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USING AN INFERENTIAL MODEL TO ESTIMATE DRY DEPOSITION OF SO_2 AND NO_X (AS NO_2) IN LEPHALALE IN THE WATERBERG-BOJANALA PRIORITY AREA.

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

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(Signature of candidate)

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ABSTRACT

Lephalale is the home of Matimba, one of Eskom's coal-fired power stations. Matimba is the biggest power station with a dry cooling system in the world. There are other industries (including coal mines) currently in operation in close proximity to the station. This industrial area is expected to grow as more industrial activities are planned for the following years. These activities will aggravate the levels of air pollution and possibly result in it being a "hot spot" for air pollution. The impact of air quality on health is covered by the National Ambient Air Quality Standards (NAAQS), but the impact of air quality on the terrestrial and aquatic ecosystem is not known. Therefore, this study focuses on the deposition of nitrogen oxides (NO_x) (as nitrogen dioxide (NO_2)) and sulphur dioxide (SO_2) within Lephalale in the Waterberg-Bojanala Priority Area. Additionally, inter-annual variability of NO_x and SO_2 ambient concentrations and back trajectories of air masses were analysed. The study obtained ambient air quality data and meteorological data from Eskom for the period 2008–2012, while additional meteorological data were obtained from the Agricultural Research Council (ARC) and the South African Weather Service (SAWS). An inferential model was used to estimate the dry deposition flux of SO_2 and NO_x (as NO_2), and the Hybrid Single Particle Langrangian Integrated Trajectory (Hysplit) Model was used to cluster back trajectories of air masses.

The results of the seasonal dry deposition velocities of SO_2 (0.17 to 0.23 cm/s) and NO_x (0.10 to 0.15 cm/s) (as NO_2) were higher in summer and lower in winter. They were also within the magnitude of the deposition velocities found in previous studies in the Highveld. The high deposition velocities in summer were attributed to photosynthetically active vegetation, turbulence and solar radiation. However, seasonal dry deposition fluxes of SO_2 and NO_x were higher in winter across the years. The higher flux values in winter were attributed to higher ambient concentrations of the trace gases. Additionally, the annual dry deposition flux of SO_2 ranged between 0.43 and 0.67 kg S ha^{-1} yr^{-1}, while NO_x (as NO_2) ranged between 0.84 and 1.05 kg N ha^{-1} yr^{-1} over the period studied. The annual deposition flux values found in the current study are lower than those found in previous studies in

the Highveld. This difference could be because of the lower ambient concentrations of SO_2 and NO_x observed in this study. There is an inter-annual variability of the ambient concentrations of SO_2 and NO_x during the period 2008–2012. However, the difference is not large or statistically significant. The dominant direction of the back trajectories of air masses is east and southeast across all seasons for the entire period of 2008–2012. This lack of seasonal pattern in back trajectories and source regions cannot explain the seasonal changes in ambient concentrations (SO_2 and NO_x). Hence, climatic factors (e.g. change in weather) or seasonal changes in combustion source intensity must be responsible.

PREFACE

The National Department of Environmental Affairs (DEA) has already identified the Waterberg as a national air quality Priority Area due to the projected growth in industrial activity and the resultant predicted increase in air pollution. Within the vicinity of the Matimba power station and surrounding coal mines, Medupi power station is already under construction. There are also plans for more coal mines to be built. This area requires an air quality management action plan to ensure that the air pollution levels of this area remain within the National Ambient Air Quality Standards (NAAQS) (DEA, 2012). In addition, the air quality managers and relevant stakeholders need to be informed about potential threats and impacts. In this location, based on a literature search, no studies have been done on deposition. The impact of air quality on health is covered by the NAAQS, but the impact of air quality on the terrestrial and aquatic ecosystems is not known. Therefore, this study focuses on the deposition of nitrogen oxide (NO_x) (as NO_2) and sulphur dioxide (SO_2) within Lephalale in the Waterberg-Bojanala Priority Area.

This dissertation comprises six chapters. **Chapter 1** outlines the rationale of the study, and presents the aim and objectives of the study. **Chapter 2** outlines the literature review. **Chapter 3** outlines the data and methods used in the analysis. **Chapter 4** outlines the results of ambient air quality and dry deposition. **Chapter 5** outlines the discussion of the results of ambient air quality and dry deposition. **Chapter 6** outlines the conclusion, limitations and recommendations.

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- CSIR Emerging Researcher Symposium, International Convention Centre, Pretoria, 29–30 October 2013.

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NOMENCLATURE

ADOM	Acid Deposition and Oxidant Model
ANOVA	Analysis of Variance
ARC	Agricultural Research Council
ARL	Air Resources Laboratory
CCAM	Conformal Cubic Atmospheric Model
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CSIR	Council for Scientific and Industrial Research
DEA	Department of Environmental Affairs
F	Deposition flux
GDP	Gross domestic profit
GIS	Geographic information system
H_2S	Hydrogen sulphide
HPa	Hectopascals
Hysplit	Hybrid Single Particle Langrangian Integrated Trajectory
IPP	Independent Power Producer
IUAPPA	International Union of Air Pollution Prevention and Environmental Protection Associations
LAI	Leaf Area Index
MATCH	Multi-scale Atmospheric Transport and Chemistry
N	Nitrogen
NAAQS	National Ambient Air Quality Standards
NCAR	National Center for Atmospheric Research
NCEP	National Center for Environmental Prediction
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides (includes NO and NO_2)
NOAA	National Oceanic and Atmospheric Administration
O_3	Ozone
PM	Particulate matter
ppb	Parts per billion

R_a	Aerodynamic resistance
R_b	Boundary layer resistance
R_c	Canopy resistance
S	Sulphur
SANAS	South African National Accreditation System
SANBI	South African National Biodiversity Institute
SAWS	South African Weather Service
SMHI	Swedish Meteorological and Hydrological Institute
SO_2	Sulphur dioxide
StatsSA	Statistics South Africa
USEPA	United States Environmental Protection Agency
$\mu g.m^{-3}$	Micrograms per cubic meter
v_d	Deposition velocity

CHAPTER 1: INTRODUCTION

This chapter provides information on the rationale of the study, key questions, aims and objectives.

1.1 Rationale for the study: Introduction

South Africa is a developing country that is rich in mineral resources. This has led to the development of mining and other industries, making it one of the biggest economies on the African continent. However, the rapid growth of these industries has led to an increase in emissions of air pollutants such as sulphur dioxide (SO_2) and nitrogen oxides (NO_x) (Zunckel et al., 1996, 1998, 1999; Mphepya and Held, 1999; Mphepya, 2002; Mphepya et al., 2004, Ferguson, 2009). Escalations in the emission of air pollutants from these industries can cause serious environmental concerns; nonetheless, these industries are the country's major economic drivers (Martins, 2009).

In this country, air pollution has received much attention due to the increase in industries, as well as communities residing close to industrial areas. Both poor air quality and the deposition of pollutants are a concern in many parts of the country and are a potential threat to sustainable development because of their negative environmental impacts. Fourie (2000) highlighted that while job creation and economic growth are of great importance to the South African government, environmental impacts might increase due to this rapid growth of industries if the country does not have appropriate planning and management strategies in place to protect its natural resources. Additionally, sustainable development needs to be achieved in order to afford the future generation a safe environment. This needs sound decision-making so that all the negative impacts on the environment are well understood. This can be achieved by prioritising the acquisition of a better understanding of atmospheric chemical transformations and the removal of pollutants (Bessagnet et al., 2005).

Research on deposition has been done in many countries, and there is evidence to suggest that gaseous pollutants such as NO_x and SO_2 can have a major impact on ecological systems when these pollutants or their reaction products are deposited (Wesely et al., 1982; Erisman and Draaijers, 1995; Zunckel et al., 1996, 1999, Mphepya, 2002; Mphepya et al., 2004; Ilyas et al., 2009; Scorgie and Kornelius, 2009a, Martins, 2009, Martins, 2007; Josipovic et al., 2011). These environmental impacts include damage to forests, reduction in biodiversity, acidification of lakes, oceans and rivers, and a decrease in the nutritional value of soil (EPA, 2002). Therefore, it is crucial to understand the long-term measurement of pollutant concentrations of gaseous species and to estimate their deposition rates in order to assess their impacts on the terrestrial and aquatic ecosystems. Such information will aid in understanding the relationship between the atmosphere and biosphere (Held et al., 1996).

South Africa is in the southern hemisphere of the African continent and is regarded as one of the largest industrialised economies in this hemisphere (Sivertsen et al., 1995; Rorich and Galpin, 1998). Most of these industries are located in the Highveld Priority Area in Mpumalanga, and are responsible for 90% of the emissions of gaseous pollutants (SO_2 and NO_x) and particulate matter (PM) in the country (Josipovic et al., 2011). However, in the country, areas such as Rustenburg, Lephalale and Burgersfort are currently experiencing a growth in industries such as mining and electricity generation. As a result of this industrial growth, air quality and the deposition of acidifying species have received much attention, especially in these industrialised areas.

Lephalale is situated in the Waterberg District Municipality in Limpopo. There is a residential area located within the vicinity of the Lephalale industrial area, namely Marapong (northeast of the industrial area). The Lephalale industrial area is characterised by operations such as mining, electricity generation and agriculture, which play a major role in the economy of Limpopo. Further growth in the area is expected in the next few years due to the planned expansion and development of industrial activities, such as the Medupi power station, Boikarabelo coal mine, an independent power station, Sekoko coal mine and a similar development in

Botswana. It is anticipated that these activities will increase the levels of air pollution and possibly result in it being a “hot spot” for air pollution. The national Department of Environmental Affairs (DEA) identified this area as an air quality Priority Area on 15 June 2012 (DEA, 2012). This area was declared a national Priority Area because, in the future, the ambient air quality of the area might surpass the National Ambient Air Quality Standards (NAAQS). Additionally, the area is likely to experience transboundary air pollution from Botswana and the Bojanala Municipality in North West (DEA, 2012).

The predicted increase in air pollution and transboundary air pollution may impact negatively on the air quality of Lephalale; hence, it requires national air quality management action to ensure that the pollutant concentrations in the area continue to be compliant with the NAAQS. Industrial emissions from the projected growth in industries in Lephalale may result in emissions that are detrimental to ecological systems. Of particular concern are the emissions of SO_2 and NO_x, the principal acid-forming pollutants, into the atmosphere. Deposition of these acid-forming pollutants can change the chemical composition of the soil, decreasing its fertility and affecting the growth and development of plants. Rorich (2004) has reported that the terrestrial ecosystem of Lephalale is likely to be sensitive to negative environmental impacts because of sparse rainfall in the region and the buffering capabilities of the soils. Additionally, the local air pollution community forum in Lephalale has highlighted that trees are dying and fence corrosion is taking place because of air pollution. Therefore, it is important that the air quality and deposition rates of acid-forming pollutants are studied in the area, and that they are understood to develop effective management strategies for air pollution and its potential deposition impacts.

The monitoring of pollutants is common in most countries, including South Africa. The use of monitored air quality data is very important if air quality management efforts are to be improved (Ozden et al., 2008). Additionally, these monitored air quality data are needed to promote ecosystem recovery from acid deposition (Driscoll et al., 2001). Eskom monitored the following pollutants at the Marapong air quality monitoring station: SO_2, NO_x, nitric oxide (NO) and nitrogen dioxide (NO_2). These pollutants were monitored for the period between 2007 and 2012 when there were additional developments, such as the Matimba power station and brick-making

operations, as well as associated population growth. Bearing in mind the planned industrial activities that may impact on the area's future air quality, it is critical to examine at these existing data and determine the status of NO_x and SO_2 deposition to inform air quality managers and relevant stakeholders about potential threats and impacts. The findings of this study are of paramount importance because the deposition of these gaseous pollutants may damage the stability of the terrestrial and aquatic ecosystem in Lephalale.

Dry deposition of pollutants is the process where gases are deposited directly from the atmosphere to land surface. It is governed processes such as: concentration of the pollutant, turbulent transport in the atmospheric boundary layer, gravitational settling, molecular diffusion, the chemical and physical nature of the deposition species and the capacity of the surface to absorb gases. However, there numerous direct methods to measure dry deposition, but these are complex, needing high technology equipment and infrastructure. Therefore, an inferential technique is an alternative to these direct methods. This model makes use of measured ambient concentrations and modelled deposition velocity to calculate deposition flux. The modelled deposition velocity is calculated using meteorological and vegetation data.

1.2 Aims

The primary aim of this research is to evaluate SO_2 and NO_x (as NO_2) dry deposition rates for the period 2008–2012 within Lephalale in the Waterberg-Bojanala Priority Area. In addition, a secondary aim is to understand the regional air masses that can affect NO_x and SO_2 concentrations seasonally.

1.3 Research questions

- Are there any inter-annual variations in ambient SO_2 and NO_x concentrations for the period 2008–2012?
- What are the dry deposition rates of NO_x (as NO_2) and SO_2 during the period 2008–2012?

- Are there any seasonal variations of NO_x (as NO_2) and SO_2 deposition rates during the period 2008–2012?
- Is there any relationship between concentrations of ambient SO_2 and NO_x and the modelled back trajectories of air mass origin?

1.4 Objectives

- To evaluate the inter-annual variability of NO_x and SO_2 ambient concentrations for the period 2008–2012.
- To calculate the annual dry deposition rates of NO_x (as NO_2) and SO_2 for the period 2008–2012.
- To assess seasonal variations of NO_x (as NO_2) and SO_2 dry deposition rates during the period 2008–2012.
- To identify seasonal regional sources of air pollution for the period 2008–2012 using the Hybrid Single Particle Langrangian Integrated Trajectory (Hysplit) Model.

CHAPTER 2: LITERATURE REVIEW

This chapter provides information on the general air pollution sources in South Africa and Lephalale. It also gives information on the transportation of air pollutants and dry deposition measurement and modelling.

2.1 Air pollution sources in South Africa

Air quality and deposition of air pollutants have received much attention on a national and international level due to their associated environmental problems, such as acid precipitation, radiative effects due to an increase in short-lived climate forcing pollutants, etc. (Pham et al., 1996; Zunckel, 1998; Mphepya, 2002, Mphepya et al.; 2004; Beukes et al., 2012). Industrialisation has been highlighted as one of the biggest contributors of primary atmospheric pollutants worldwide, particularly SO_2 and NO_x (Annegarn et al., 1996a; Pham et al., 1996; Zunckel et al., 2000; Smith et al., 2001; Mphepya et al., 2004). To understand the origin of the chemical species deposited from the atmosphere to the earth at a specific point or over a region, one needs a comprehensive knowledge of the emission sources both regionally and globally (Else, 1985; Else, 1987). In South Africa, the heavily industrialised Highveld region in Mpumalanga has been associated with heavily polluted air and has been declared an air quality Priority Area (DEA, 2007). Most deposition and air quality studies were focused on this area, compared to other industrialised areas (such as the Waterberg, Rustenburg, Tubatse and the Vaal, which also have industries) as there are more industrial activities resulting in the emission of precursor gases, which are harmful to the environment. Similar to the Highveld Priority Area, Lephalale is the economic hub of the Waterberg District Municipality. More industrial activities are planned in the area, thus making the area more likely to have high levels of air pollution. As mentioned above, it has also been declared a Priority Area, indicating the importance of evaluating ambient concentrations and their deposition rates in Lephalale.

Josipovic (2009) reported that air pollution in South Africa has characteristics of a developing and developed country. Industrial emissions and emissions from motor

vehicles are characteristic pollution sources in developed countries, while a developing country is characterised by burning fuels used in the domestic household (low-grade fuel, which costs less) for cooking and space heating (Elsom and Longhurst, 2004; Khare and Kansal, 2004), as well as vehicle and industrial emissions. Additionally, Blight et al., (2009) stated that the air quality in South Africa is declining as a result of an increase in ambient concentrations of both trace chemicals (SO_2 and NO_x) and PM from industries, households and power stations. Additionally, wood and coal are commonly used for domestic heating and cooking, mostly in rural areas. The common sources of air pollution and their examples from a South African perspective are listed below in Table 2.1.

Table 2.1: Common pollution sources in South Africa (Blight et al., 2009).

