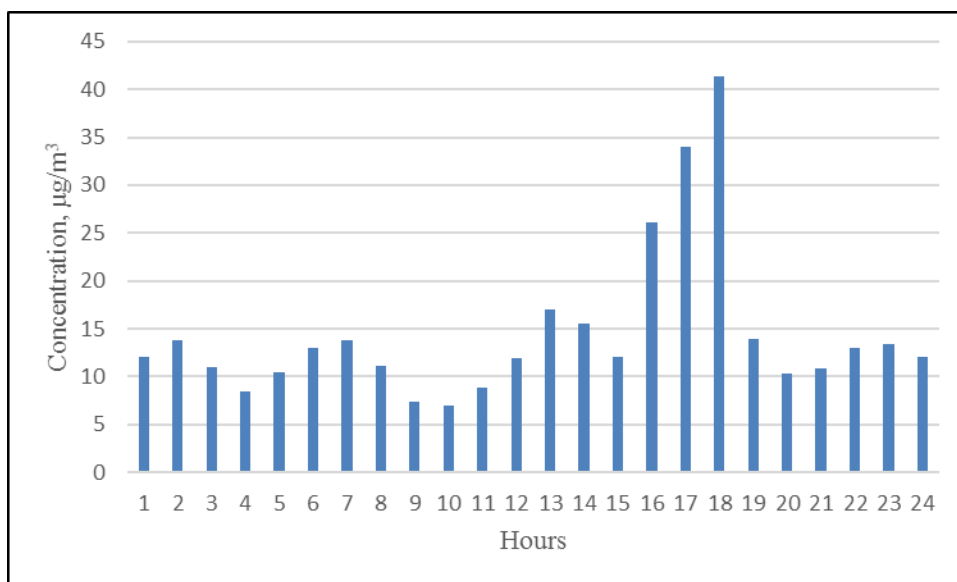


Figure 33: 24 hours concentrations of NO₂ , September 2008 at Elandsfontein air quality monitoring station

4.1.2.2 Seasonal variation of nitrogen dioxide

Data for December, March, October and November 2008 are missing from the Elandsfontein monitoring station. This has resulted in the analysis of available monthly data in each season. NO₂ show variations for different seasons most appropriately indicated by monthly averages in each season. NO₂ for the summer reached a maximum of 13.374 µg/m³ during January 2008 and a minimum of 6.8217 µg/m³ in February 2008 (Figure 34). No data was available for December 2008. Decline of concentration from December to January 2008 might have been caused by the wind direction away from the monitoring station. The two-month average concentration of NO₂ reached 19.9957 µg/m³ during the summer season (Figure 34).

The autumn concentrations of NO₂ during April and May 2008 showed a maximum of 73.609 µg/m³ and a minimum of 14.550 µg/m³ respectively (Figure 35). No data was available for March 2008. Atmospheric conditions during autumn are towards a stable condition and therefore able to keep pollutants near the surface. The total average of NO₂ over the two months during autumn reaches 88.159 far higher the 19.9957 µg/m³ total average concentration over two months of the summer season.

Data for all three months of the winter time have been analyzed for seasonal variation. June had an average of $13.015 \mu\text{g}/\text{m}^3$ July of $15.0482 \mu\text{g}/\text{m}^3$ and August had an average of $12.135 \mu\text{g}/\text{m}^3$. Although averages during winter were lower than summer averages during 2008, they are less than averages of NO_2 for autumn season during 2008. A two months (July and June 2008) total average for the winter season reached $28.1505 \mu\text{g}/\text{m}^3$ which is higher than $19.9957 \mu\text{g}/\text{m}^3$ of the summer season. The stable atmosphere and presence of inversion during winter keeps pollutants near the surface and are captured by the ground based Elandsfontein air quality monitoring station. Only September 2008 data for NO_2 has been observed and reached $15.135 \mu\text{g}/\text{m}^3$. seasonal variation of NO_2 showed higher concentration during autumn, followed by winter then lower concentration during summer and spring.

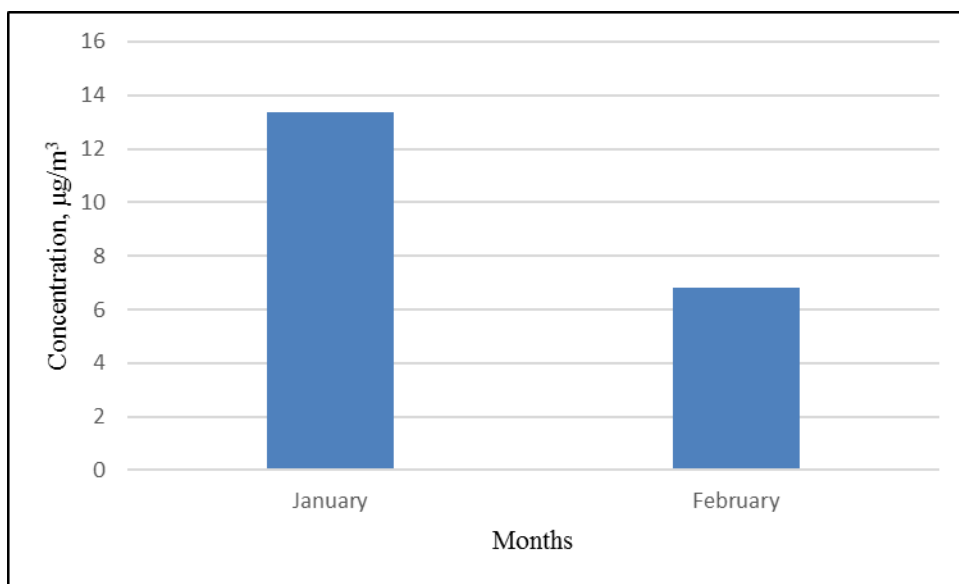


Figure 34: Summer monthly average concentrations of nitrogen dioxide at Elandsfontein (FJ) 2008