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Pollution source	**Examples**
Fuel combustion in stationary activities	Boilers, industrial and chemical processes
Fuel combustion in mobile activities	Vehicles
Solid waste disposal	Incineration
Land surface disturbances giving rise to dust	Unpaved roads, agricultural emissions and mine dumps

2.2 Air pollution sources in Lephalale

Figure 2.1 below displays common sources of air pollution in Lephalale. Details of each pollution source are given below.

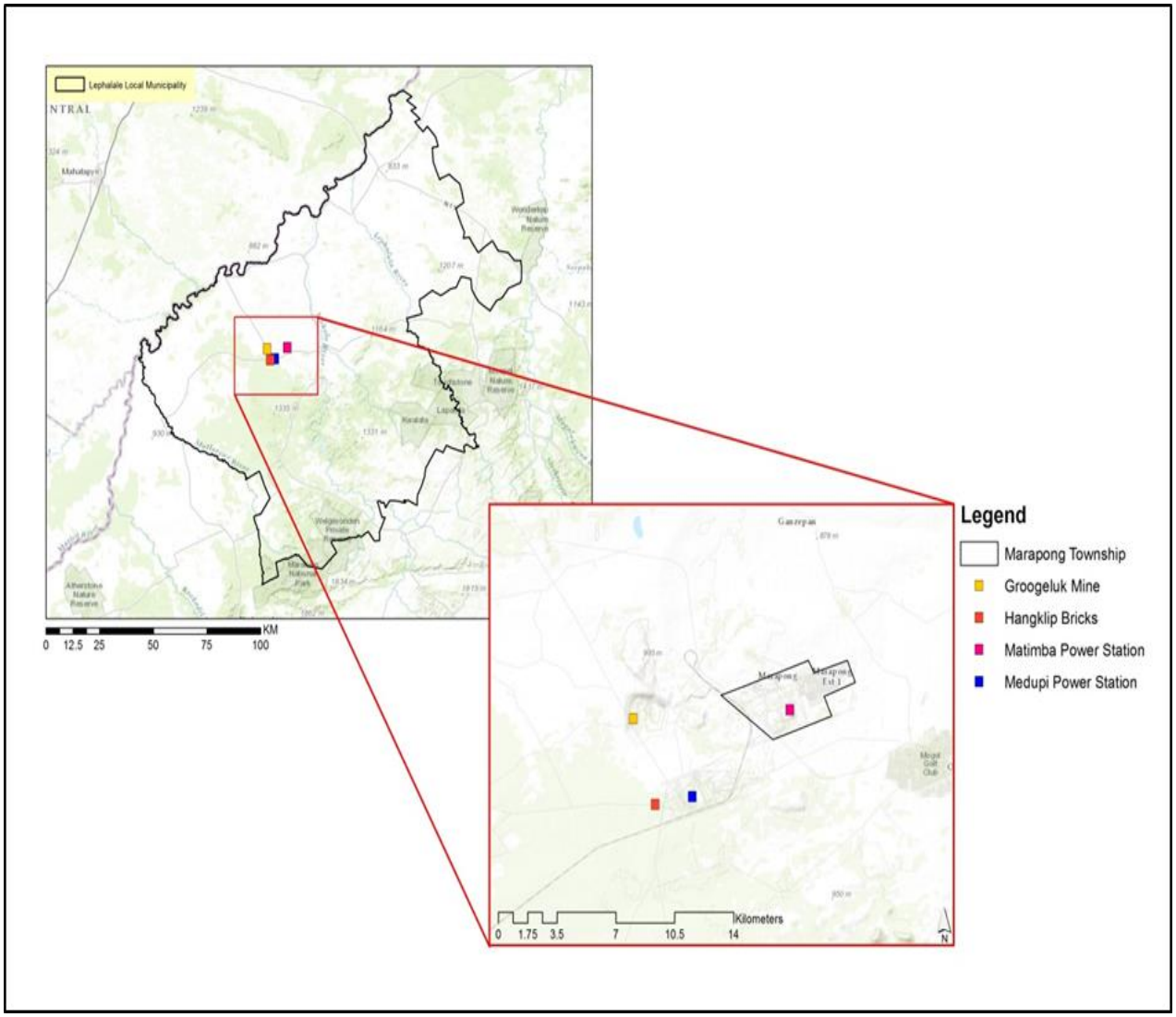


Figure 2. 1: Air pollution sources and Marapong Township in Lephalale Local Municipality.

2.2.1 Power generation: Matimba power station

Matimba power station is situated at ~14 km from Lephalale town and is classified as one of the biggest power stations with a dry cooling system in the world. This station was designed with a dry cooling system as a result of water scarcity in the area of Lephalale (Walton and Ngcukana, 2009). This station releases pollutants such as SO_2, nitric oxide (NO), carbon dioxide (CO_2), nitrogen dioxide (NO_2) and small quantities of mercury (Walton and Ngcukana, 2009). The newly built Medupi power station will also release the same pollutants once it is operational. Another source of atmospheric pollutants in the vicinity of Matimba includes windblown pollutants from

ash dumps and stockpiles. Additionally, this station was quantified as the major contributor of SO_2 in Lephalale (Walton and Ngcukana, 2009).

2.2.2 Mining: Grootegeluk mine

Grootegeluk is an open-cast mine situated ~7 km from Matimba power station and ~25 km from Lephalale. Coal from this mine is transported via a conveyer belt to Matimba (Muthige, 2013). The main sources of fugitive dust from the mine include drilling, dragline, crushing and transportation (IDP, 2012; UMoya-NILU, 2013; Walton and Ngcukana, 2009). Blasting also results in gaseous emissions such as NO, carbon monoxide (CO), as well as small quantities of SO_2. Small quantities of pollutants such as NO_x, SO_2, CO and hydrogen sulphide (H_2S) are formed due to a spontaneous combustion process at Grootgeluk mine (Walton and Ngcukane, 2009).

2.2.3 Domestic fuel burning

Domestic fuel burning is common in low income townships and rural areas in South Africa. This is because some areas are not electrified, while other households prefer to save electricity by making use of coal, wood and paraffin. This is no different for Marapong Township in Lephalale, where coal, paraffin and wood are commonly used for cooking and space heating. Coal and biofuel have been highlighted as the most common sources of energy in townships in South Africa for cooking and space heating, as they are affordable (Mdluli and Vogel, 2010; Tummon et al., 2010). According to Statistics South Africa (StatsSA) (2011), 60.4% of the houses in Lephalale are electrified, but 39.6% still rely on paraffin, wood, candles, coal or animal dung for heating and cooking. Piketh et al., (1999) stated that – from a South African perspective – during cold months, coal and biomass are the main contributors of emissions on the surface. The most common pollutants as a result of coal combustion include PM and gaseous pollutants, such as SO_2. Pollutants emitted from wood combustion include NO_x (NO and NO_2), SO_2 and CO, while pollutants emitted from paraffin are NO_2, CO and SO_2 (The World Resources Institute, 1998; Ezzati et al., 2004).

2.2.4 Biomass burning

In South Africa, biomass burning (such as veldfires) has been indicated to be one of the sources of air pollutants such as PM and gaseous pollutants (NO_x and SO_2) (Li et al., 2003; Scholes and Andreae, 2000). In this country, most wild and natural fires are caused by lightning, while some areas are set alight for land management purposes (Roy et al., 2005). Granier et al., (2011) highlighted pollutants such as NO_x, CH_4 and CO as common pollutants from flaming combustion during the burning of savanna and scrubland, while the combustion of grasslands forms pollutants such as NO_x and carbon dioxide (CO_2) (Korontzi et al., 2004).

In South Africa, biomass burning occurs during the dry season (Roy et al., 2005). However, Lephalale and the Waterberg district as a whole, have less density of fires compared to the neighbouring districts of Sekhukhune in Limpopo and Bojanala in North West Province (Walton and Ngcukana, 2009). It has also been indicated that emissions from fires in these neighbouring districts will impact on the air quality of the Waterberg. However, biomass burning at a regional level might also impact on the air quality of the Waterberg.

2.2.5 Vehicular emissions

The Waterberg area has been experiencing an influx of people over the past few years as a result of growing economic activity. An increase in an economically active population usually results in more people using public and private transport. Currently, Nelson Mandela Road (D1675), which is the main road to the mine and power station in Lephalale, is currently experiencing increasing volumes of traffic (IDP, 2013). Vehicles within the power station, coal mines and brick firms, as well as Lephalale, which are ~ 8 km from the Lephalale industrial area, also release air pollutants. Rhys-Tyler et al., (2011) identified SO_2, NO_x, PM and CO as the main pollutants resulting from transportation. When the temperature and pressure are high inside the engine, there is a reaction between oxygen and nitrogen, which results in the formation of NO_x, while fuels containing sulphur result in SO_2 formation (Walton and Ngcukana, 2009).

2.2.6 Hangklip Brickworks

Hangklip Brickworks makes use of clamp kilns to make bricks, and produces 24 million bricks annually (Walton and Ngcukana, 2009). Clamp kilns are no longer used in most parts of the world (especially developed countries) as they are considered an old way of brickmaking due to continuous kilns and mechanisation being introduced (UNEP, 2014). However, in South Africa, they are still common as they are considered affordable. The process of brickmaking is comprised of extracting and crushing the material. The material is then screened and blended so that it can be ready for shaping and eventually drying and heating. Major air pollutants released from this combustion process include SO_2, NO_2 and CO.

2.2.7 Additional sources from 2012 and beyond

In conjunction with the construction of Medupi power station, there have been road developments since the inception of Medupi in 2011 (Muthige, 2013). Other than the sources mentioned above, according to the Lephalale Local Municipality IDP (Integrated Development Plan) (2013), a Sintel char plant has also been under construction in the area since 2012. Two coal mines are being planned, namely Sekoko and Boikarabelo, which will emit pollutants similar to those emitted at the Grootegeluk coal mine. Thabemetsi mine will be constructed close to Grootegeluk in 2016. Plans are also under way by Limpopo Independent Power Producer (IPP) to build an independent coal fired power station.

2.2.8 Summary of sources

In general, the main sources of air pollution in Lephalale are the Matimba power station, Grootegeluk mine, vehicular emissions, biomass burning, domestic fuel burning (from Marapong Township) and Hangklik Brickworks. Additionally, Medupi power station and other planned coal mines (Thabemetsi, Sekoko and Boikarabelo), as well as the planned independent coal fired power station by Limpopo IPP, will also contribute to air pollution in the area. The common pollutants emitted from these sources include SO_2, NO_x (NO and NO_2) and CO.

2.3 Atmospheric transportation of air pollutants

How pollutants are moved, diluted, dispersed and accumulated in the troposphere depends on the presence of thermal and turbulence processes in the boundary layer (Garstang et al., 1996; Tyson and Preston-Whyte, 2000; Scorgie and Kornelius, 2009a). Pollutants can be transported both vertically and horizontally (Garstang et al., 1996; Bradshaw et al., 2000; Tyson and Preston-Whyte, 2000; Savage et al., 2004). Vertical transportation is dependent on the stability of the atmosphere and the surface mixing height. Horizontal transportation mainly depends on large synoptic-scale circulation. Local winds also play a role in transporting pollutants within the neighbourhood of the source. These local winds originate from geomorphologically and topographically different features" areas such as valleys, seas, mountain plains. Mountain plains winds also transport pollutants around the area of the source (Tyson and Preston-Whyte, 2000).

South Africa is located within a subtropical high-pressure belt and is affected by high pressure cells, as well as other circulation systems from tropical and temperate latitudes (Tyson et al., 1988). It is dominated by three semi-permanent high-pressure cells: the South Atlantic high pressure off the west coast, the South Coast Indian high pressure off the east coast and the continental high pressure over the interior. These three high-pressure cells cause the atmospheric circulation to be anticyclonic, thus resulting in stable atmospheric conditions across the country (Tyson et al., 1976; Tyson et al., 1988; Cosijn and Tyson, 1996; Garstang et al., 1996). These anticyclones occur more frequently in winter (70%) and less frequently in summer (30%) (Tyson et al., 1996). The dominance of these anticyclones results in stable conditions in the atmosphere, which leads to an accumulation of pollutants, resulting in high concentrations of pollutants.

Several studies have indicated that inversions restrict the vertical distribution of pollutants, thus resulting in horizontal transportation within the layers (Tyson et al., 1996a; Tyson et al., 1996; Tyson and Gatebe, 2001). Multiple elevated inversions occur in the middle to upper troposphere due to large anticyclonic subsidence. Three elevated inversions are located at the altitudes of ~3 km (with an air pressure of 700 hPa), ~5 km (with an air pressure of 500 hPa) and ~7 km (with an air pressure of 300

hPa) on the interior plateau with 800 hPa occurring on the coast of the South African subcontinent (Cosijin, 1996; Cosijin and Tyson, 1996). Latitudinal and longitudinal position plays a role in the differences in height and persistence of these elevated inversions. In winter, the first elevated inversion is situated at an altitude of ~3 km over the plateau, while in summer, the first elevated inversion increases to 4 to 5 km over the plateau (Cosijin, 1996).

The three stable layers (700 hPa, 500 hPa and 300 hPa) trap pollutants. The 500 hPa layer is the most persistent and sometimes prevails with no disruptions. However, the 700 hPa layer is not persistent and gets disrupted on a weekly basis by the passage of frontal disturbance due to the vertical mixing of particles and gases to the 500 hPa layer (Cosijin, 1996; Cosijin and Tyson, 1996). Freiman and Tyson (2000) indicated that the 500 hPa layer plays a role in the dispersion of pollutants in the country. Additionally, the ~ 300 hPa stable layer is different from the other layers because it is lowest in summer and highest in winter. This layer plays a role in seasonal variation in height because of the constant presence of inversion layers. The occurrence of these stable layers is not affected by circulation variations because the main type of circulation in the country is anticyclonic.

Recirculation also plays a role in moving pollutants. In South Africa, it occurs often as a result of anticyclonic circulations, which are frequent in the country (Garstang et al., 1996; Freiman and Piketh, 2003). Additionally, this type of transportation is limited to layers below 200 hPa (Tyson et al., 1996a) and can occur at any scale (at both the regional and continental level) (Tyson and Preston-Whyte, 2000; Freiman and Piketh, 2003). Direct transportation or recirculation plays a role in exiting 75% of the air circulation from this country into the Indian Ocean, but little of the transportation takes place to the Atlantic Ocean (Tyson and Gatebe, 2001). In addition to the above, Garstang et al., (1996) stated that the transportation of trace gases and particulates are controlled by the following factors:

- The position of the downward limb of the Walker circulation;
- The easterly waves of the Southern African subcontinent; and,
- The westerly waves in the mid-latitudes.

The photochemistry of an area can be affected by the long-range transportation and recirculation of trace gases and particulates in the air (Freiman and Piketh, 2003). Garstang et al., (1996) stated that pollutants are recirculated in the subcontinent for days after they have been released from the source. Industry and biomass are the main sources of transboundary pollution, thus resulting in authorities facing the challenge of air pollution being transported outside the country's borders.

2.4 Deposition

There has been great concern about the deposition of acidifying pollutants on the natural environment globally. Human-induced activities have increased the concentrations of trace gases such as SO_2 and NO_x, as well as PM in the atmosphere. These pollutants are removed from the atmosphere by three processes: chemical transformation, dry deposition and wet deposition. However, the deposition of acidifying pollutants can pose a potential threat to the natural resources, terrestrial and aquatic ecosystems, and building materials. Examples of impacts resulting from the deposition of acidifying pollutants are biodiversity loss, eutrophication and the acidification of lakes, streams and rivers (Rodhe et al., 2002; Bobbink et al., 2010; Flechard et al., 2011; Liu et al., 2013a; Adon et al., 2013). The deposition of acidifying pollutants such as NO_x and SO_2 adds reactive nitrogen (N) and sulphur (S) to the ecosystem (soil, water and vegetation) (Nowlan et al., 2014). This process has been regarded as the main source of nitrogen deposited on terrestrial and aquatic ecosystems compared to biological nitrogen fixation (Holland et al., 1999).

Dry deposition can be defined as a process through which pollutants are removed from the atmosphere in the absence of rainfall. The dry deposition of pollutants is governed by atmospheric turbulence, chemical and physical properties of depositing species, and the ability of the surface to absorb or capture deposited pollutants (Erisman and Draaijers 1995; Seinfeld and Pandis, 1998). The transportation of pollutants from the atmosphere to the earth's surface is mainly controlled by turbulence, which is dependent on buoyancy, as well as wind shear (Erisman and Draaijers, 1995). The rate at which pollutants are transported to the surface is controlled by turbulence, but the solubility and chemical reactivity of the trace gases

affects the surface uptake, while vegetation is one of the natural surfaces that promote dry deposition (Seinfeld and Pandis, 1998).

Several studies have confirmed that NO_x has a low solubility in water (Asman et al., 1998; Seinfeld and Pandis, 1998; Wesely and Hicks, 2000), but Watt et al., (2004) indicated that although NO_x is emitted as NO, in terms of deposition, its main pathway is in the form of NO_2. Additionally, gases such as SO_2, which are more soluble, but less reactive, are absorbed through the stomata and leaf cuticle of the vegetation on which they are deposited (Grennfelt, 1987). These pollutants can be absorbed at the surface of the leaf, as well as by the soil (Hicks et al., 1988).

2.5 Measuring dry deposition

There are different methods or techniques that have been utilised to measure dry deposition (Businger, 1986). Dry deposition can be measured directly or indirectly (Seinfeld and Pandis, 1998). Indirect methods determine flux by measuring secondary quantities, which include average concentrations or the vertical gradients of the average concentrations of the depositing pollutant. These secondary quantities are related to flux. However, direct methods require more effort as they need sophisticated instruments and infrastructure. Direct methods; to measure deposition, include micro-meteorological methods, surface accumulation methods, throughfall and watershed mass balance.

2.5.1 Micro-meteorological techniques

Micro-meteorological techniques (using local meteorology for deposition flux estimation) are ideal for determining the dry deposition of gaseous pollutants. An example of this methodology is eddy correlation, whereby deposition flux is determined from the measured vertical component of the wind velocity and concentration of the pollutant. The gradient method is another example of micro-meteorology whereby deposition flux is determined from concentrations of the depositing gas at two or more heights. Hicks (1986) indicated that measuring these

concentrations at different heights is very difficult because accuracy is needed to derive the deposition flux of the gases.

The advantage of the micro-meteorology technique is that it allows for the continuous measurement of flux. These measurements are done above the surface. However, the limitation of this methodology is that the measured flux values cannot be extrapolated to larger areas because the measurement must be in the constant flux layer limited between five and ten metres above the vegetation. Furthermore, with this technique, it is difficult to determine flux in a terrain that is complex or close to the source of the pollutants, because the flux layer is not well developed. Developing a constant flux layer is challenging, as the atmosphere above the surface should have no sources or sinks. The presence of sources and sinks in the atmosphere above the surface could result in rapid chemical reactions. Additionally, there should not be significant differences in pollutant concentrations with time (Hicks et al., 1987; Baldocchi et al., 1988). Thus, these results in micro-meteorological techniques are not suitable for routine applications. Therefore, the applicability of this technique is in studying deposition processes, as well as validating other measurement methods and models. Even though this type of technique has been used in South Africa there is no published literature on this technique.

2.5.2 Surface accumulation techniques

Surface accumulation techniques involve measuring deposition to natural surfaces (using throughfall technique) or surrogate surfaces (using fallout buckets). These techniques are used to quantify the deposition of large particles, in which collection vessels intercept particles before they reach the surface. However, the limitation of this technique is that the collection surfaces do not simulate vegetation. In addition to the above surface accumulation techniques, microscope counting, stomatal conductance and the wind tunnel are other techniques of surface accumulation techniques. Below are two examples of surface accumulation techniques.

2.5.2.1 Throughfall techniques

In order to estimate deposition, this technique makes use of water dripping from vegetation canopies, as well as stem flow down tree trunks. Rainfall washes away material deposited on the canopy and the net throughfall flux of the ion below the canopy provide information on dry deposition (Beir et al., 1992). The advantage of this technique is that it is considered affordable, and less effort is required. It also provides long-term average flux values and total deposition (wet and dry deposition combined). The limitation of this technique is that it does not differentiate between gas and particle deposition, and direct dry deposition to the floor forest is not measured (Lindberg et al., 1986). This technique has been used in South Africa by Olbrich and Du Toit (1993) to quantify canopy fall in commercial forests on the Mpumalanga escarpment.

2.5.2.2 Surrogate surfaces

The technique of surrogate surfaces is utilised when the surface characteristics are not taken into account. This is used more specifically for particles than gases. This technique makes use of filter substrates to collect deposited material. It is dependent on the presence of aerodynamic resistance (R_a) (Seinfeld and Pandis, 1998).

In comparing the two techniques above, surface accumulation techniques give deposition fluxes on a spatial scale, which is representative of the foliage or surrogate surface element. Micrometeorological methods yield data that represent flux at a larger spatial scale compared to the surface accumulation technique. In general, micrometeorological techniques often accomplish the criteria of no variation, in comparison to surface accumulation methods that meet the criterion of the representativeness of the surrounding area.

2.6 Dry deposition modelling

2.6.1 Examples of dry deposition models

It is important that models are developed and used for dry deposition estimation, due to the fact that it is challenging to make direct measurements (Brook and Padro, 1995). Atmospheric deposition models are essential because they can be used to summarise current conditions, identify management options, extrapolate spatial or temporal deficiencies in a monitoring programme, and predict changes in deposition due to economic growth and regulatory changes.

Deposition velocities of pollutants, when extrapolated to larger areas, yield errors, especially in areas with complex terrain, because deposition velocities are site-specific. However, atmospheric models at regional levels and chemistry models have been used to determine flux. For example, two studies made use of the one-layer trajectory model to predict concentrations of SO_2 and sulphate, and deposition velocities of 0.8 cm/s and 0.2 cm/s were assumed in order to calculate dry deposition flux in Scandinavia and Europe (Eliassen, 1977; Eliassen and Saltbones, 1983). Another model, the Acid Deposition and Oxidant Model (ADOM) was developed in North America and funded by the governments of Canada, Ontario and Germany, as well as the Electric Power Research Institute. This model uses grid average meteorology data as an input. The outputs of this model are grid-averaged deposition velocities. These deposition velocities were calculated for each land-use type and averaged arithmetically to give the yield grid-averaged deposition velocity of each pollutant.

Additionally, the Swedish Meteorological and Hydrological Institute (SMHI) developed a model called the Multi-scale Atmospheric Transport and Chemistry (MATCH) model, which assists in estimating dry deposition flux if direct measurements are not available (Robertson et al., 1999). This model is a three dimensional model to determine horizontal and vertical transportation, vertical dilution, dry deposition, wet deposition and chemical transformations. The inputs of the model required to understand the transportation and chemical transformation of pollutants are emissions and meteorology. In order to estimate dry deposition flux,

the estimated pollutant concentration is used together with assumed deposition velocities from literature. This model was utilised successfully in Sweden (e.g. Langner et al, 1995), Asia (e.g. Robertson et al., 1995) and over the continents of Africa (Zunckel et al., 2000) and South America (e.g. Robertson, 1996).

2.6.2 Inferential technique

The inferential technique is another direct technique, according to Hicks et al., (1987). Understanding the processes involved in dry deposition can help to estimate dry deposition flux from routinely measured pollutant concentrations, as well as meteorological parameters. Flux is calculated as the product of deposition velocity and pollutant concentrations. Dry deposition velocity can be estimated by utilising a multiple-resistance transfer model. There are three resistances (aerodynamic, near surface (quasi-laminar) and surface resistance) responsible for transferring deposition material to the earth's surface. They act parallel to each other.

This technique has been employed in many studies conducted at international and national level to estimate dry deposition (e.g. Meyers and Yeun, 1987; Meyers et al., 1991; Matt and Meyers, 1993; Zunckel et al., 1996; Zunckel et al.,1999; Zunckel et al., 2000). For example Meyers et al., (1991) used this model in the USA to determine nitrogen deposition. They found that dry deposition contributed between 30 and 50% of total nitrogen deposition in the eastern USA. This model was also used in Switzerland where it was shown that dry deposition was higher than wet deposition (Hesterberg et al., 1996). In the Czech Republic, 61% of total nitrogen deposition in the region was attributed to dry deposition (Zapletal, 1998). In South Africa, it was used in the heavily industrialised area of Mpumalanga and has not yet been applied to other industrial areas of the country (for example, Lephalale, Rustenburg and Tubatse). Therefore, it is important that this technique is applied in other industrial areas, since they are becoming heavily industrialised and will also have deposition of pollutants, which are harmful to the environment. It is important to estimate the dry deposition rates of these harmful pollutants. Several deposition studies that have been undertaken in the Highveld Priority Area in South Africa have highlighted that dry deposition is possibly more significant in South Africa than wet

deposition (Wells, 1989; Turner, 1993; Wells, 1993). The reason is that the South African climate in the interior is mostly arid and these areas do not receive much rainfall. These conditions make it important to estimate the dry deposition rates of chemical species (SO_2 and NO_x).

In the current study, an inferential model was used to estimate dry deposition velocity and flux. Many studies have highlighted inferential modelling as the best technique to determine the dry deposition of acidifying species because they are difficult to measure (Hicks et al., 1987; Wesley, 1989; Meyers et al., 1991; Zunckel et al., 1996; Zunckel, 1998; Brook et al., 1997; Mphepya et al., 2004; Ferguson, 2009; Held and Mphepya, 2000; Josipovic, 2009; Josipovic et al., 2011). Furthermore, this model was selected because it makes use of routinely measured air concentrations, meteorology and permits for the consideration of site-specific characteristics.

2.6.2.1 Examples of dry deposition studies in the Highveld Priority Area, South Africa, using the inferential technique

A number of studies have been conducted in South Africa to understand the dry and wet deposition of NO_x and SO_2 (for example, Piketh and Annegarn, 1994; Zunckel et al., 1996; Zunckel, 1999; Zunckel et al., 1999; Zunckel et al., 2000; Mphepya et al., 2004; Scorgie and Kornelius, 2009a; Scorgie and Kornelius, 2009b; Josipovic et al., 2011). These studies are important because they were done in areas which have similar climatic conditions as Lephalale. Studies on dry deposition in the Highveld Priority Area were conducted in response to rising concerns regarding an increase in emissions from industries and their impacts on the terrestrial and aquatic ecosystem (Scorgie and Kornelius, 2009b). Most of these studies were conducted in the Highveld Priority Area in Mpumalanga, because the area is highly industrialised and most of the country's coal fired power stations are situated in this area. A few studies have also been done in the Free State, Gauteng (Scorgie and Kornelius, 2009) and Limpopo (Louis Trichardt) (Mphepya, 2002). Wells et al., (1996) highlighted the fact that the Highveld Priority Area was given much attention because it was responsible for 90% of the scheduled emission of pollutants such as SO_2, NO_x and particulates in

South Africa in 1993 (Table 2.2). Additionally, the fact that this country is semi-arid highlights the importance of dry deposition in South Africa.

Table 2.2: Scheduled emissions from South Africa and the Highveld industrial region (metrics tonnes per year) in 1993.

Pollutant	South Africa	Highveld Industrial region	Percentage of total
Particulates	331 339	285 405	86
SO_2	2 120 452	1986 193	94
NO_x	1 004 716	913 486	91

Source: Wells et al., 1996

In South Africa, this inferential model was used for the first time by Zunckel et al., (1996) at Elandsfontein, central Mpumalanga. This study found the total dry deposition of sulphur to be 13.9 kg S ha^{-1} yr^{-1}. Similarly, Zunckel (1999) used an inferential model to understand the dry deposition of SO_2 in three climatic regions in Mpumalanga. The study utilised air quality and meteorological data collected at Elandsfontein and Palmer from June 1996 to May 1997. Similar data were collected at Blyde and Skukuza. The total dry deposition flux observed in Elandsfontein was 13 kg S ha^{-1} yr^{-1}, with Palmer having 3.1 kg S ha^{-1} yr^{-1}, while 3.9 kg S ha^{-1} $yr^{-1}$and 3.1 kg S ha^{-1} yr^{-1}were observed for Skukuza and Blyde, respectively (Figure 2.2). Seasonal variation of flux was observed, but it was not strong. The highest flux was recorded in summer and the lowest was recorded in winter for Elandsfontein and Palmer (Figure 2.2). Maximum fluxes were recorded in winter, with summer having the minimum. Additionally, Zunckel et al., (1999) did a similar study to the above in a remote rural site on the south-eastern escarpment (Ben MacDhui Mountain located in the Eastern Cape near Lesotho and the Drakensberg). This study reported an annual dry deposition flux of sulphur as 1.1 kg S ha^{-1} yr^{-1}. This deposition flux was attributed to the regional transportation of gases in South Africa.

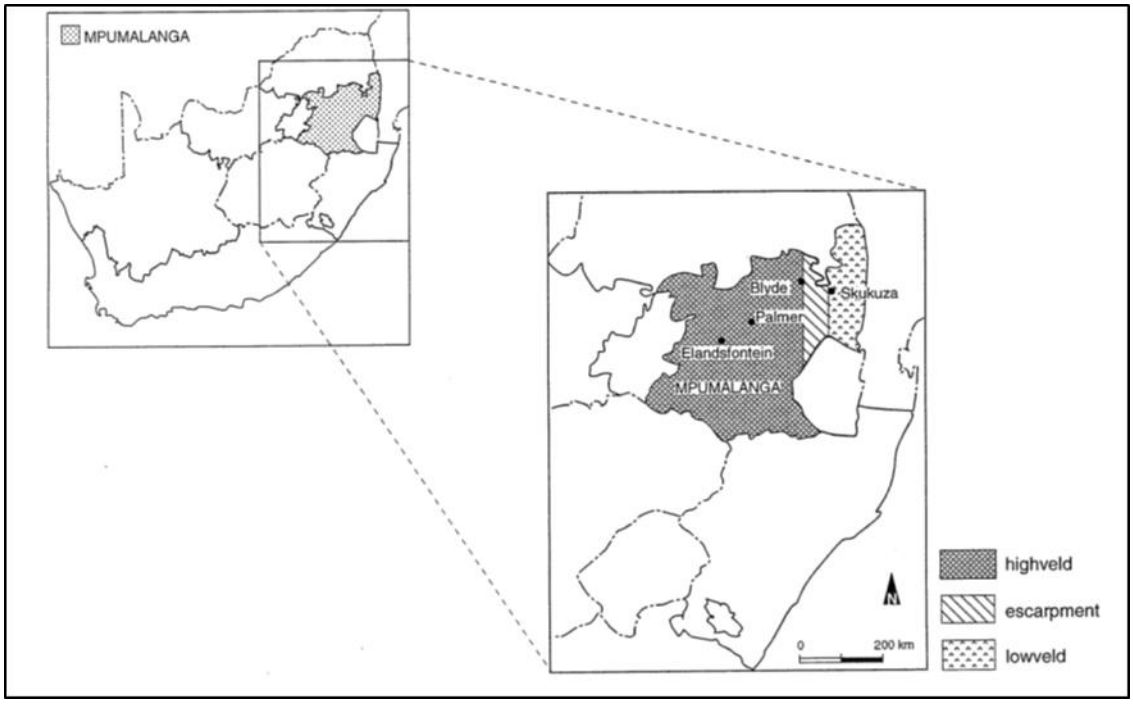


Figure 2.2: Location of air quality monitoring stations in Mpumalanga (Zunckel et al., 2000).

Zunckel et al., (2000) used the inferential model and the MATCH model to understand the dry deposition of SO_2 in the Highveld, as well to see if they yielded different results. Regardless of the differences in the modelling approach, the dry deposition results from MATCH agreed with those of the inferential model. In this study, a dry deposition flux greater than 10 kg S ha^{-1} $yr^{-1}$was observed in the central Highveld. Furthermore, Scorgie and Kornelius (2009) also did their study in the Highveld Priority Area, as well as in Gauteng and the Free State. They calculated annual dry deposition of SO_2 to be above kg S ha^{-1} yr^{-1}in most parts of the Highveld. However, the central Highveld had the highest deposition flux of kg S ha^{-1} yr^{-1}. This study indicated that the high increase NO_x concentrations, over the three decades, are responsible for elevated nitrogen deposition in the central Highveld.