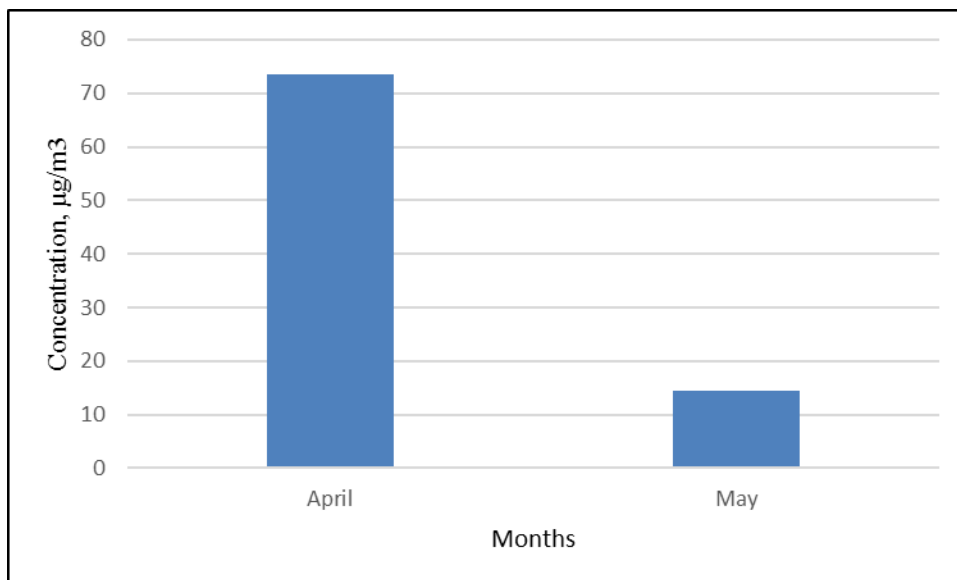


Figure 35: Autumn monthly average concentrations of nitrogen dioxide at Elandsfontein (AM) 2008

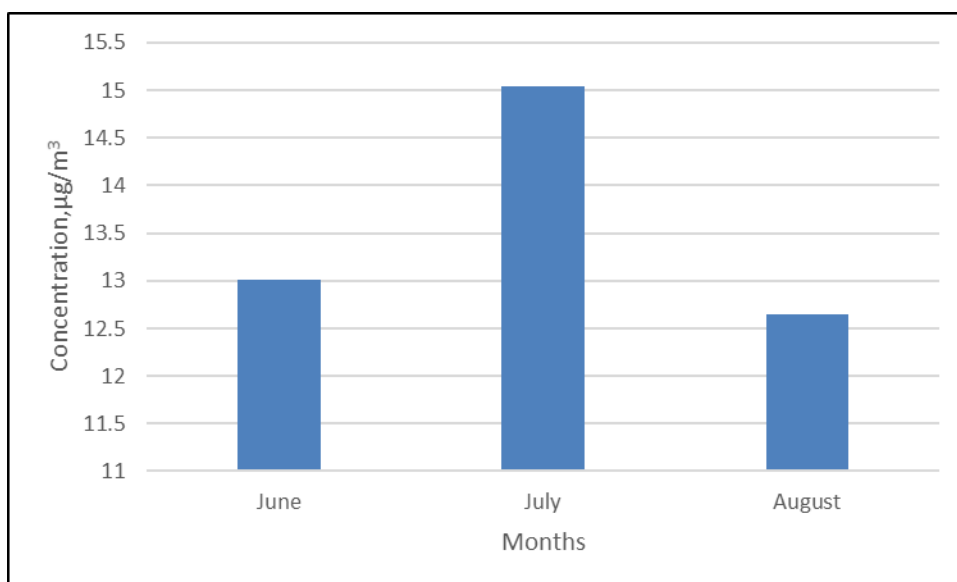


Figure 36: Winter monthly averages of nitrogen dioxide at Elandsfontein monitoring station, (JJA) 2008

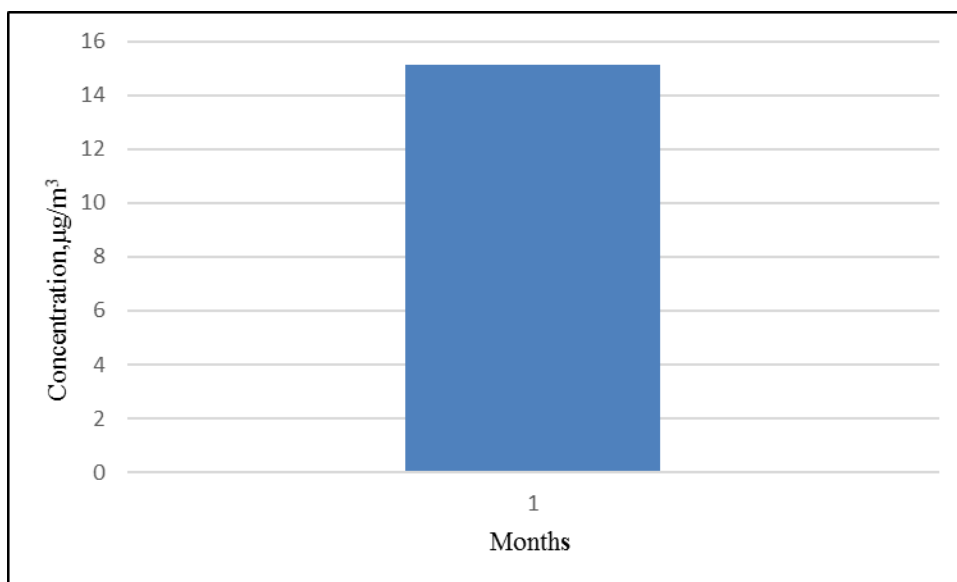


Figure 37: Spring monthly averages of nitrogen dioxide at Elandsfontein monitoring station (S) 2008

4.1.2.3 Diurnal variation of nitrogen dioxide

The data for different months of the seasons show different diurnal variations of nitrogen oxides. The concentration of both NO and NO₂ are low during the day and high during the night (Figure 29). January data indicate diurnal variability of NO₂ including other nitrogen oxides species for different times of the day. Hourly concentration over 24 hours indicate the lowest concentration of 4 µg/m³ during the eleventh and 12th hour peak of 55 µg/m³, occurred during the 20th hour (Figure 30). The rise in concentration during the 20th hour may be caused by emissions from vehicles and households. Concentrations over 24 hours are much higher during the day and night for April 2008. A minimum concentration of 40 µg/m³, occurred during the 12th hour and a maximum of 126 µg/m³ (Figure 31). In both seasons maximum concentrations of NO₂ occurred around 20:00 where pollutants are being generated from transport and households especially informal settlements in the Mpumalanga Highveld. For the June month a maximum concentration of 20 µg/m³, occurred during at 21:00 also corresponding closely with the maximum concentrations during January and April 2008 and a minimum concentration of 4 µg/m³, occurred at 16:00 (Figure 32). During September maximum concentration of NO₂

occurred at 18:00 reaching $42 \mu\text{g}/\text{m}^3$, and a minimum of $7 \mu\text{g}/\text{m}^3$, occurred at 10:00 (Figure 33). The 24 hours' data for a January, April, June and September showed diurnal variations of NO_2 with a minimum concentrations occurring during early hours and maximum concentrations occurring at around 20:00. The lower inversion layer during winter days and nights traps pollutants near the surface and are captured by ground based measurements. This is enhanced by tailpipe emissions from traffic and households' activities after work.