Josipovic et al., (2011) conducted a dry deposition study in the Highveld Priority Area to understand the acidic atmospheric pollution deposition of SO_2 and NO_x. This study collected data of NO_2 and SO_2 from August 2005 to September 2007 at 37 passive monitoring sites. However, this study did not estimate the dry deposition velocities of NO_2 and SO_2. Rather it used the deposition velocities of 1996–1998, which were estimated by Mphepya (2002). The deposition velocities used by Josipovic et al.,

(2011) are presented below in Table 2.3. The study of Josipovic et al., (2011) mostly focused on critical loads resulting from the deposition of NO_2 and SO_2. Critical loads can be defined as “a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” (United Nations Economic Commission for Europe,1988). It has also been discovered from this study that some parts of the Highveld are experiencing critical load exceedances, while those downwind of the source indicate low levels of critical load exceedances. Exceedances of these critical loads imply that the ecosystems are at risk.

Table 2.3: Daily and nocturnal seasonal dry deposition velocities (cm/s) of SO_2 and NO_2 in Palmer and Elandsfontein for the period 1996–1998 (Mphepya, 2002) as applied by Josipovic et al., (2011).

Pollutant	Station	Autumn		Winter		Spring		Summer	
		Day	Night	Day	Night	Day	Night	Day	Night
SO_2	Palmer	0.26	0.12	0.14	0.1	0.24	0.12	0.37	0.15
	Elandsfontein	0.26	0.12	0.15	0.1	0.22	0.11	0.35	0.15
NO_2	Palmer	0.13	0.04	0.05	0.04	0.12	0.04	0.24	0.08
	Elandsfontein	0.14	0.1	0.05	0.04	0.1	0.05	0.26	0.08

Collet et al., (2010) studied the atmospheric nitrogen budget in the Highveld Priority Area. The study was done for the period 2005–2006, and made use of deposition velocities from literature. The deposition velocity of NO and NO_2 taken from literature varied from 0-1.5 cm/s, while NO_3 had deposition velocities between 0.12 and 1.2 cm/s. This study reported that the dry deposition flux of NO, NO_2 and NO_3 was at its peak in winter. This was attributed to atmospheric stability causing higher concentrations to be obtained during this season. Additionally, the annual dry deposition flux of nitrogen in the Highveld was between 6.7 kg N ha^{-1} $yr^{-1}$and 13.1 kg Nha^{-1} yr^{-1}. It was also stated that these deposition flux amounts do not pose a threat to the environment in Mpumalanga, but power generation contributed about 4 to 15% of the nitrogen emissions and the remainder was advected out of the region. The deposition fluxes found in this study are lower than those found by Josipovic et al., (2011) and this could be due to the use of different deposition velocities when calculating flux.

2.7 Environmental impacts of SO_2 and NO_X deposition

SO_2 and NO_x emitted into the atmosphere undergo physical and chemical transformation, which eventually leads to acid deposition. Environmental impacts because of acid rain (resulting from the deposition of trace gases of SO_2 and NO_x) remain a worrying factor in both developing and developed countries (Josipovic et al., 2011). The Waterberg district in South Africa is no different from other areas all over the world that have concerns about acid deposition due to emissions from industries. This area has been declared an air quality Priority Area. The expected increase in industrial activities makes it more vulnerable to poor air quality in the future. Therefore, it is important to estimate and understand the current deposition rates of chemical species such as NO_x and SO_2. This will aid relevant stakeholders to understand the likely impacts of acid deposition on ecological systems. Additionally, according to DEA (2014), there is a poor understanding of the ecological impacts of the deposition of chemical species such as SO_2 and NO_x in the Waterberg Priority Area in general. However, scientific studies on acid deposition are yet to be done to understand these impacts. This makes it important for this study to

estimate the deposition rates of acid-forming chemical species such as NO_x and SO_2.

2.7.1 Nitrogen oxides

Nitrogen oxides is the generic term used to describe the sum of NO and NO_2. These nitrogen oxides are released into the troposphere (Atkinson, 2000), but NO_x has an atmospheric lifetime of about a day in the lower atmosphere (McElroy, 2002). The formation of NO_x occurs under high temperature combustion (Beirle, 2004; Horri et al., 2006; Ma, 2010). NO is the primary pollutant that is emitted directly into the atmosphere. It is formed by the reaction between N_2 and O_2. NO_2 forms as result of the reaction between NO and O_2.

NO_x plays a major role in the formation of ozone and smog (Levine et al., 1996; Atkinson, 2000; Fan et al., 2010). Ozone is formed as a result of photolysis in the presence of NO_2 and NO available in the atmosphere. This process usually occurs during the day in the presence of sunlight, which is needed to break the bonds of NO and NO_2. Sources of NO_x include soils, motor vehicles, industries (power stations), aircrafts, biomass burning, fossil fuel burning and lightning (WMO, 1994; Atkinson, 2000; Leue et al., 2001; Horri et al., 2005). Environmental impacts of NO_x include vegetation mutations and biological imbalances, and can hamper the growth of plants, and cause loss of biodiversity, corrosion of material and eutrophication (Bobbink et al., 1998; Rodhe et al., 2002; Liu et al., 2013a). In addition, NO_x affects visibility. This results in decreases in regional air quality (Fenger, 2002; Mauzerall et al., 2005). NO_x also takes part in the formation of tropospheric ozone, which itself is an air pollutant (Levine et al., 1996; Atkinson, 2000). Thus, increases in NO_x concentrations can lead to highly elevated tropospheric ozone concentrations (Munger et al., 1998). Examples of ozone impacts include plant growth and productivity reduction and reduction in plant photosynthesis (Felzer, et al., 2007; Karnosky et al., 2007).

2.7.2 Sulphur dioxide

SO_2 is a non-stable gas. As a result, the highest concentrations of SO_2 coincide with sources of emissions, reducing with increasing distance downwind. Subsequently, after SO_2 has been released, it can be converted into sulphate via the process of oxidation (Pham et al., 1996; Hewit, 2000). SO_2 can be oxidised to sulphate via several process, such as gas phase, photochemical and radical processes, aqueous processes and heterogeneous process (Pienaar and Helas, 1996). The oxidation rate of SO_2 decides the lifetime of the pollutant (Khoder, 2002). The rate of the abovementioned removal processes, combined with the rate of SO_2 emissions, determines the residence time of SO_2 in the atmosphere. This ranges from about two to eight days (Katz, 1977). Hidy (1994) gives residence times of SO_2 in the lower atmosphere as one to three days. The general environmental impacts of acid rain resulting from oxidation and dissolution of SO_2 to form sulphuric acid (H_2SO_4) include damage to vegetation, soil, animals (especially in aquatic ecosystems, such as fish and insects), monuments and drinking water (Zunckel et al., 2000; Wang et al., 2003; Collett et al., 2010; Josipovic et al., 2011, Nowlan et al., 2014)

With all these impacts on the environment, it is vital to investigate the impacts of these pollutants in areas that are highly industrialised, as well as those on the verge of industrialisation. It is important to get a broader idea of exactly what is happening in these areas in terms of deposition. This will assist in minimising the impact of pollutants, and will aid in achieving sustainable development by mitigating the impact of pollutants on the environment.

CHAPTER 3: DATA AND METHODS

The chapter provides information on the study area, data and methods used in the study.

3.1 Study area

The north-western part of the Waterberg District Municipality is the home of Lephalale (see Figure 3.1 below) in Limpopo, South Africa. The Waterberg district is situated in the western part of Limpopo and is considered the largest district in the province. It covers 49 504 km^2 of land and has an estimated population of 622 734 (StatsSA, 2011). This region is considered to be one of the areas with the largest platinum reserves (the Bushveld complex) in the country. Lephalale is also located 40 km from Botswana border and about 280 km from Pretoria. It experiences a summer rainfall with an annual average rainfall between 350 and 400 mm, with summer temperatures around 32 °C and winter temperatures about 21 $^{\circ}$C.

Lephalale contributes about 59.21% of the gross domestic product (GDP) to the mining sector in the district. However, on the national GDP, electricity from this area adds 11.33%, while on district level, it contributes 69.65%. Sectors such as agriculture and manufacturing also contribute to the GDP of the district.

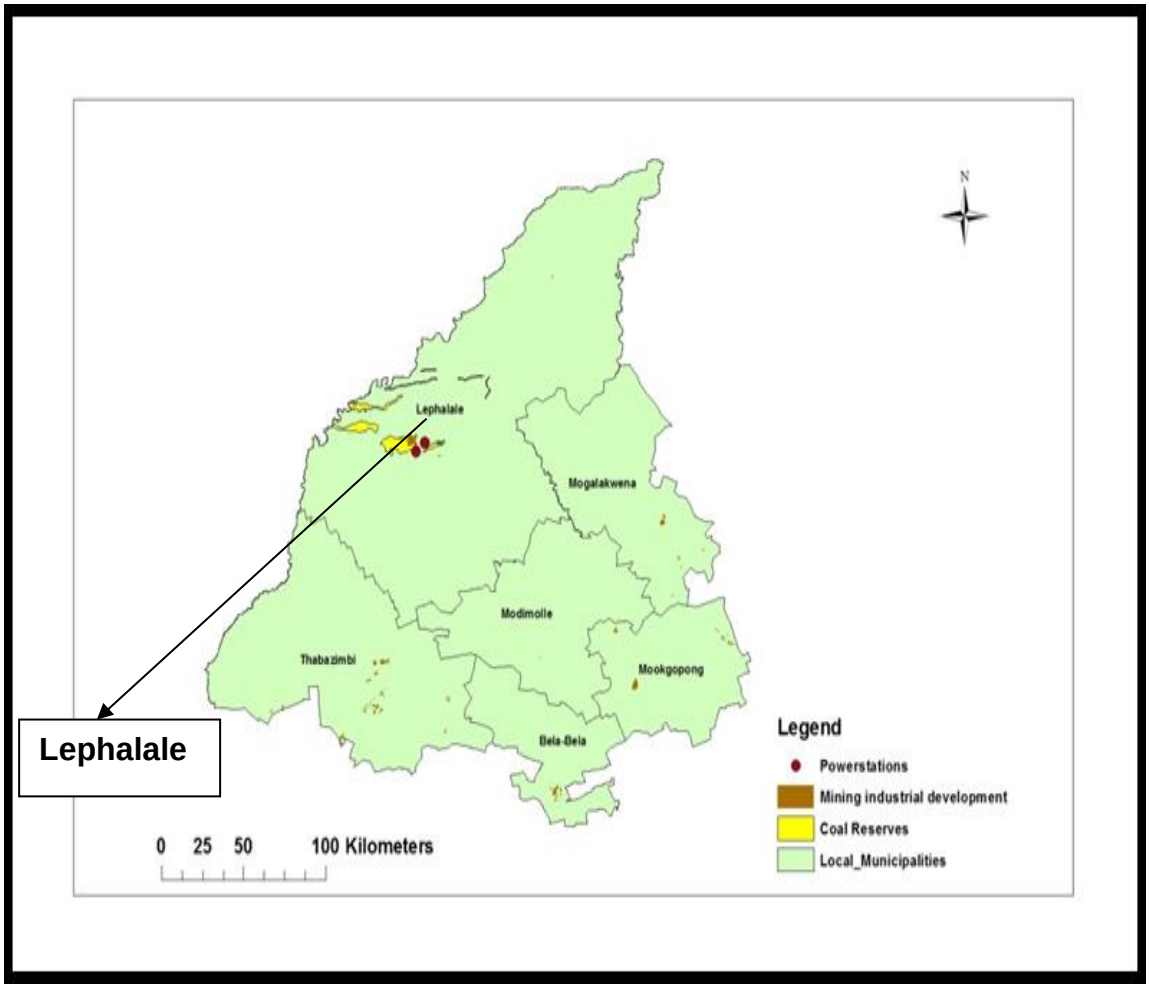


Figure 3.1: A map showing the Waterberg district with its local municipalities, coal reserves and power stations.

3.2 Data and methods

3.2.1 Data requirements for inferential model

In this study, flux values of dry deposition were calculated using the inferential method, which infers deposition to the surface by deriving deposition velocity from meteorological data and uses measured concentrations. The meteorological parameters used for the prediction of deposition velocity are the standard deviation of wind direction (σ_θ), ambient temperature, humidity, solar radiation and rainfall. A set of five years of data (2008–2012) for the parameters SO_2 and NO_x, and the abovementioned meteorological data were used to calculate the dry deposition flux at Marapong. Details of the source of the meteorological data used at the Marapong station to do this modelling are provided below in Table 3.1.

Table 3.1: Hourly data used at the Marapong station for dry deposition modelling.

Parameters	2008	2009	2010	2011	2012
Temperature	X[1]	X	X	X	X
Wind speed	Marapong[2]	Marapong	Marapong	Marapong	Marapong
Wind direction	Marapong	Marapong	Marapong	Marapong	Marapong
Humidity	Marapong	2008 and 2010[3]	Marapong	2008 and 2010	2008 and 2010
Solar radiation	Model[4]	Model[5]	Model	Model	Model
Rainfall	Lephalale[6]	Lephalale	Lephalale	Lephalale	Lephalale

The inferential model is Excel-based and was created by the National Oceanic and Atmospheric Administration (NOAA). It was first used in the USA in 1984 (Hales et al., 1987; Hicks et al., 1991). The limitations of this model include the following (Brook et al., 1997):

- Complex terrain results in uncertainty when deposition velocities are extrapolated to larger areas than represented by the site.
- There is limited information or knowledge about realistic modelling of vegetation behaviour with regard to water and heat stress.
- Another limitation is that initially the study planned to estimate dry deposition rates at Lephalale in the Waterberg-Bojanala Priority Area, as it was initially believed that there were multiple monitoring stations. However, this is a single-point model. Therefore, deposition velocities observed in this study cannot be extrapolated to other stations. Marapong was the only station used to estimate dry deposition. The reader must interpret the results with caution

[1] X means missing data were generated using linear regression from data measured in Lephalale of Lephalale station see section 3.2.2.1 below

Marapong means Marapong data were used for that specific year

[3] means humidity data from 2008 and 2010 were used for that specific year

[4] Model means modelled CCAM data

[5] Lephalale means data from Lephalale station

because only one station was used to estimate the dry deposition rates and this may not give a good representation of the deposition rates across Lephalale.

3.2.2 Ambient air quality and meteorology data

Adequate air quality and meteorological monitoring information in the Waterberg District Municipality is limited. This makes it difficult to quantify the current state of air quality and deposition in the district, as well as surrounding areas (Walton and Ngcukana, 2009). However, Eskom (Matimba power station) has done some ambient air quality and meteorological monitoring campaigns since 1984 around Lephalale (see Figure 3.2) (Walton and Ngcukana, 2009; Singleton, 2010). Eskom conducted these campaigns to understand the impact of the Matimba power station in Lephalale. Table 3.2 displays all the monitoring stations, meteorological data and periods for which Eskom monitored ambient air concentrations. Table 3.2 also shows the pollutants of interest in this current study, which were collected during these campaigns, as well as their averaging period. The aforementioned monitoring stations were also moved around the area. The Zwartwater monitoring station monitored data from 2001 until 2003 (Singleton, 2010). This station was first moved to Groostryd and then relocated to Marapong as result of environmental authorisation conditions given to the new power station (Medupi). Currently, one of these campaigns turned into a permanent monitoring station (Marapong), but there are no longer-term data from a single site, or multiple concurrent sites to compare. These campaigns and the current monitoring station mostly collected the following continuous data: SO_2, PM, CO_2, ozone (O_3), NO_2, NO, NO_x, wind speed, wind direction, humidity and temperature, although there are also some data for mercury (Hg) and hydrogen sulphide (H_2S).

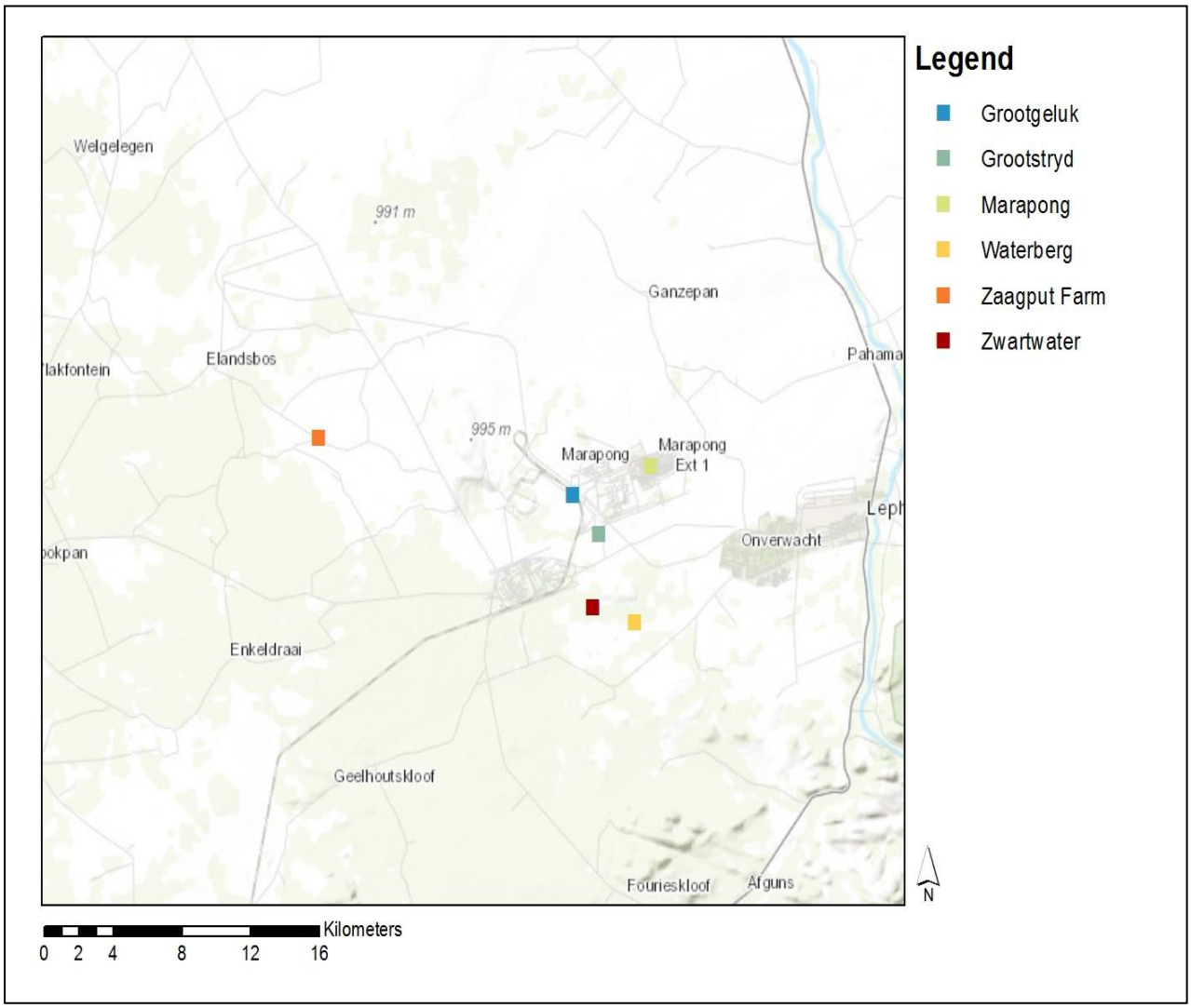


Figure 3.2: Location of Eskom monitoring campaigns and Marapong station in Lephalale.

Table 3.2: Air quality and meteorological data monitoring stations and the period the measurements were taken (note that there are no overlaps).

Station name	Measured hourly meteorological data	Measured hourly air quality data for SO_2 and NO_x	Years
Marapong	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	2006–2013
Groostryd	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	2003–2006
Zwartwater	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	2001–2003
Zagput	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	2000–2001
Grootegeluk	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	2000
Waterberg substation	Wind speed, wind direction, Temperature humidity	SO_2,NO,NO_2 and NO_x	1984–1992

These stations are operated according to United States Environmental Protection Agency (USEPA) standards (Muthige, 2013) and have been accredited by the South African National Accreditation System (SANAS) (Singleton, 2010). The image in Figure 3.3 depicts a typical example of Eskom's air quality monitoring station, indicating analysers for different pollutants.

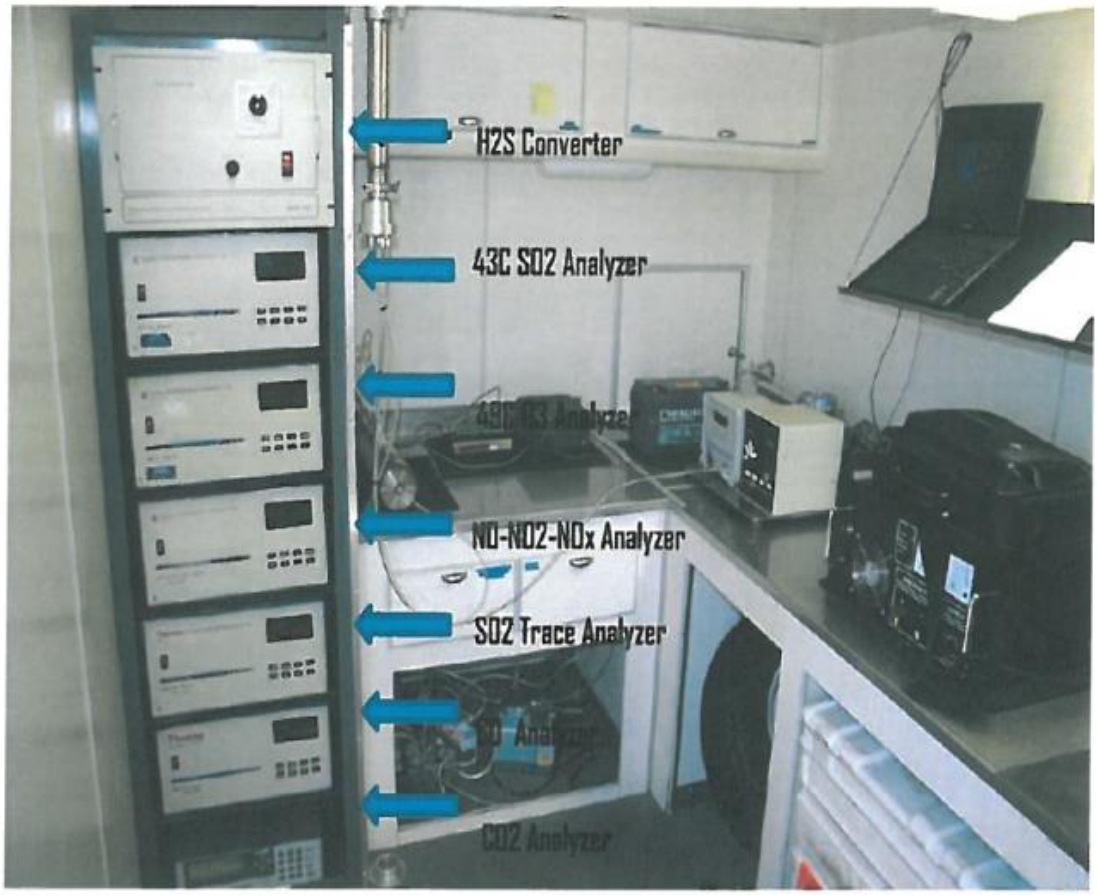


Figure 3.3: Example of an air quality monitoring station at Eskom (Muthige, 2013).

During the past two years, the DEA started collecting air quality and meteorological data in the district (in Lephalale, Thabazimbi and Mokopane). Since it has been expected that the air quality of the area is likely to deteriorate because of additional industrial activities, additional monitoring campaigns are being undertaken by organisations such as Grootegeluk mine.

In this study, the ambient air quality parameters that were considered are SO_2 and NO_x. This study selected Marapong as the appropriate station for the study area. One reason is because of its longer record of data, which is critical to assess trends and do atmospheric modelling (Ministry for the Environment, 2009). These data also show a good completeness; hence this will help in investigating on how the pollutants studied (SO_2 and NO_x) changed over the selected period.

3.2.2.1 Available and unavailable meteorological data at Marapong station

Excellent data availability is essential in doing dry deposition modelling because insufficient data can have a significant effect on the conclusions that can be drawn from the data. Furthermore, it is essential that a data set is complete during modeling because, gaps in data preclude the accurate calculation of seasonal or annual ambient concentrations and deposition flux. If a data set is not complete seasonal or annual summary statistics can be affected by gaps that increase the influence of non-missing data in the calculation. This is important because deposition varies over time (Hicks et al., 1993). For example, if there is a single high or low sample in a season with many data gaps the seasonal average could be skewed higher or lower as a result of that low or high sample. In order to account for this variability, missing data should be estimated. Different statistical methods can be used to estimate the missing data provided there are neighbouring stations which can be used to estimate these data. This procedure involves doing a linear correlation between the station with missing data and neighbouring stations to determine if there is any relationship. If a strong relationship exists between the station with missing data and one of the neighbouring stations, then that neighbouring station would be used as a proxy for the station with missing data and linear regressing modeling would be used to estimate the missing data.

Marapong station did not have all the meteorological data needed for modelling dry deposition, specifically solar radiation, rainfall and humidity. Therefore, additional surface hourly meteorological data for this study were obtained from the South African Weather Service (SAWS) and the Agricultural Research Council (ARC) stations (Lephalale and Werkendam, respectively) for the period 2007–2012. Table 3.3 below shows the available meteorological data at Marapong for the period 2007–2012. However, 2007 did not have meteorological data, while 2009, 2011 and 2012 did not have relative humidity data. Additionally, rainfall was completely unavailable at Marapong station.

Table 3.3: Available and unavailable Meteorological data at Marapong station for the period 2007–2012 (note that "Yes" means available data and "No" means no data).

Parameters	2007	2008	2009	2010	2011	2012
Temperature	No	Yes	Yes	Yes	Yes	Yes
Wind speed	No	Yes	Yes	Yes	Yes	Yes
Wind direction	No	Yes	Yes	Yes	Yes	Yes
Relative Humidity	No	Yes	No	Yes	No	No
Solar radiation	No	No	No	No	No	No
Rainfall	No	No	No	No	No	No

The SAWS and ARC stations are ~8 km (Lephalale) and ~14 km (Werkendam) from the Marapong air quality monitoring station respectively (Figure 3.4). Table 3.4 and Table 3.5 show all the available and unavailable meteorological data for these two monitoring stations.

Table 3.4: Meteorological data available at Lephalale meteorological station (note that "Yes" means available data and "No" means no data).

Meteorological parameters	2007	2008	2009	2010	2011	2012
Temperature	Yes	Yes	Yes	Yes	Yes	Yes
Wind speed	Yes	Yes	Yes	Yes	Yes	Yes
Wind direction	Yes	Yes	Yes	Yes	Yes	Yes
Relative Humidity	Yes	Yes	Yes	Yes	Yes	Yes
Solar radiation	No	No	No	No	No	No
Rainfall	Yes	Yes	Yes	Yes	Yes	Yes

Table 3.5: Meteorological data available at Werkendam meteorological station (note that "Yes" means available data).

Meteorological parameters	2007	2008	2009	2010	2011	2012
Temperature	Yes	Yes	Yes	Yes	Yes	Yes
Wind speed	Yes	Yes	Yes	Yes	Yes	Yes
Wind direction	Yes	Yes	Yes	Yes	Yes	Yes
Relative Humidity	Yes	Yes	Yes	Yes	Yes	Yes
Solar radiation	Yes	Yes	Yes	Yes	Yes	Yes
Rainfall	Yes	Yes	Yes	Yes	Yes	Yes

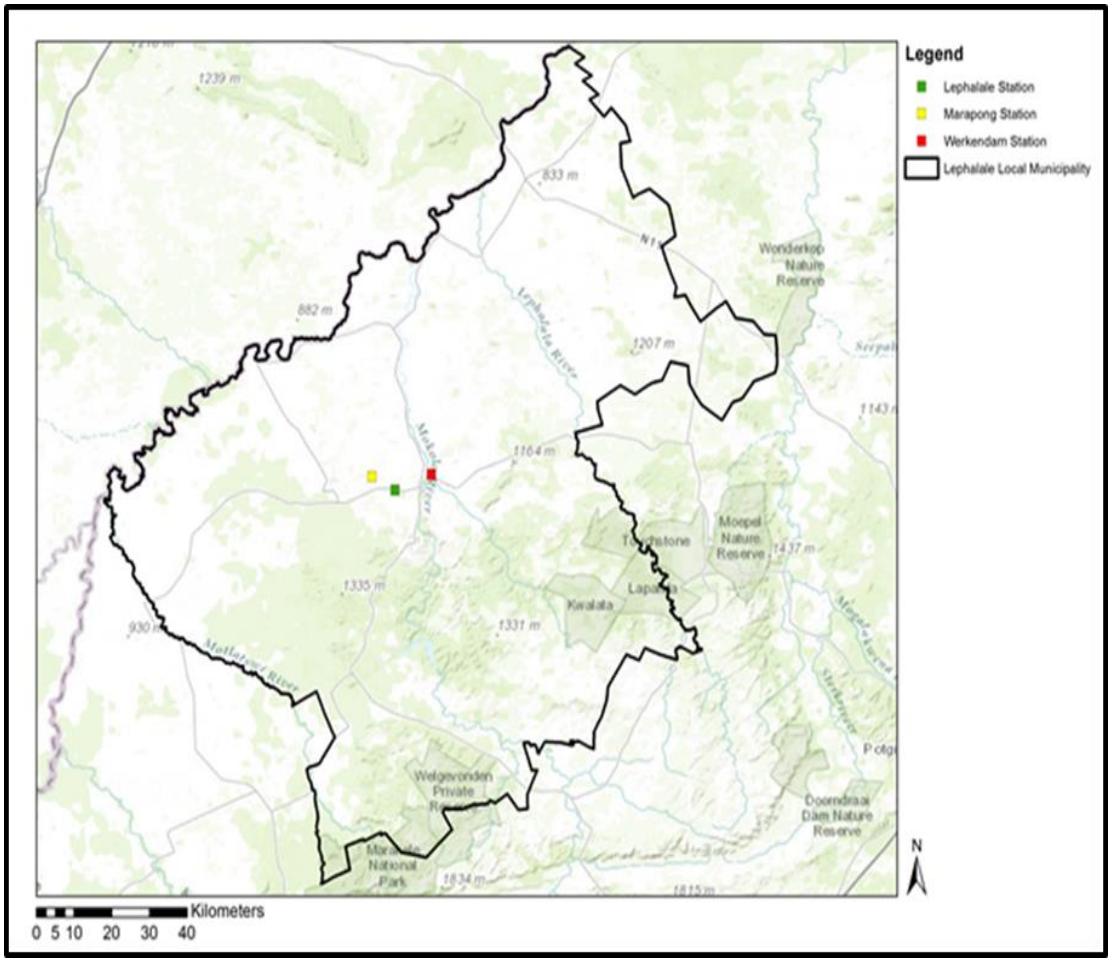


Figure 3.4: Map showing air quality and meteorological stations in Lephalale.

3.3 Data quality control

3.3.1 Data cleaning

There are many sources of error in the measurement of data from monitoring stations. Some of these errors are as a result of instrument noise errors, drift, power cuts, etc. All the hourly data for this study were screened for data quality and data completeness. In performing data quality control, an attempt was made to identify these errors. The following rules, in accordance with SANAS (2012) and the New Zealand Good Practice Guide for Air Quality Monitoring and Data (Ministry for the Environment. 2009), were used:

- Negative values (except for temperature) were discarded. According to Ministry for the Environment (2009), negative values may be replaced with zero if they are a valid measurement. However, if the values were the result of instrument problems, such concentrations could be discarded. In this study, the department responsible for data collection at Eskom confirmed that the negative values were as a result of instrument problems.

- Identical values and some of the zeroes were removed. Identical values were considered to be hourly values repeated three times in a row; values with a threshold of 0.03 were considered common. Additionally, zeroes (except for precipitation), which repeated more than four times, were considered invalid.

The meteorological data were considered erroneous in the following cases (ASOS, 1998; WMO, 2004; Fiebrich, et al., 2012; Journée and Bertrand, 2010):

- Wind direction should range between 0 and 359 degrees in order for it not to be considered erroneous.
- Precipitation with negative values was discarded.
- Relative humidity values of 0% or 100% were discarded.

3.3.2 Data completeness and recovery

In order to ensure acceptable data quality, all the hourly data (meteorology and air quality from Marapong, Werkendam and Lephalale stations) were cleaned in MS Excel 2010 using the criteria explained above. Data completeness was considered when averaging time series data. A 70% data completeness rule was used when averaging data across time scales (i.e. if more than 30% of one-hourly data points were missing from a day, then the daily average could not be calculated from one-hour data points).