4.2 The spatial distribution of Nitrogen dioxide in the Mpumalanga Highveld

Both data sets were classified into monthly, seasonal and diurnal data sets. Data from Elandsfontein monitoring station has hourly figures for 24 hours per days, this allowed diurnal analysis of the data. Some data values were distorted and therefore it was imperative that a 24 hours' period with undisturbed data set be chosen for analysis. The satellite data presents the vertical columns of NO_2 in different pixels during the satellite overpass in the Mpumalanga Highveld. Having been presented in $10^{15} \text{mol}/\text{cm}^2$, satellite data has been plotted in bar charts for comparison with the surface data which is presented in $\mu\text{g}/\text{m}^3$. Different pixels were shown by coordinates on the surface and were not all in the location of Elandsfontein monitoring station, but covers area close to Standerton, Amersfoort and Volkstrust. This means that satellite monitoring covers a high surface resolution than the stationery Elandsfontein Monitoring station. The latter has been placed strategically on the well elevated position to capture pollutants which are blown by westerly and north-westerly winds from point sources to the station.

The spatial resolution covered by OMI makes it difficult to compare satellite data with the ground monitoring. NO_2 between ground measurements and satellite borne instrument may not agree. The reason being that the tropospheric column densities which is affected by the changes in emissions, temperature and dynamics of the boundary layer may create different mixing ratio from surface mixing ratio estimations. Tropospheric NO_2 columns are easily affected by priori NO_2 profile shapes. The dynamics in the boundary layer and vertical mixing with height in vertical NO_2 column creates disagreements between the ground and satellite borne measurements. The boundary layer concentrations are not uniform throughout, but in some areas

they form small fraction of the tropospheric column and influence the mixing ratios in the surface NO₂ column

Both data sets show seasonal variability of data values between summer and winter of 2008. The highest concentration of NO₂ occurred during winter as a result of a very stable atmospheric condition that limited the amount of atmospheric dilution, (Piketh *et al.*, 2010). Peak of NO during this period may be ascribed to industrial emissions into the stable atmospheric conditions and the lower thermal layer that prevents upward mixing. NO₂ concentrations showed to be variable during different seasons, lower concentrations were experienced during January, February April and September 2008. During winter, temperature inversions occurred almost every night near the surface, this is showed in the high peaks during June, July and August. NO that is emitted during the night remains above inversion and is not captured by ground monitoring. This is because emission stacks are 200 meters above the ground and air quality monitoring stations below this level do not capture nitrogen oxide which is emitted from these tall stacks during the night. Low inversions during the night are caused by the stable atmospheric conditions. NO₂ concentration peak during the day when inversion has dissipated. This midday peak shows that most NO₂ remain above the inversion layers during the night because they are emitted by the high stacks of power station in the Mpumalanga Highveld.

There is a peak in the concentration of NO₂ during autumn months, high concentrations during June, July and August months (Figure 8, figure 9 and figure 12). This is caused by the stable atmospheric conditions and absence of surface inversion. Higher concentrations of NO₂ during August may be ascribed to the biomass burning which usually takes place during this time in the Mpumalanga Grassland. Both satellite and ground measurements shows the same trend of pollutant distribution in the Mpumalanga Highveld. With the westerly and north westerly air flow during winter, the Elandsfontein air quality monitoring station is able to capture ground pollutants from industrial sources, while vertical column densities of the satellite measurements cover high spatial resolution data. The Elandsfontein monitoring station makes hourly recording of pollutants. A satellite data contains averaged observations that have been taken over a large

field of view that covers several hundred square kilometers rather than a ground measurement with its limited coverage. A number of pixels are indicated in a single rotation of the OMI and capture data in the large area than ground measurements. Satellite data must first be retrieved from the instrument before analyzed. The main keys to successful retrievals are accurate calibration and simulation of the measurements (Liu *et al.*, 2010).

Retrieval of trace gases from the troposphere species occurs with uncertainties which are associated with clouds, the surface albedo, the trace gas profile, the stratospheric trace gas column and aerosols. Such uncertainties create difficulties in comparing satellite with ground measured data. A tropospheric column density is found by subtracting the stratospheric slant column from the total slant column. The total tropospheric slant column is converted to tropospheric vertical column density by making use of the AMF. The DOAS retrieval method makes a difference between NO₂ columns from the stratosphere and Troposphere. The air mass factor is applied to convert the tropospheric slant column into NO₂ vertical column through the following equation:

$$X_{tr} = N_s - N_{s,st}$$

$$M_{tr}(X_a, b) \quad (22)$$

N_s indicates the slant column and M_{tr} , the tropospheric air mass factor. The air mass factor depends on the priori profile of NO₂. When this preparation of the vertical tropospheric vertical column density occurs, a priori assumption about the surface albedo, vertical column aerosol, clouds and NO₂ must be made. The uncertainties that relate to the total column amounts may be created from those uncertainties from (1) the fitted NO₂ slant columns, (2) the stratospheric air mass factors, and (3) the algorithm used to separate the stratosphere and troposphere (STS) (Bucsela *et al.*, 2013). Uncertainties of satellite data retrieval that may prevent proper comparison with the ground monitored data from Elandsfontein air quality monitoring station are discussed below.

4.3. Modelling satellite data for ground measurement

The satellite data which has been used is the tropospheric vertical column which has been presented in 10^{15}mol/cm^2 . Comparison between the two data sets has been done by firstly converting the unit for measuring satellite data into the $\mu\text{g/m}^3$. Ground measured data occurs in ppb and has also been converted to $\mu\text{g/m}^3$ before making comparing between the two data sets

The satellite data is given in $(10^{15}/\text{cm}^2)$ and has been converted to $\mu\text{g/m}^3$, the same units as the ground measured data as follows:

$$\begin{aligned} &= \frac{10^{15}}{\text{cm}^2} \times 10000 \text{ cm}^2 \times g \times \frac{1000000 \mu\text{g}}{g} \\ &= 10^{25} \mu\text{g/m}^3 \end{aligned}$$

Under standard pressure and temperature, an ideal gas contains 2.69×10^{19} molecules or $(2.69 \times 10^{25} \text{m}^{-3})$

Mixing ratio which represents the gas concentration to the dry air will be

$$\begin{aligned} X &= \frac{1 \times 10^{25} \text{g} \cdot \text{m}^{-3}}{2.69 \times 10^{25} \text{g} \cdot \text{m}^{-3}} \\ &= 0.371 \text{-----} (23) \end{aligned}$$

This factor has been used to multiply the satellite data to convert it to $\mu\text{g/m}^3$

The converted satellite data is then compared with the ground measured data from Elandsfontein air quality monitoring (Figure 41). Arnot satellite overpass, Elandsfontein satellite overpass and Camden satellite overpass data which also occur on 10^{15}mol/cm^2 have also been converted into $\mu\text{g/m}^3$ before compared with the ground measured data. the Arnot overpass data has been compared with the ground measured data from Hendrina air quality monitoring station, the Elandsfontein satellite overpass data with Secunda air quality monitoring station and Camden satellite overpass has been compared with Ermelo air quality monitoring station. Comparison of the paired data sets has been resented in plots (Figure 39, Figure 40 and Figure 41). Full data of NO_2 for 2008 is available for August 2008 for all air quality monitoring stations for the study area which have been used for analysis. The 2008 OMI data for August 2008 has been converted to $\mu\text{g/m}^3$ and used for comparison.