3.3.2.1 Meteorological data

Table 3.6 details the percentage of meteorological data recovered for Lephalale and Werkendam after performing data quality control procedures. These data indicate that the data completeness for both the stations is good with most of the data completeness above 80%. Similarly, Werkendam also had data completeness above 80%.

Table 3.6: Percentage data recovered at Lephalale and Werkendam stations for the period 2007–2012.

	Lephalale station					Werkendam station				
Year	**Temperature**	**Rainfall**	**Wind speed**	**Wind direction**	**Humidity**	**Temperature**	**Rainfall**	**Wind speed**	**Wind direction**	**Humidity**
2007	97.0%	94.3%	97.0%	97.0%	96.7%	88.3%	97.3%	90.3%	90.3%	89.1%
2008	94.4%	92.0%	94.5%	94.5%	93.2%	86.3%	96.3%	89.3%	89.3%	95.3%
2009	84.0%	89.2%	84.0%	84.0%	89.2%	90.3%	94.7%	80.3%	80.2%	92.6%
2010	92.8%	89.5%	86.6%	86.6%	93.9%	93.2%	90.6%	94.3%	94.3%	94.3%
2011	94.5%	90.2%	75.6%	75.6%	95.6%	94.3%	92.5%	93.1%	93.1%	85.6%
2012	96.3%	89.6%	97.1%	97.1%	91.1%	91.3%	93.8%	96.3%	96.3%	90.5%

3.3.2.2 Air quality data

The Marapong station also had a high SO_2 data completeness ranging from 76.0 to 92.7% for the period 2007–2012 (Table 3.7). Furthermore, NO_x and NO_2 also had good data completeness from 74.0 to 92.3%. During this study, meteorological data for 2007 were not made available. However, 2008–2012 meteorological data were above 70% for wind speed and direction, except in 2009 and 2012 (Table 3.7).

Table 3.7: Percentage data recovered at Marapong station for the period 2007–2012.

Year	SO_2	NO_x	NO_2	Wind speed	Wind direction	Temperature	Humidity
2007	88.8%	79.7%	79.7%	No data	No data	No data	No data
2008	81.8%	74.0%	77.5%	73.2%	70.5%	75.0%	70.0%
2009	76.0%	75.9%	78.9%	69.8%	69.5%	85.0%	No data
2010	88.8%	88.6%	90.1%	80.4%	80.3%	75.0%	72.0%
2011	92.7%	92.3%	89.2%	84.3%	84.3%	76.0%	No data
2012	90.3%	90.3%	91.6%	69.9%	69.6%	72.0%	No data

3.3.3 Solar radiation data validation

The Lephalale and Marapong stations do not collect solar radiation data, as indicated above. Thus, hourly solar radiation model results obtained from the Conformal Cubic Atmospheric Model (CCAM) were used for this study (McGregor, 2005, McGregor and Dix, 2008). These modelled data were obtained from the Climate Studies Modelling and Environmental Health Research Group at the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa. African studies (Engelbrecht, 2002; Olwoch et al., 2008; Engelbrecht et al., 2009) have indicated that this type of modelling has been used in South Africa and tropical Africa for the past ten years to simulate present-day climate and future climate change. Additionally, this model is capable of providing realistic daily climate statistics over Southern Africa (Potgieter, 2009).

For this study only one neighbouring station (Werkendam) measured ground-based solar radiation data. However, as that station is ~ 14 km from the study site, it was not certain that the solar radiation data would be applicable. Thus, the Werkendam solar radiation data were compared to the model outputs. This comparison was performed to validate the model data so that it can be utilised in this study, and just like any other model, there are limitations. The limitation of the CCAM output is that the modelled data have a coarse spatial resolution of 15 km. In addition, to the aforementioned data information, the limitation of this study is that one station was used (Werkendam) to validate the modelled data.

The relationship between the two data sets (modelled and measured solar radiation) was analysed through linear correlation. This type of correlation determines the strength of the relationship between two variables without fitting a line. This analysis was performed on each year of available monitored solar radiation data (2008–2012). Figure 3.5 below displays an example of the relationship between annual modelled CCAM data and monitored Werkendam solar radiation data in 2008. These two data sets have a strong positive correlation (R =0.82). Additionally, similar results were obtained for the other four years (2009, 2010, 2011 and 2012). Their graphs are included in Appendix 1. Since the relationship between monitored and modelled data at Werkendam is strong, it is assumed that the modelled values will be an appropriate proxy for measured data at the study site of Marapong. Therefore, the modelled data were used for Marapong and it was assumed to be reliable and representative of Marapong.

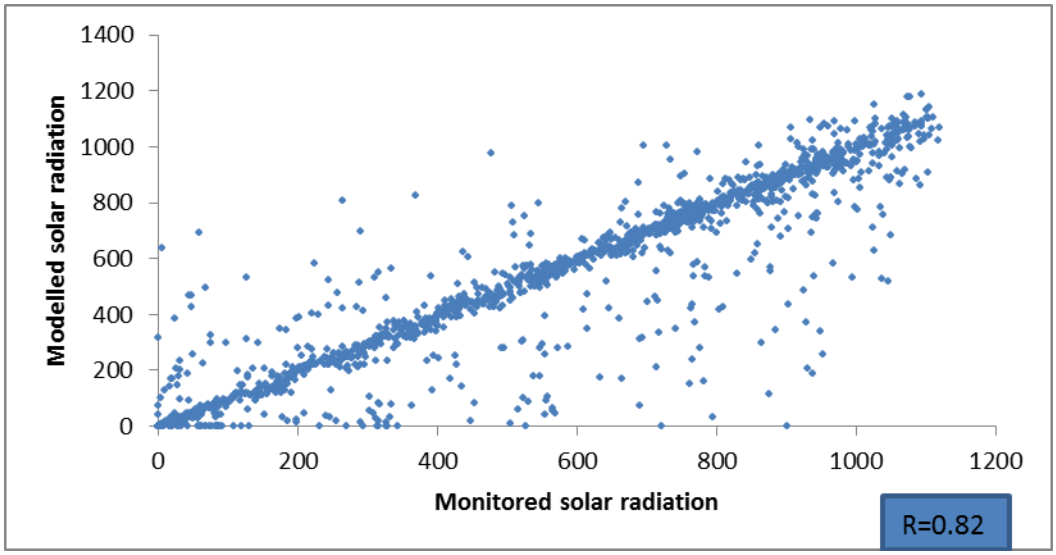


Figure 3.5: Example of 2008 linear correlation analysis results of modelled CCAM data and monitored Werkendam solar radiation data (W/m^2).

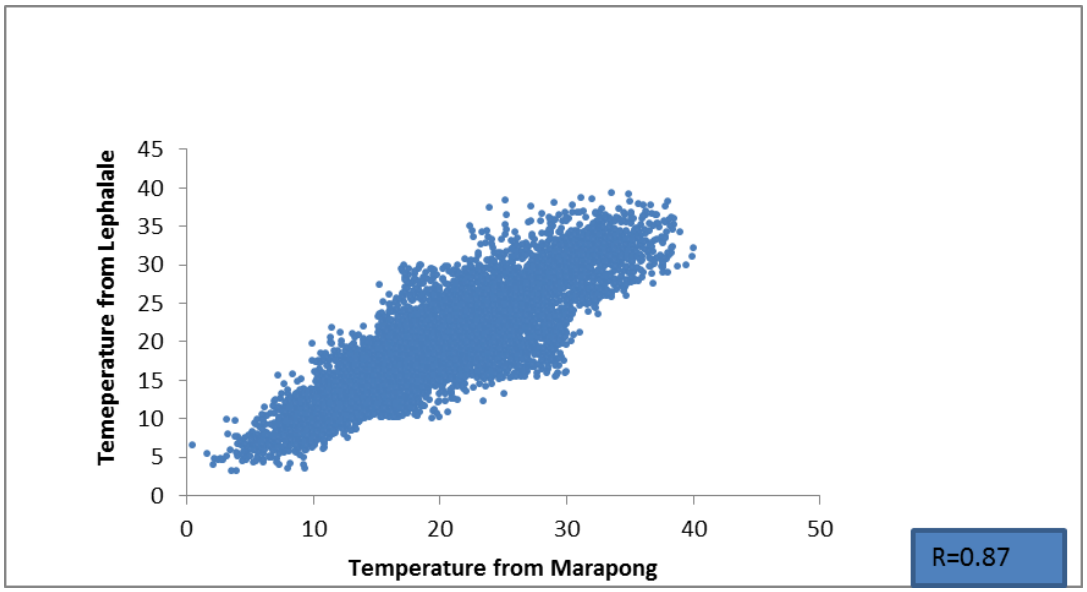
3.3.4 Other Meteorological data validation

Hourly meteorological data from Marapong station, such as temperature, humidity, wind speed and direction, were correlated with those of Werkendam and Lephalale because Marapong had poor data availability in terms of wind speed and wind direction in 2009 and 2012. Humidity data were also not available in 2009, 2011 or 2012, as mentioned above. Therefore, it was crucial that missing data be estimated using available data from the nearest other stations. This was done to determine if there is any relationship between these stations and Marapong, because there is limited meteorological data and stations available in the area. However, if there was a relationship between Marapong and one of the other meteorological stations, it was assumed that this station would provide accurate information when modelling the missing meteorological data at Marapong.

The relationships between Marapong and Lephalale, and between Marapong and Werkendam was also analysed through linear correlation for each year (2008–2012). Figure 3.6a and Figure 3.6b display an example of the linear correlation of temperature data between Marapong and Lephalale, and between Marapong and Werkendam in 2008. The results indicate that temperature has a strong positive correlation (R ranging between 0.82 and 0.87) between Marapong and these

meteorological stations. Similarly, the results for the period 2009–2012 (in Appendix) 2 also show a strong positive correlation.

a)



b)

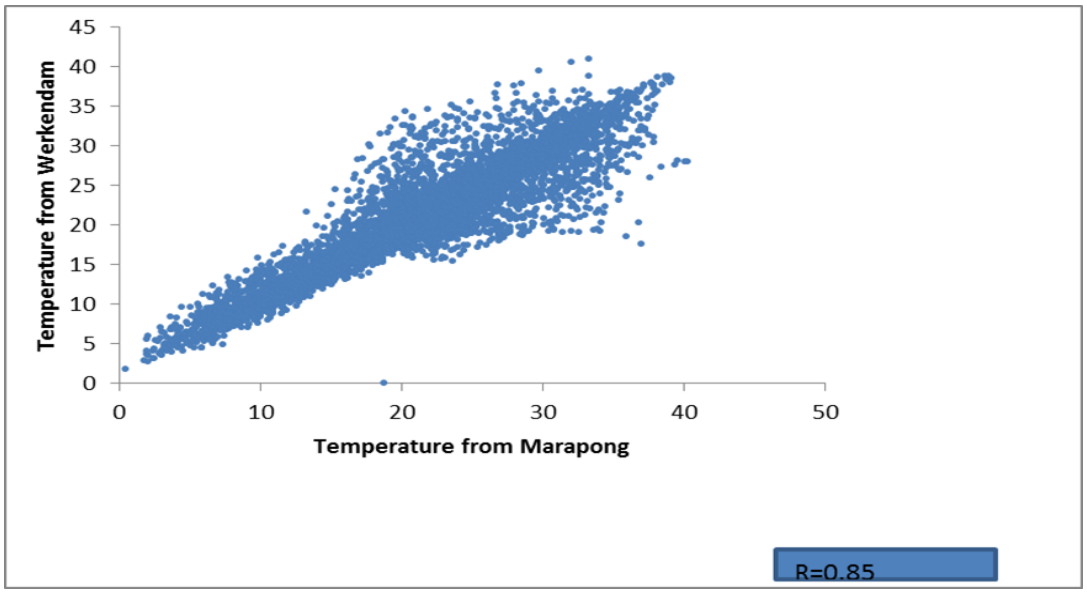
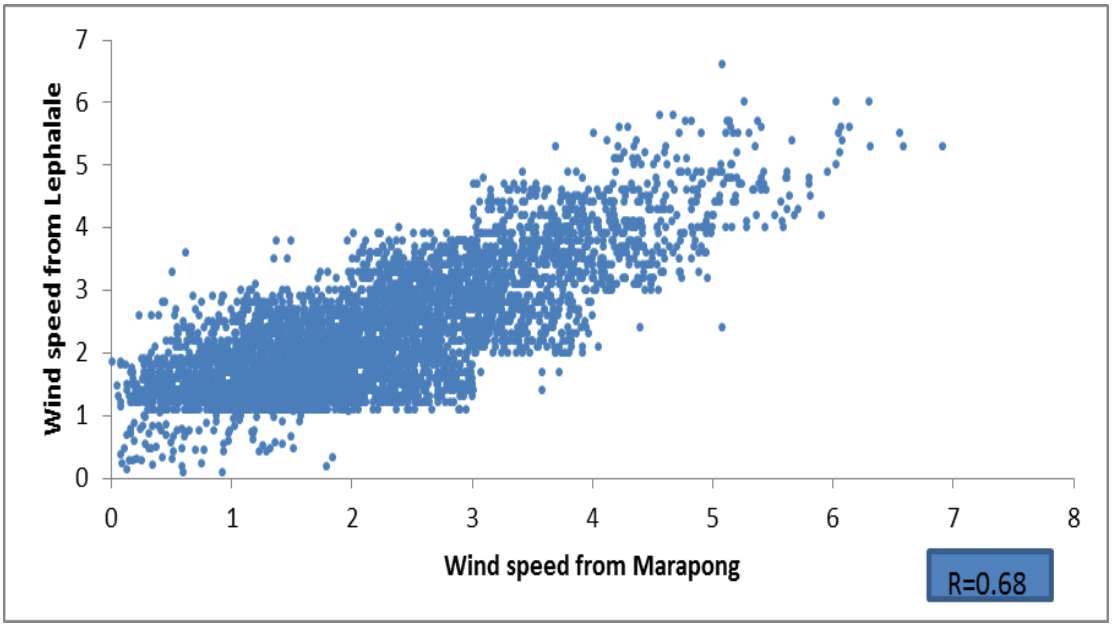


Figure 3.6: Example of linear correlation analysis results of temperature (˚C) data between Marapong and Lephalale, and between Marapong and Werkendam in 2008.