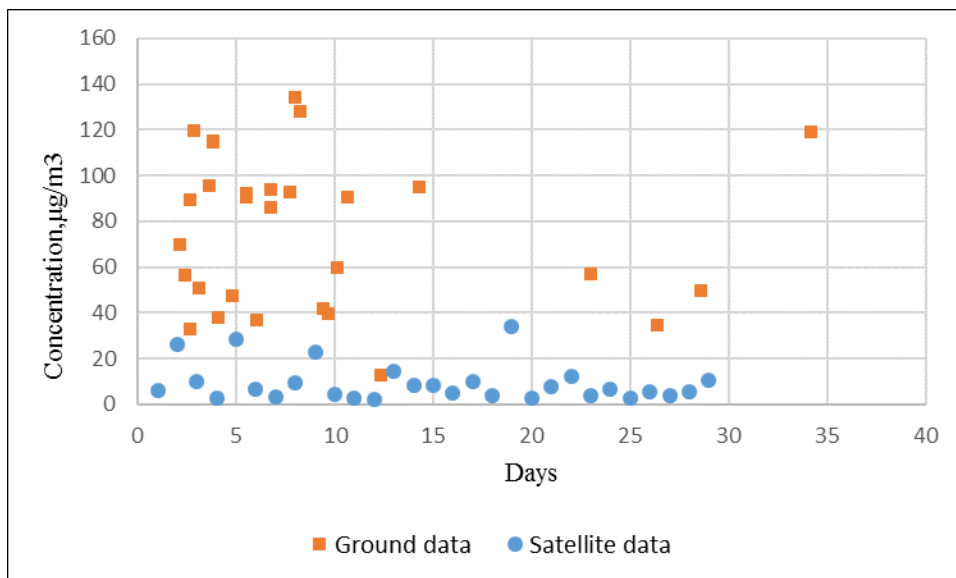


Figure 38: Ground data versus modelled satellite data at Ermelo and Camden overpass, 2008

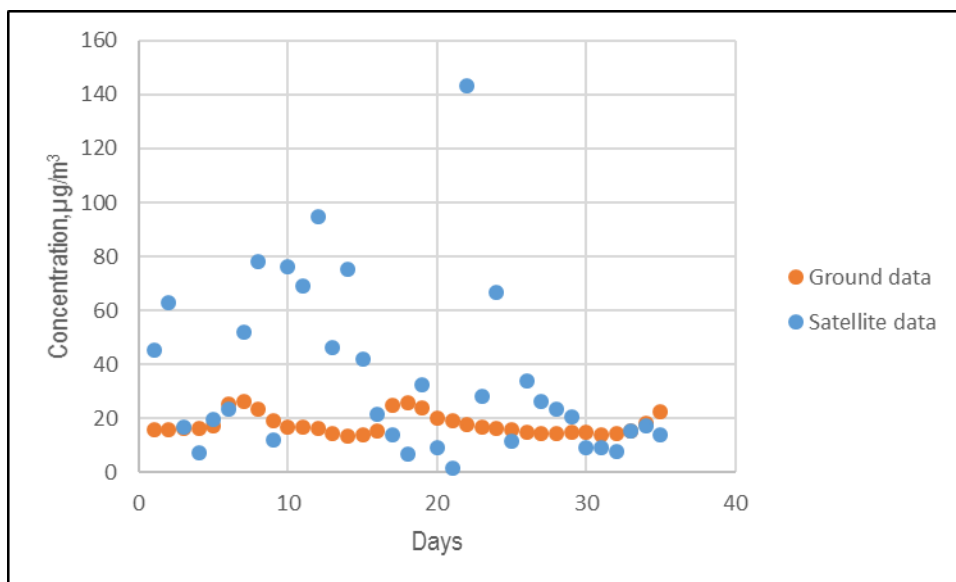


Figure 39: Ground data versus modelled satellite data at Hendrina monitoring station and Arnot Satellite overpass, 2008

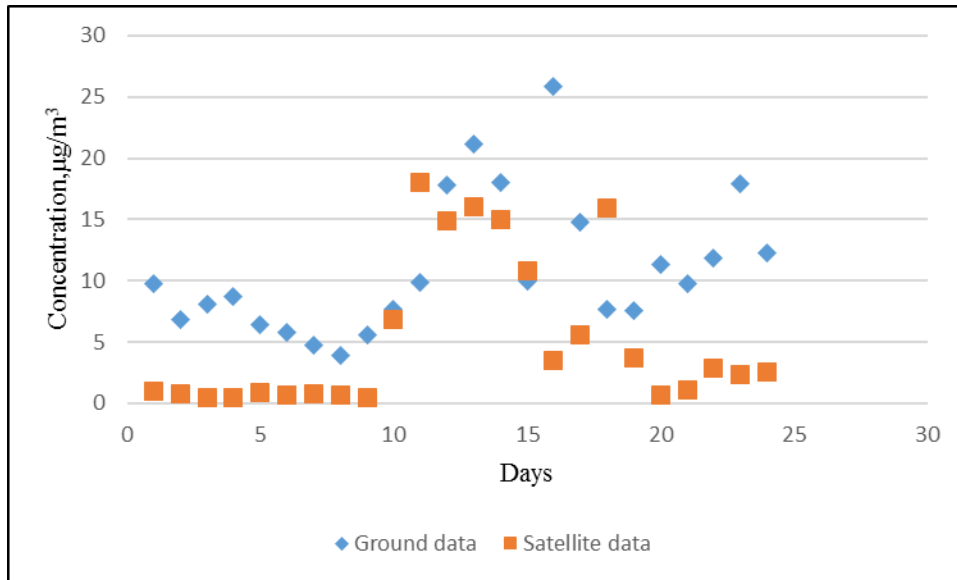


Figure 40: Ground data versus modelled satellite data at Elandsfontein monitoring station 2008

4.4 Influence of diurnal variation

The Mpumalanga Highveld as part of the Highveld is located in the subsiding edge of Southern Hadley and Ferrel cells and experiences mean anticyclonic circulation throughout the year. As the vortex strengthens in winter, westerlies expand, forcing the semi-permanent high pressure northwest over the southern part of the African continent. As part of the Mpumalanga Priority Area, the weather of Mpumalanga Highveld is characterized by hot summer day time (25-32°C) and cooler winter day time (15-19°C). The late summer afternoons are characterized by thundershowers while the winter night time temperatures drop to below the freezing point resulting into morning frost. Anticyclones over Southern Africa occur with convergence in the upper levels of the troposphere, subsidence in the middle of the troposphere and divergence near the surface of the wind field. The circulation type over Southern Africa influences air quality through transport pathways and local meteorological conditions.