The correlation between the wind data of Marapong and Lephalale, and between Marapong and Werkendam was determined for the period 2008–2012. Figure 3.7a and Figure 3.7b illustrate the relationship between Marapong and Lephalale, and between Marapong and Werkendam in 2008 in terms of wind speed. Figure 3.7a and

Figure 3.7b indicate that there is a weak relationship between Marapong and the abovementioned meteorological stations in terms of wind speed because wind speed is highly variable. Additional results of wind speed data between Marapong and Lephalale, and between Marapong and Werkendam for the period 2009–2012 are displayed in Appendix 3. These results also show a weak linear relationship. The linear correlation results show that while the relationship between the data for Marapong and Lephalale looks much better than that between Marapong and Werkendam, the relationship between these two data sets is not strong. In general, the results for the period 2008–2012 show that there is no relationship between Marapong and Lephalale, or between Marapong and Werkendam in terms of the data set for wind speed.

a)



b)

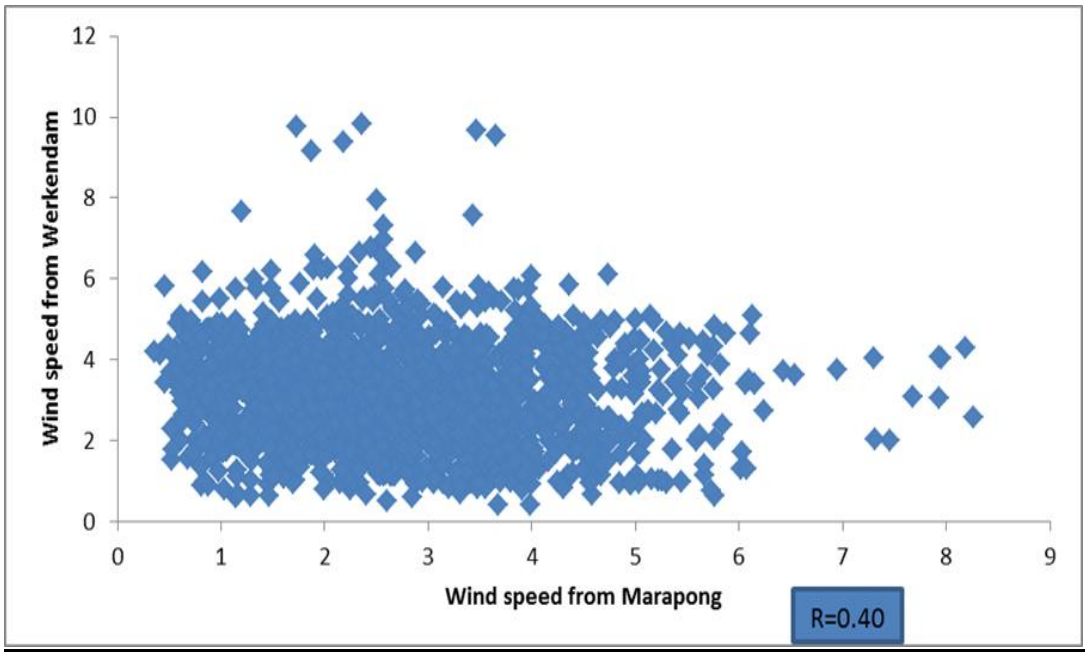
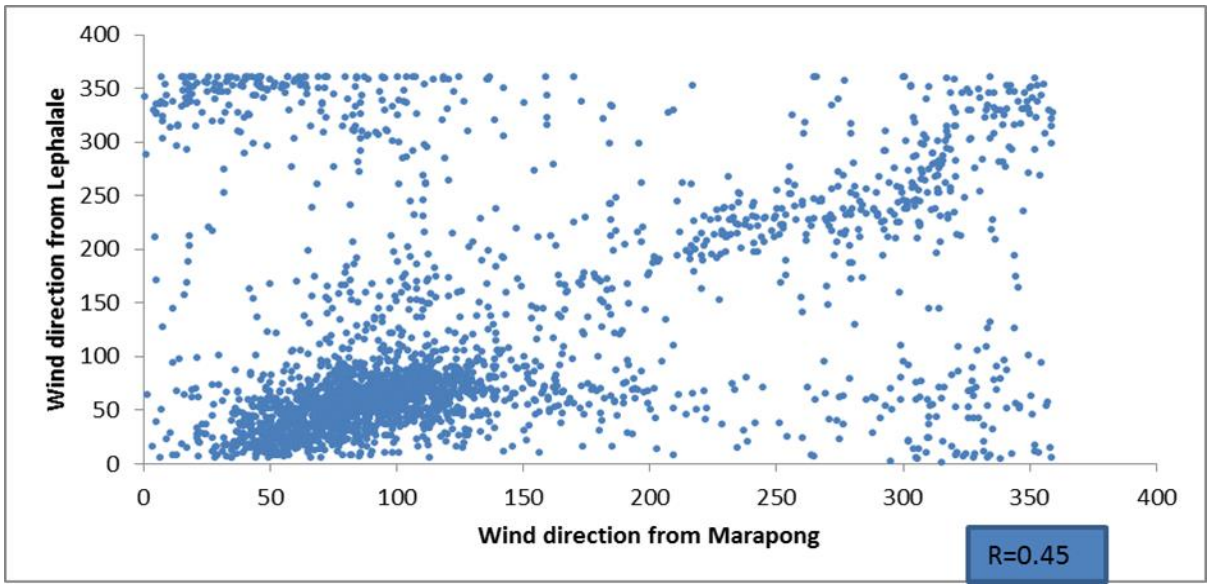


Figure 3.7: Example of linear correlation analysis results between Marapong and Lephalale, and between Marapong and Werkendam in 2008 in terms of wind speed (m/s).

In addition, Figure 3.8a and Figure 3.8b below display the correlation between Marapong and Lephalale, and between Marapong and Werkendam in terms of wind direction. Wind direction data for Lephalale and Werkendam stations were compared to those of Marapong, and a very weak correlation was observed. This means that there is no relationship between these stations. Appendix 4 shows similar results, where there is no correlation between Marapong and Lephalale, or between Marapong and Werkendam for the years 2009–2012 in terms of wind direction.

a)



b)

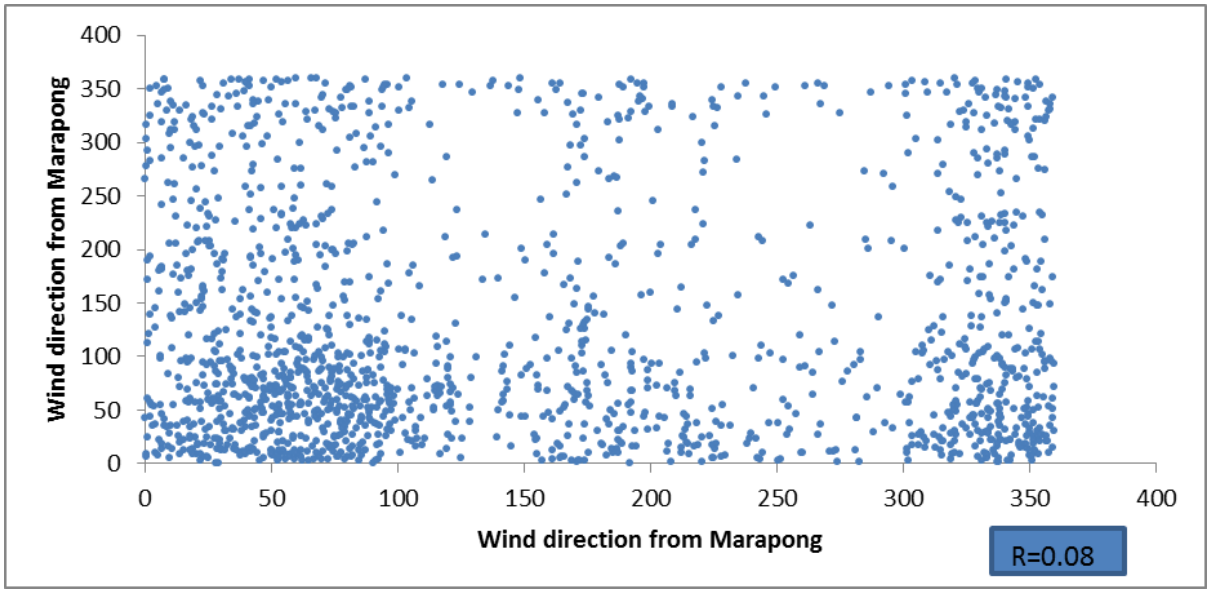
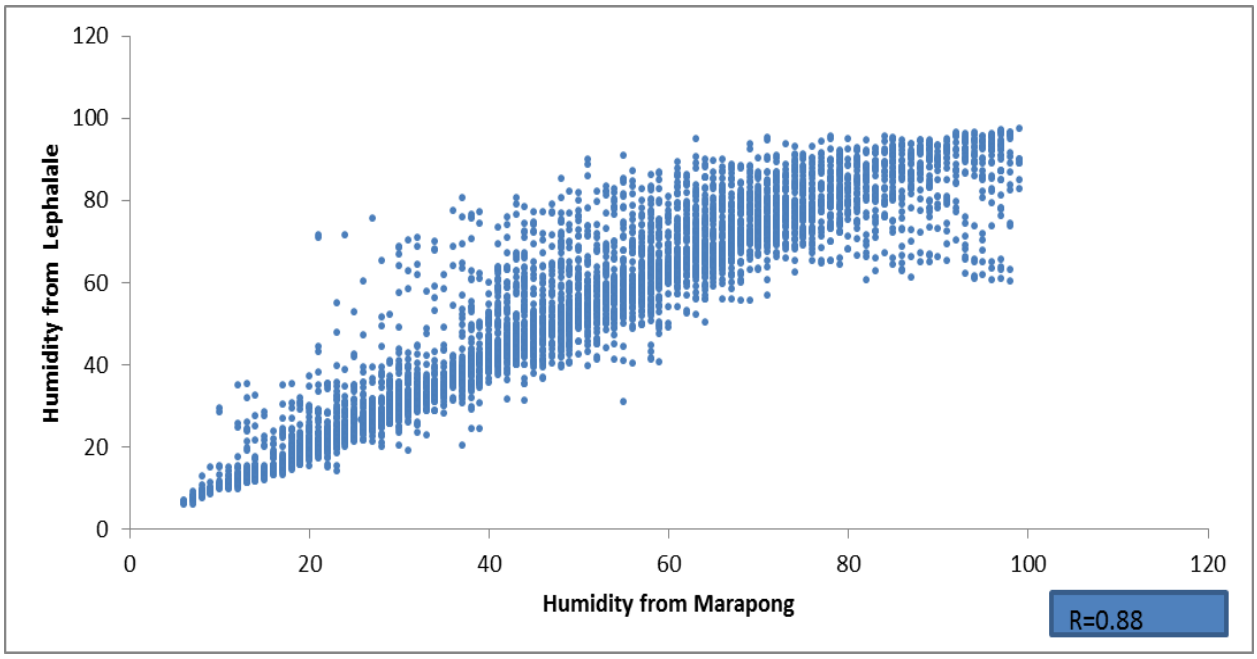


Figure 3.8: Example of linear correlation analysis results of wind direction (°) data between Marapong and Lephalale, and between Marapong and Werkendam in 2008.

Figure 3.9a and Figure 3.9b show a linear correlation analysis of humidity data between Marapong and Lephalale, and between Marapong and Werkendam in 2008. In general, the humidity data of Marapong in relation to Lephalale, and Marapong in relation to Werkendam show a good correlation, with both having an R above 0.80.

Appendix 5 shows the additional correlation of humidity data between Marapong and Lephalale, and between Marapong and Werkendam for the year 2010. The results also show a good relationship between the humidity data of Marapong in relation to those of both Lephalale and Werkendam.

a)



b)

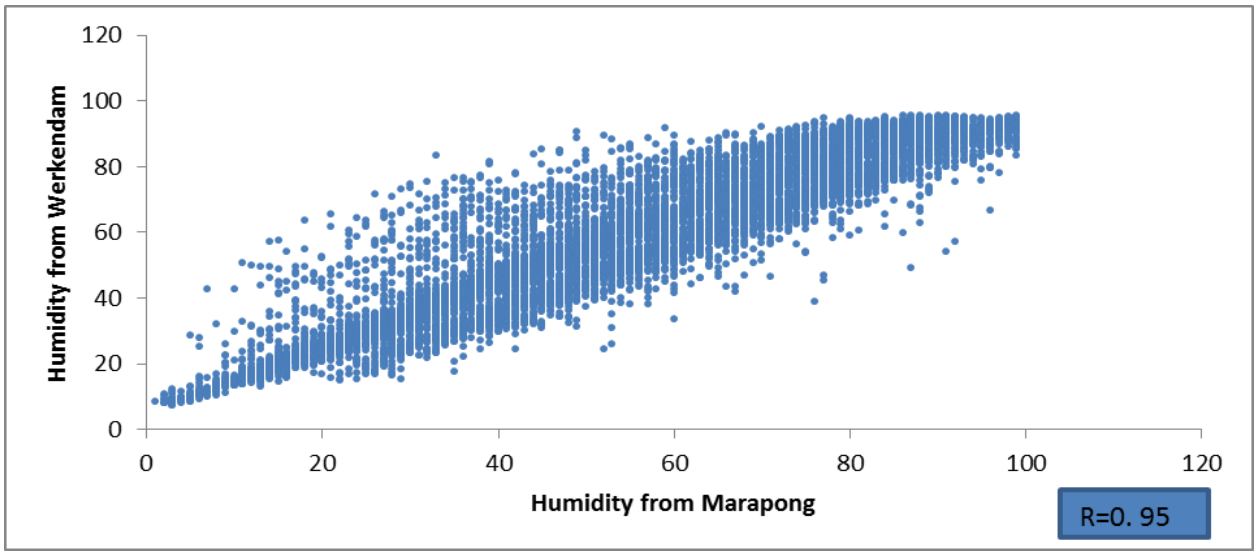


Figure 3.9: Example of linear correlation analysis results of humidity (%) data between Marapong and Lephalale, and between Marapong and Werkendam in 2008.

3.3.5 Linear least squared regression

The relationship between the two data sets (modelled and measured solar radiation) was analysed through a linear least squares regression (Johnson and Bhattacharyya, 1992; Moore and McCabe, 1998; Helmis and Nastos, 2012). This type of modelling determines the relationship between two variables by fitting a linear equation squared to observed data. Table 3.8 shows linear regression results for the period 2008–2012. The measured versus modelled data relationship for the 2008 results show that there is a strong positive relationship (with a slope of 0.93) between the modelled and measured solar radiation data with an R^2 (Coefficient of determination) of 0.93. In addition, the p-values of these data sets were calculated, with a confidence interval >95 percentage. This p-value explains if the results are statistically reliable (statistical significance), so any data with a p-value below 0.05 were considered statistically significant in this study. This analysis was performed on each year of available measured solar radiation data (2008–2012). Therefore, results in Table 3.8 for 2008 show that 92% of the modelled and measured data a strong relationship, and there is a 95% confidence that these data are reliable (statistically significant) because the p-value is below 0.05. The entire Table 3.8 also shows the results for the period 2009–2012, which also indicate a strong significant correlation. Since the relationship is strong between modelled and measured data, it was assumed that the modelled values will be an appropriate proxy for measured data at the study site of Marapong. Therefore, the modelled solar radiation data were used for Marapong, and they were assumed to be reliable and representative of Marapong.

Table 3.8: Linear regression results of modelled versus measured solar radiation.

Year	Linear equation	R^2	p-value (at 0.05 significance level)
2008	y = 0.93x + 7.3	0.92	0.0003
2009	y = 0.86x + 2.2	0.81	0.0007
2010	y = 0.85x + 3.5	0.85	0.0006
2011	y = 0.89x + 4.4	0.90	0.0004
2012	y = 0.91x + 8.8	0.91	0.0002

Table 3.9 below shows linear regression results of temperature, humidity, wind speed and wind direction at Marapong in comparison to the Lephalale station for the period 2008–2012. In general, the linear regression results below indicate that there is a strong relationship between the temperatures at Marapong in relation to Lephalale because their R-square ranged between 0.83 and 0.90, and their p-value is between 0.0002 and 0.0008, which indicates that there is a statistically significant difference. Similarly, humidity showed a strong relationship with R-squared ranging between 0.83 and 0.89 and p-value (0.0001 to 0.0007) being less than 0.05. However, wind speed and direction did not show a strong relationship and there is no statistically significant difference because they are highly variable.

Table 3.10 below shows linear regression results of temperature, humidity, wind speed and wind direction at Marapong in comparison to the Werkendam station for the period 2008–2012. In general, the linear regression results below indicate that there is a strong relationship between the temperature and humidity of Marapong and Werkendam because their R-squared ranged between 0.79 and 0.85, and the results were significantly different with p-values <0.05. Similarly, humidity showed a strong relationship with R-squared ranging between 0.84 and 0.87, and p-value being less than 0.05. However, wind speed and direction did not show a strong relationship because they are highly variable.

In summary, some of the meteorological parameters were not available or complete in Marapong. Therefore, this resulted in validating and modelling the meteorological data in Marapong using nearest meteorological stations, because poor data availability can yield unreliable results. Linear correlation assisted in validating modelled vs measured solar radiation as well as other meteorological parameters (wind speed and direction, temperature and humidity) to determine if there is any relationship between the stations of Marapong vs Werkendam and Marapong vs Lephalale. Furthermore, this assisted in selecting Lephalale station and modelled CCAM data as the appropriate proxies for measured data at the study site of Marapong. Also, the linear least squared regression assisted in modelling missing meteorological data.

Table 3.9: Linear regression results of temperature, humidity, wind speed and wind direction at Marapong in comparison to the Lephalale station for the period 2008–2012 (the p-value is at 0.05 significance level).