4.5 Summary of satellite data over the Mpumalanga Highveld

4.5.1 *Monthly variation of nitrogen dioxide*

Concentration of NO₂ from the satellite data has been given in 10¹⁵/cm². Monthly, seasonal and diurnal averages have been calculated and plotted in the charts for analysis. Concentrations of NO₂ were in the peak during the winter months and didn't show the same peak during August 2008 (Figure 8). The peak in concentrations during winter and autumn is ascribed to stable conditions, lower thermal layer and no rainfall. The pattern in of NO₂ concentrations from the satellite measurements shows similar trends with ground measurements taken from Elandsfontein Monitoring station.

The satellite data was taken between the hours of 11:00 and 12:45 and do not show concentrations of NO₂ during the night. NO conversion to NO₂ requires O₃ which is not produced during the night, and therefore the production of NO₂ from NO and O₃ stops at this time. High ozone concentration occurs over Mpumalanga Highveld which confirms the presence of NO_x as precursor elements for ozone formation. The ozone concentration exhibits seasonal and diurnal changes, with the minimum occurring before sunrise and maximum values in the early afternoon, thereafter decreasing steadily. This indicates abundance of NO_x oxides and its reactivity during the day to form secondary products. Diurnal changes of ozone are related to the production of NO₂ from the oxidation of NO during the day. Due to air flow and photochemical processes which result into ozone formation, the highest ozone concentrations do not occur at Elandsfontein air quality monitoring station which is located closer to point sources that include electricity generating stations and petrochemical industry in Secunda.

The satellite measurement is able to capture concentrations in high resolution and in vertical columns than ground measurements. Pollutants which are emitted by 200-300 meters elevated stacks of the power stations, steel manufacturing and petrochemical factories in the Mpumalanga Highveld are captured by the satellite measurement and may not be captured by ground measurement during winter when those stacks are above an inversion. It also peaks at midday in

summer. The nitrogen oxide concentrations which result from the photochemical processes accumulate below the boundary layer under these conditions. The NO_2 is high during spring than during autumn which may be caused by the biomass burning in the Mpumalanga grassland that produces NO, a reactive species of nitrogen oxides. NO reacts with atmospheric oxygen to produce nitrogen dioxide and ozone.

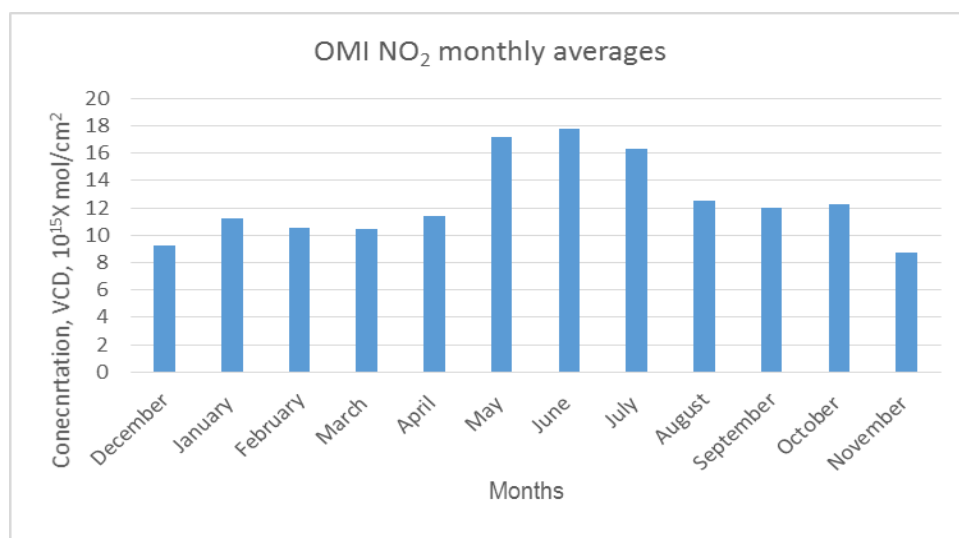


Figure 41: 2008 NO_2 monthly average concentrations from satellite measurement

4.5.2 Seasonal variation of nitrogen dioxide

Concentrations of NO_2 were $11 \times 10^{15} \text{ mol/cm}^2$ during December, January and February 2008 (Figure 41). March concentration of NO_2 was $10.5 \times 10^{15} \text{ mol/cm}^2$, peaked to $11.5 \times 10^{15} \text{ mol/cm}^2$ in March and reached $17 \times 10^{15} \text{ mol/cm}^2$ in May. The increase in concentration of NO_2 in the vertical columns may be caused by the presence of aerosols in the atmosphere and near stable atmospheric condition near the surface. The latter condition may affect the part of the vertical column near the surface. NO_2 concentrations reached $19 \times 10^{15} \text{ mol/cm}^2$ in June, gradually dropped to $16.2 \times 10^{15} \text{ mol/cm}^2$ in July and $12.5 \times 10^{15} \text{ mol/cm}^2$ in August. This decrease in concentrations of NO_2 may be caused by the dissipation of inversions towards the end of winter. The September concentration was at $12 \times 10^{15} \text{ mol/cm}^2$, $8.5 \times 10^{15} \text{ mol/cm}^2$ in October and remained at $9 \times 10^{15} \text{ mol/cm}^2$ in December. The satellite data is presented in 10^{15} mol/cm^2 but show the same seasonal variation as the ground data.

4.5.3 Diurnal variation of nitrogen dioxide

The satellite data do not show hourly averages of NO₂ oxides in the specific area. This is because the satellite instrument has an overpass time at a particular area. The data which is being analyzed has been taken in different pixels formed by the vertical columns of nitrogen oxides. But the seasonal and annual trends of nitrogen dioxide concentrations in the satellite measurements is similar to the ground measurements although the units of measurements are not the same for both data sets. The atmospheric stability during different times of the year applies to both the satellite and ground measured data. The atmospheric stability occurs more in during the night than during the day which prevents upward migration of pollutants which therefore remain close to the surface. Most satellite data for the study area has been made available for 11:00 to 12:45 because of the overpass occurring during this time interval. A lack of hourly data from the satellite data except for the overpass time limits the space of comparison between the two data sets.

The modeled satellite data show high concentration as compared with the ground measured data. This may be ascribed to the mixing ratios between the ground and satellite borne concentrations. Dividing the satellite concentrations which have been converted from 10¹⁵ mol/cm² to µg/m³ does not result into a significant change of concentrations. The elevation of the inlet channel for data collection at Elandsfontein air quality monitoring station is only three meters above the roof level, which implies that the height above the surface is 6 meters. The tropospheric vertical column occurs within the 3000 meters of the Planetary Boundary layer. After conversion from mol/cm², the satellite data turn to have values below those of the ground measured data and at other points above the ground measured data. Pollutants including NO₂ above the level of the ground measured data may only be captured by the satellite instrument and therefore the two data sets may not be the same. Figure 40 indicates that the satellite concentrations of NO₂ are above the ground measured data within the first five days but drops further to the right from the 5th day to the 30th day. The satellite data remains below the ground measured data for the rest of whole 30 days in the region of less than 30µg/m³. The ground measured data reached 70µg/m³ and 80µg/m³ (Figure 40 and in figure 41). A large spatial distribution of NO₂ occurs in the

satellite pixel than of ground measured data sets which gives result in smaller satellite values than ground values when the two data sets occur in the same measuring unit.

4.6 Retrieval uncertainties related to clouds,

Cloud data must be analyzed because of the impact it has on the NO₂ vertical columns. Not all instruments for calibration may be taken on flight which is the reason to perform ground calibration before the inflight calibration. Clouds have a large influence on the transfer of radiation in the atmosphere, making proper cloud detection and corrections are important for trace gas retrievals in passive remote sensing (Sneep *et al.*, 2008). The retrieval of cloud pressure from OMI is needed for cloud correction for the satellite measured NO₂. Some pixels with the cloud fraction of more than 0.2 are screened of the data to prevent disagreement with ground measured data. The O₂-O₂ absorption is used for cloud retrieval on the 447 nm band to retrieve the cloud pressure that is considered in the analysis of satellite NO₂. It gives the pressure level near the middle of the cloud instead of the pressure on top of the cloud. Clouds occur in different levels from the surface and affected differently by temperature. Ambient temperature and noise made by clouds creates uncertainty on the near ground NO₂ columns retrieval. Clouds complicate AMF calculations. This shows that the retrieval uncertainties are dominated by the uncertainty in the estimate of the tropospheric air mass factor, which is of the order of 20 – 30% for polluted pixels (Zhou *et al.*, 2009). Clouds increase the visibility of NO₂ above them (e.g. from lightning), but the main effect is that they shield the polluted boundary layer (Beirle *et al.*, 2004). This suggests that nitrogen oxides below the boundary layer may not be picked by the satellite measurements in the presence of clouds and the data taken at this level creates disagreement with the satellite borne measurements

The cloud pressure retrieval considers the cross section of the cloud with a fixed temperature. It is also retrieved by using the Differential Optical Absorption Spectroscopy. Clouds can have a different influence on the satellite measurement, they can increase the signal for NO₂ lying above the clouds, e.g. Coming from lightning events, and they can shield parts of NO₂ lying beneath the clouds (Wening *et al.*, 2003). Clouds, temperature and absorption cross sections create

uncertainties of the total columns densities. Temperature has an influence in the photolytic chemistry of trace gases in the boundary layer and it also reflects the amount of surface radiation. Its variation may create uncertainties in the vertical NO_2 column. Thus NO_2 that lie above the clouds may be picked by satellite measurements but not by ground measurement. Since the cloud albedo is much higher than the ground albedo during the cloudy times, the light which may be observed for satellite measurement comes predominantly from the clouds and that underestimates the boundary layer NO_2 . An inaccuracy of the calculated column may occur because of the height of a boundary layer for the seasonal, daily, and diurnal variations. This is because of the shield effect of clouds in which trace gases underneath the cloud level may not be picked by the satellite instrument. Ground measurement pick trace gases under the cloud but on a limited spatial resolution as compared to the spatial distribution of trace gases in the satellite pixel. This may create quantitative disagreements between the satellite and ground based measurements.

4.7 Retrieval uncertainties related to surface albedo

The satellite and ground measured data sets have been taken from different spatial distributions but in the same industrial extent in the Mpumalanga Highveld. Data sets from satellite and ground measurement show lower vertical NO_2 columns over industrial pollution sources in summer than those in winter. The ambient temperature, cloud factor and absorption across the pixel near the ground may have errors that must be accounted for in the ground measurement. Uncertainties in this aspects may be responsible for the differences between the two data sets. Higher NO_2 columns over industrialized areas may not be the same as those over non industrialized areas because of high variability of NO_2 in the troposphere near pollution sources. This spatial heterogeneity of on NO_x fields may yield differences in the NO_2 total columns. The difference in the areas of spatial foot print between ground and satellite measurements may give different results in measurements if not accounted for. Spatial gradients in the NO_2 field around the measurement site may also result into differences between satellite and ground measurements.

Different topographical features may affect data capturing by the ground measurement which may be captured by the satellite instrument. Similar effect may result when the wind direction blows pollutant away from the ground instrument. The abundance of NO₂ in the ground measured data may be caused by the location of the ground monitoring station near the industrial sources and wind direction towards the Elandsfontein air quality monitoring station. The satellite data indicate the slant and vertical NO₂ densities while ground measurements indicate surface data in smaller radius than the one which is covered in a wide spatial resolution by a satellite measurement. The tropospheric mass factor (AMF) is used to convert the tropospheric slant columns of NO₂ into vertical columns of NO₂. The latter represents the integrated abundance NO₂ along the average photon path from the sun, through the atmosphere to the satellite. Seasonal trends of NO₂ concentrations for ground and satellite measurements differ during the spring and autumn seasons. Emissions from the mine dumps and traffic accumulate at the ground level and increase NO₂ concentration which is captured through ground measurement. They can replace NO₂ concentrations which are emitted above inversion layers during autumn season. The pixel which is free from clouds is based on the ground reflection and Rayleigh scattering in the atmosphere. This part gives the total NO₂ vertical column.

4.8 Retrieval uncertainties associated with aerosols

Aerosols are tiny solid or liquid particles dispersed in gases and may be found in the vicinity of clouds. Biomass burning is also a major source of atmospheric aerosols (Kaufman *et al* 1998) and emits submicron particles composed mainly of partially oxidized organic materials. Because backscattering is related to optical thickness and color ratio is related to particle size, the shift implies that particles become larger and have a greater optical thickness near clouds (Vànai *et al.*, 2013). The layer of aerosols above the NO₂ may reduce the sensitivity of the satellite measurement. The largest change by a factor of approximately 2 relative to the situation without aerosols, was found when a low layer of aerosol of 600m was combined with a similar NO₂ layer of 1.0 km (Leitão *et al.*, 2010). If the elevated aerosol layer is not accounted for, the computed NO₂ column may be too low resulting into high underestimation. The 2008 satellite data for this study do not have correction factor for the aerosol effect, and therefore may present an underestimated NO₂ data. The amount of aerosol, like trace gases can be retrieved through the

backscattered solar radiation. This backscattered solar radiation is the primary signal that is used for the satellite detection of atmospheric aerosols (Husar, *et al.*, 2001). Retrieving tropospheric NO₂ from solar backscattered radiation requires information about the vertical sensitivity of NO₂. Such information will give indication of the influence of tropospheric vertical profile on the satellite data to be compared with ground measurement.

The amount of the aerosols in the atmosphere will react with the trace gases measured through back scattered radiation and influence the sensitivity of the satellite measurement. When mixed with trace gases, including NO₂ even if not on the full scale of the boundary layer, aerosols will through effective albedo multiple scattering and enhance NO₂ retrieval. The sensitivity of satellite measurement is determined through the air mass factor. The retrieved NO₂ column is sensitive to the NO₂ profile which is used in the calculation of tropospheric air mass factor. The higher the air mass factor the higher the sensitivity of the satellite measurement becomes. They may enhance the light path within its aerosol layers as a result of multiple scattering and increase the absorption signal from the path between the scattering events. This may increase the sensitivity within and above its layer from larger scattering and these paths contribute to the radiance observed at the satellite and decrease sensitivity below its layer during back scattering of aerosols to the satellite before reaching this altitude. The findings about the influence of aerosols on the vertical NO₂ column retrieval from satellite measurement suggests that errors on satellite data may not give similar trends with the surface concentration.

4.9 Weather influence of nitrogen dioxide distribution in the Mpumalanga Highveld

South Africa occurs in the Sub-tropics where high pressure and subsidence exist. A low pressure system develops in Southern Africa leaving high pressures on the surrounding pacific and Indian oceans. Circulation patterns which develop as a result of continental intrusion attracts moisture from the tropics which results into rainfall. Rain falls with the HNO₃ having resulted from the photolytic reaction of NO with the OH in the troposphere. Air temperature affects rates of photolytic chemistry and the amount of surface radiation. While urban air quality can vary in response to changes in the pollutant emission, and weather conditions, the emission of air

pollutants also depends on meteorological condition in some cases (Zhang *et al.*, 2012). Enhanced evaporation occurs over the warm pole in the southwest Indian Ocean, and this moist air is advected towards southern Africa as a result of the low pressure anomaly generated over this pole, which strengthens the offshore flow (Reason *et al.*, 2001). The atmospheric circulation over the whole of South Africa is anti-cyclonic throughout the year and anticyclones over the continent occur with convergence in the upper levels of the troposphere, strong subsidence throughout the troposphere and divergence near the surface. Subsidence occurs at the level where air is cooler and dense while the convergence near the surface occurs where air is warm and less dense.

The anticyclonic circulation over South Africa is caused by the dominance of the three pressure cells, i.e. South Atlantic High Pressure cell in the west coast, the South India High Pressure cell in the east coast and the continental High Pressure cell over the interior. Clear skies, light wind and atmospheric stability are related to High Pressure systems. Low pressure systems are associated with cloudy skies, heavy winds and atmospheric instability. During winter, South Africa experiences intensified pressure belt which moves northwards, with the upper level circumpolar westerlies that expands to displace the upper tropical easterlies towards the equator. In winter the anticyclonic belt becomes weak and shifts towards the South, making the tropical easterly flow to influence South Africa. Anticyclone occur most frequently during winter over the interior of South Africa and minimal during December. Cold fronts occur during winter and are caused by the movement of cold air from the south and southwest northwards and are responsible for the formation of cold snaps. Warm fronts occur when the two air masses, cold and warm masses develop sharp boundaries with respect to temperature, but the warm air approaches the cold air while the cold air retreats. Warm front occurs during the summer months.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Trace gases are of great concern regarding to their impact on air quality and environment in general. The Elandsfontein and other air quality monitoring stations in the Mpumalanga Highveld measure trace gases including NO_2 which are generated from its eight power generating stations, traffic from the nearby roads, informal settlements and petrochemical industry in the Mpumalanga Highveld. The flat terrain and elevation of the Mpumalanga Highveld allows Elandsfontein monitoring station to capture NO_2 concentrations which are formed from oxidation of NO produced from point sources, including the power stations, steel processing industries and the petrochemical industry in Mpumalanga Highveld. The OMI data identifies global images which indicate the hotspots for NO_2 generation. The Mpumalanga Highveld is one of the identified hotspots (Figure 7). Formation of NO_2 occurs from the photolytic oxidation of NO during the day. The conversion of NO to NO_2 occurs in the chemical reaction between NO and O_3 (Equation 3). Biomass burning in the Mpumalanga Highveld during winter particularly in August contributes to ground and space borne concentrations.

Low income houses in the informal settlements in the Mpumalanga Highveld burn coal for household energy and the smoke that result from this burning contributes to ground concentration of nitrogen dioxide in the atmosphere. Trace gases are captured once the wind direction blows towards the monitoring station, otherwise those which are generated far from the site undergo photochemical changes to secondary species before they may be captured by Elandsfontein monitoring station. The satellite borne data of trace gases including NO_2 is taken around the earth for 24 hours. A satellite overpass in the Mpumalanga Highveld occurs between 11:00 to 12:45. A 2008 satellite data from OMI has been used for comparison with data from Elandsfontein monitoring station, only data of the overpass over areas that are monitored by Elandsfontein monitoring station would compare appropriately to the satellite data (Figure 41). The figure shows higher concentrations of satellite data taken from a pixel over Elandsfontein air quality monitoring station than the corresponding ground measured data. Satellite data taken from the pixel over Camden in Ermelo is higher than the corresponding ground measured data

taken from Ermelo air quality monitoring station (Figure 39). The same applies with the satellite data taken from a pixel over Arnot, near Hendrina which is higher than the ground measured data taken from Hendrina air quality monitoring station (Figure 40). Tropospheric vertical columns of a satellite overpass may be converted into a ground mixing ratios while considering a conversion error. The vertical column of NO₂ within the troposphere contains more accurate data in a flat terrain than would be in less flat area.

Satellite data is taken from high spatial and spectral resolutions for trace gases around the earth. The data contains different pixels over Mpumalanga Highveld including Elandsfontein. Ground measured data has been taken from air quality monitoring stations located at Balfour, Ermelo, Hendrina, Middelburg, Secunda, Standerton and Witbank. Total vertical columns from the OMI are subjected to cloud pressure which shields NO₂ away from the ground measurements, similarly ground concentrations of NO₂ may be shielded away from satellite borne measurements during the cloudy days. Other retrieval errors for satellite data includes those created by surface albedo and aerosols. The vertical height of emissions stacks from power plants in the Mpumalanga Highveld escapes some pollutants from ground measurement when there is an inversion and are captured once inversions have dissipated. Ground measurements indicate high concentration of NO₂ during the night, autumn and winter periods. Elandsfontein monitoring station has a trace gas capturing pipe which is elevated for 3 meters above the roof of the station and therefore may not capture NO₂ fraction from the stratosphere, except after atmospheric deposition. It becomes part of the satellite data after its conversion from the stratospheric NO₂ to vertical NO₂ columns through the use of AMF. Its inclusion in the satellite borne measurement creates point of non-similarity with ground measurements.

The instability in the boundary layer is created by emissions and temperature influence on data capturing by OMI. The satellite data is measured in 10¹⁵mol/cm² while ground data of nitrogen oxides occurs in ppb. Conversion of satellite and ground measured data to µg/m³ has been done for comparison of the two data sets but satellite data plots have been done with the data in mol/cm² to observe the trend of data (Figure 42). Trends in both satellite and ground

measurements indicated a peak of NO₂ during the autumn, high concentration during winter and in August 2008. The peak in June and July is ascribed to atmospheric stability and inversion and high NO₂ concentrations in August is caused by biomass burning in the Mpumalanga Highveld which is covered by grassland. OMI and Elandsfontein data do not agree quantitatively because of differences in spatial and spectral resolutions, with the satellite coverage of the stratospheric NO₂.

5.1.1 Temporal variability of nitrogen dioxide over Mpumalanga Highveld

Temporal variability of the NO₂ has been determined by the monthly, seasonal and diurnal trends. Monthly variability covers both seasonal and diurnal variation of NO₂ in the Mpumalanga Highveld. On the annual scale, NO₂ concentration may show an increasing trend from one year to the other. The increasing trend may be caused by industrial development, traffic volume increase and residential developments. The latter includes low cost houses which use coal combustion for energy. Seasonal variability occurs from one season to the next. NO₂ average concentration are low during summer than in autumn (Figure 35 and Figure 36). A maximum average of 13.374 µg/m³ occurred during summer whilst a maximum average of 73.609 µg/m³ occurred during autumn. This showed an influence of a change from unstable atmospheric condition during summer to a near stable condition during autumn. The spring concentrations of NO₂ were low with the maximum in September reaching 15.135 µg/m³ and in summer the maximum average was 13.374 µg/m³ and a minimum of 6.821 µg/m³ from ground monitoring. Temporal variability of the NO₂ in the Mpumalanga Highveld show lower NO₂ concentrations in summer, increased concentrations in autumn, higher concentrations in winter and decreasing concentrations in spring. The reason for this variability is the stable atmospheric condition and presence of inversion during winter which keeps pollutants near the surface. Atmospheric circulations during spring and summer promotes vertical and horizontal transportation of pollutants away from the source thereby keep concentrations low.

Hourly NO₂ concentrations have been analyzed for the ground data and this was not done for the satellite data, the reason being that the satellite data shows the overpass time. Concentration of

NO₂ show to be higher during the night and lower during the day. Diurnal concentrations also show seasonal variations in which winter hourly concentrations are higher than summer hourly concentrations. Generally, pollutants concentrations are higher in the afternoons when there is an inversion. Pollutants including nitrogen dioxide are generated by the traffic, household's coal burning, coal dumps and pollutants that fall on the ground near the source due to fumigations. NO₂ concentrations in the Mpumalanga Highveld appear to be low during the night and rise in midday of the winter months. This is because NO₂ are created as a result of chemical conversion of NO emitted from emission stacks of power stations to NO₂. Concentrations of NO₂ remains above inversion that develops during the night of the winter season in the Mpumalanga Highveld. The above inversion concentrations of nitrogen dioxide accumulate because an inversion act as a barrier for downward dispersion of nitrogen oxides which is formed by the oxidation of NO from the power plant smoke stacks. During the day, the inversion dissipates and northwesterly wind blows them away from sources.

5.1.2 Spatial distribution of nitrogen dioxide from the satellite measurements

Satellite data covers observations over a large field of view, which suggests a couple of hundred square kilometers. It operates through Aura which is a space borne programme that covers the tropopause and the lower troposphere. The satellite data covers high horizontal spatial resolution up to 200 square kilometers as indicated by the TEMIS data coordinates for the pixels in the Mpumalanga Highveld. The satellite data covers both horizontal and vertical resolution for a complete column. The DOAS is a spectrometer for retrieving NO₂ from OMI and covers a spatial resolution of 13 x 24 square kilometers at nadir with daily coverage. The vertical resolution of the spectroscopy covers from 7 to 11 kilometers in the stratosphere and from 10 to 14 kilometers in the troposphere. This shows an extent of vertical and horizontal coverage of the satellite instrument. OMI takes measurements of concentrations of different trace gases from solar irradiance which is scattered and absorbed in the atmosphere. OMI has an overpass time when it creates pixels and capture the data. Unlike a stationery monitoring instrument, OMI records data in a particular location giving horizontal and vertical resolutions.

5.1.3 Use of satellite data to estimate surface concentrations of nitrogen dioxide

The position of the actual pixel that captured the Mpumalanga Highveld pollution hotspot must be identified for the accurate data that may be compared with ground monitoring taking into account the spatial resolution and tropospheric NO₂ vertical column. The overpass time of the satellite instrument must correspond with the day, time and season for ground measurement. For the OMI data, the overpass time occurs between 11:00 to 12:45 whilst, ground measured data is given on hourly intervals over 24 hours. A discrepancy on the time for the data between the two instruments may be affected by diurnal changes in NO₂ concentrations in the boundary layer. Spatial smoothing differs depending on the ground resolution of the instruments. Satellite NO₂ may give different signal with ground measurements with steep gradients in the tropospheric NO₂ columns. The spatial foot print of the ground instrument must be accounted for to make comparison with the pixel of the satellite overpass. Uncertainties of the satellite data retrieval may be a measure cause of disagreement between the satellite and ground measured data sets.

5.2 Recommendations

Satellite data do not show average concentrations of NO₂ in pixels over highly polluted areas during the overpass time, they are rather averaged with the concentration of adjacent unpolluted areas. Comparison between the two data sets must reflect data in the Mpumalanga Highveld. This only occurs during the overpass time of a space borne instrument. A satellite data retrieval depends very sensitively on the presence of clouds, and even small cloud fraction (between 5 and 20%) have a major impact (TEMIS Nitrogen dioxide NO₂). The fundamental difference between ground and satellite measurements is the spatial resolution. This means that a field of view which is represented in the satellite data, is more that the spatial resolution of a ground measured data. The ground pixel contains spatial homogeneity with larger NO₂ concentrations near or at pollution sources. The spatial difference between satellite and ground measurements disagree with the usage of a satellite measurement for ground monitoring. Satellite measurement may therefore not be used to estimate surface concentration of nitrogen oxides.

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