	Temperature			**Humidity**			**Wind speed**			**Wind direction**		
Year	Linear equation	R^2	p-value	Linear equation	R^2	p-value	Linear equation	R^2	p-value	Linear equation	R^2	p-value
2008	y = 0.9x + 2.3	0.90	0.0002	y = 0.88x + 2.3	0.89	0.0004	y = 0.26x + 1.3	0.25	0.0701	y = 0.35x + 0.3	0.31	0.0801
2009	y = 0.87x + 4.2	0.85	0.0004	y = 0.85x + 1.3	0.85	0.0001	y = 0.35x + 3.1	0.34	0.0910	y = 0.25x + 1.3	0.20	0.0630
2010	y = 0.84x + 5.2	0.83	0.0008	y = 0.84x + 0.3	0.80	0.0003	y = 0.41x +1.22	0.39	0.0940	y = 0.45x + 0.8	0.42	0.0741
2011	y = 0.86x + 4.4	0.84	0.0006	y = 0.89x + 1.3	0.84	0.0002	y = 0.34x + 2.4	0.29	0.0611	y = 0.39x + 0.21	0.34	0.0850
2012	y = 0.80x + 8.8	0.78	0.0003	y = 0.86x + 2.2	0.83	0.0007	y = 0.40x + 2.3	0.37	0.0702	y = 0.23x + 2.3	0.23	0.0625

Table 3.10: Linear regression results of temperature, humidity, wind speed and wind direction at Marapong in comparison to the Werkendam station for the period 2008–2012 (the p-value is at 0.05 significance level).

	Temperature			Humidity			Wind speed			Wind direction		
Year	Linear equation	R^2	p-value	Linear equation	R^2	p-value	Linear equation	R^2	p-value	Linear equation	R^2	p-value
2008	y = 0.80x + 2.3	0.79	0.0002	y = 0.87x + 2.3	0.88	0.0008	y = 0.16x + 1.33	0.17	0.0800	y = 0.35x + 0.3	0.30	0.0711
2009	y = 0.81x + 2.2	0.85	0.0003	y = 0.84x + 1.3	0.83	0.0006	y = 0.15x + 0.34	0.12	0.0630	y = 0.47x + 1.3	0.40	0.0901
2010	y = 0.83x + 3.2	0.82	0.0004	y = 0.85x + 4.3	0.84	0.0005	y = 0.11x + 0.26	0.10	0.0841	y = 0.54x + 0.8	0.53	0.0605
2011	y = 0.80x + 0.40	0.81	0.0002	y = 0.86x + 1.3	0.85	0.0004	y = 0.14x + 0.41	0.17	0.0703	y = 0.33x + 0.21	0.30	0.0719
2012	y = 0.81x + 0.82	0.78	0.0001	y = 0.85 x+ 2.2	0.85	0.0003	y = 0.20x + 2.33	0.19	0.0930	y = 0.43x + 2.3	0.40	0.0800

Linear regression equations of wind speed, wind direction, humidity and temperature for Marapong in comparison to Lephalale and Werkendam were utilised to model the missing data of Marapong, provided that the linear equations of these data overlap. The data estimated from each year using these equations were then used for further analysis. Marapong station does not measure rainfall data at all, therefore the nearest station to the study site was considered to see which would be more viable to use for this study area. Since the Lephalale station is only approximately 8 km from the study site, it was chosen on a criterion that the topography between Marapong and Lephalale was similar, because there are no mountains or valleys between these two stations (Dr Johan Malherbe, 2013, personal communication, 21 February). Werkendam station was considered to be situated too far from the air quality station. The mountain terrain between the two stations may yield results that are less representative of Marapong.

3.4.1 Dry deposition calculation for gases using an inferential model

In this study, NO_2 deposition velocity was used to represent NO_x because NO_x is deposited primarily as NO_2 (Scire et al., 2000). This model uses measurements of meteorological and vegetation data to estimate deposition velocity, which is then multiplied by measurements of near-surface air concentrations to estimate dry deposition flux. Dry deposition flux is determined by Equation 1, where C ($\mu g/m^3$) is the pollutant concentration of chemical species of interest, F ($\mu g/m^2/s$) is the deposition flux of the pollutant and V_d (cm/s) is the deposition velocity (Seinfeld and Pandis, 1998; Wesely and Hicks, 2000; Baumgardner et al., 2002; Gao, 2002; Marner and Harrison, 2004; Yang et al, 2005). The negative sign in Equation 1 indicates a downward flux.

$$F = -V_d C \quad (1)$$

In an inferential model, the deposition velocity (V_d) of gaseous pollutants is expressed as an inverse relationship of three resistances as follows:

$V_d = 1/(R_a + R_b + R_c)$ (2)

Where,

R_a (s/m) is the aerodynamic resistance

R_b (s/m) is the quasi-laminar

R_c (s/m) is the canopy/surface resistance

R_a (s/m) is the aerodynamic resistance, which is determined by atmospheric properties and mainly accounts for turbulent exchange. The term R_b (s/m) is the quasi-laminar boundary layer resistance, which accounts for the molecular diffusivity affecting pollutant transfer near receptor surfaces. R_c (s/m) is the canopy resistance, which includes the uptake of pollutants by leaves, the soil and other chemically absorbing materials at the surface of interest. Other possible pathways embedded in R_c for deposition to surface elements are represented as bulk resistance in Figure 3.10. This Figure 3.10 also highlights the resistance network along the transportation pathway from atmosphere to surface (vegetation and soil).

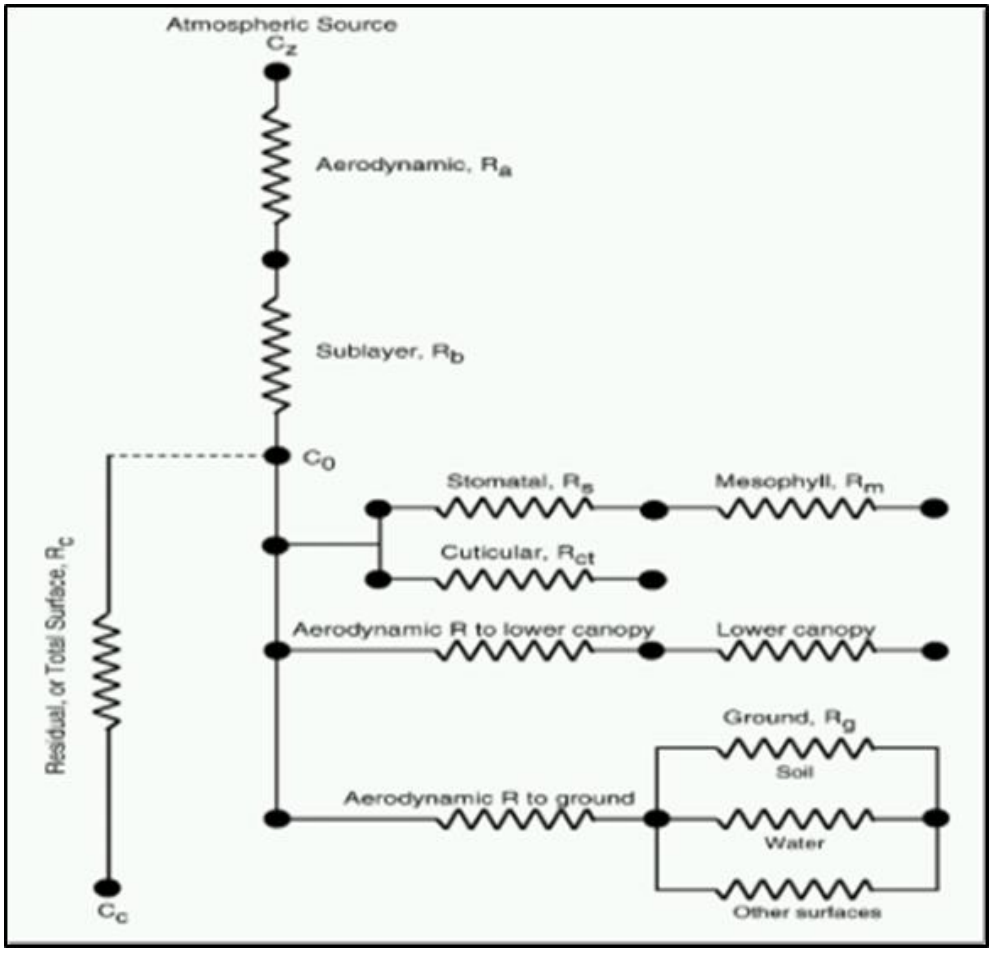


Figure 3.10: Schematic diagram illustrating the resistance network along the transportation pathway from atmosphere to surface (after Hicks et al., 1987).

3.4.1.1 Aerodynamic resistance (R_a)

The atmosphere's ability to transfer passive contaminants through vertical mixing is described by aerodynamic resistance (R_a). This resistance is controlled by atmospheric turbulence, and is hence influenced by mechanical mixing and buoyancy. Information on stability and surface roughness is provided by the standard deviation of horizontal wind direction (σ_θ) (radians). R_a can be estimated using measurements of σ_θ combined with measurements of wind speed (u measured in m/s), as indicated below in Equation 3a and Equation 3b (Hicks et al., 1987; Meyers and Yeun, 1987).

$R_a=4(u\sigma_\Theta^2)^{-1}$ for neutral to stable conditions (3a)

$R_a= 9\ (u\sigma_\Theta^2)^{-1}$ for unstable conditions (3b)

The stability conditions were defined using Pasquill classes (Table 3.11)

Table 3.11: Pasquill stability classes (Pasquill, 1961).

Wind speed (m/s)	Daytime			Nighttime	
	Incoming solar radiation			Cloud cover fraction	
	Strong	Moderate	Slight	$\geq\frac{4}{8}$	$\leq\frac{3}{8}$
<2	A	A-B	B	-	-
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D4	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Solar radiatione: Strong (>700 W/m2), moderate (350-700 W/m2) and slight (<350 W/m2)

A - extremely unstable, B - moderately unstable, C - slightly unstable, F - moderately stable, D – neutral and E - slightly stable

3.4.1.2 Quasi-laminar boundary layer (R_b)

The quasi-laminar boundary layer resistance, R_b, the resistance layer in contact with the surface, is determined by empirical expression (in Equation 4), based on experimental data (Meyers and Yeun, 1987), and is given by the following equation:

$$R_b = (2/ ku_*) (Sc/Pr)^p \quad (4)$$

Where,

- k is the Von Karman u*, (m/s) is the frictional velocity
- Sc is the Schimdt number for SO_2 (1.25) and NO_2 (1.07); constant (0.4)
- Pr is the Prandtl number for air (0.72 is used)
- Exponent *p* is 2/3

Therefore, frictional velocity u* (measured in m/s) can be estimated using R_a and wind speed (Equation 5) as follows:

$$u* = \sqrt{\frac{u}{Ra}} \quad (5)$$

3.4.1.3 Canopy/surface resistance (R_c)

The trace gas molecules diffuse across the quasi-laminar boundary layer, which is in contact with the surface (either vegetation or soil). From that point, the rate of transfer is governed by surface uptake resistance, R_c. This resistance layer consists of three pathways: transfer through either the stomata or reaction with the moist mesophyll cells, transfer though the cuticle or reaction on cuticle surface, and transfer to the ground (Scire et al., 2000). This resistance is related to effective uptake rate, composed of three parallel pathways (Figure 3.11).

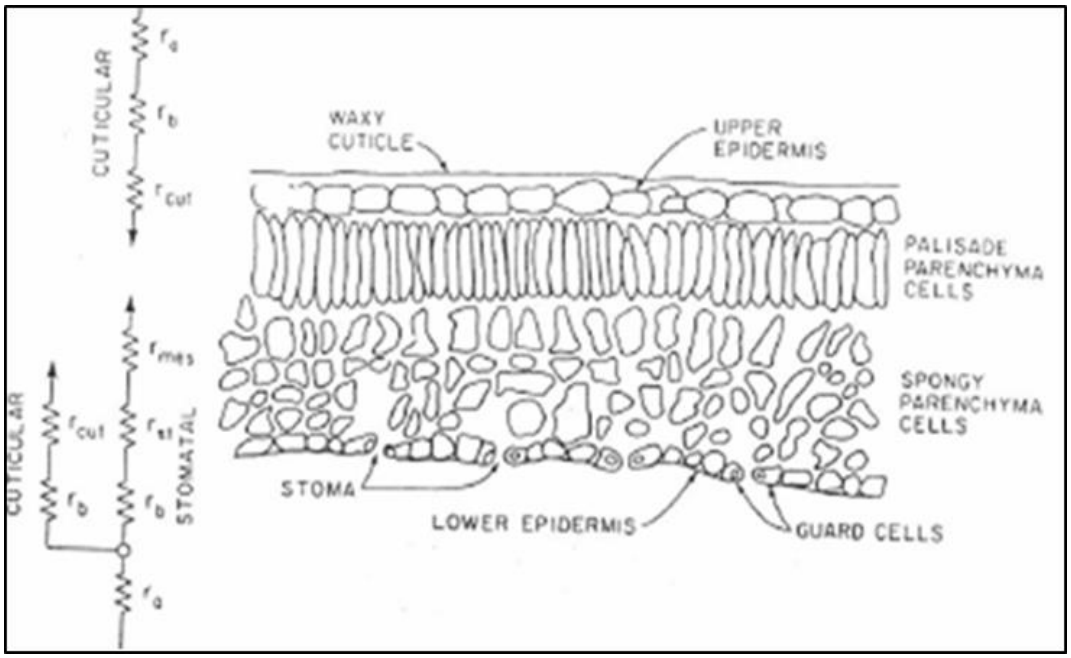


Figure 3.11: Schematic illustration of the pathways and processes for the transfer between air and plant tissue (after Hicks et al, 1987).

This resistance is therefore calculated as follows:

$$R_c = [LAI/r_f + LAI/r_{cut} + LAI/r_g]^{-1} \quad (6)$$

Where LAI is the leaf area index and $r_{f,}$ (s/m) represents the internal foliage resistance. Additionally, r_{cut} (s/m) denotes cuticle resistance and r_g (s/m) ground resistance. However, internal foliage resistance (in Equation 7) is made up of two resistances: mesophyll resistance (r_m measured in s/m) and stomatal resistance (r_s measured in s/m) (Hicks et al., 1987). Therefore, internal foliage resistance is calculated as follows:

$$r_f = r_s + r_m \quad (7)$$

3.4.3.1 Stomatal resistance (r_s)

Factors such as temperature, water stress, humidity and solar radiation are the external forces responsible for the opening and closure of the stomata, thus canopy resistance results in major seasonal and diurnal variation of deposited trace gases (Hicks and Matt, 1988; Clarke et al., 1997, Scire et al., 2000). During dry conditions, stomatal resistance controls surface resistance to absorb gaseous pollutants. When the plant is photosynthetically active and growing, the stomatal resistance is at its lowest (high deposition flux can be expected). This results in seasonal variation of deposition velocity (Hicks et al., 1987; Erisman, 1993). Availability of stomata to take pollutants is related to the growth of plants and foliation cycles. During summer, there is less stomatal resistance, especially during the day. Temperatures above 20 $^{\circ}$C play a role in the photosynthetical activity of plants, resulting in a greater uptake of pollutants. However, if the temperature is zero and below, as well as above 40 $^{\circ}$C, stomatal opening is not possible (Pleim, et al., 1984; Erisman and Baldocchi, 1994). Water deficit in the soil is also related to stomatal closure (Erisman and Baldocchi, 1994). Cuticle resistance decreases with an increase in humidity. If the surface is wet, then dry deposition of SO_2 is enhanced. The transfer through stomata is by diffusion, and stomatal resistance is inversely dependent on molecular diffusivity. Generally, stomatal resistance depends on incident photosynthetically active radiation (I_p) as in Equation 8 below. In general, an increase in stomatal resistance

as a result of less availability of photosynthesis and solar radiation may result in a decrease in deposition velocity.

$$r_s = r'_s [1 + (b'/I_p)]/ (f_e f_w f_T f_s), \quad (8)$$

Equation 8, r'_s expresses the value of stomatal resistance, which varies with the plant species (in this study, 4.5 s/m was used for the Limpopo Bushveld, which belongs to the savannah), and b' expresses an empirical constant (2.3×10^{-8} m^2). Factors f_e, f_w and f_T in Equation 8 correct for the effects of humidity, water stress and temperature, respectively (Hicks et al., 1987). The correction factor f_s modifies the stomatal resistance to account for the difference between the molecular diffusivity of the trace gas in question and the water vapour.

3.4.3.2 Mesophyll resistance (r_m)

After the pollutants have entered the sub-stomatal cavity, they are either transferred to plant cells or destroyed by chemical reactions within the stomatal cavity or interstices among mesophyll cells. This type of resistance mainly depends on the solubility and reactivity of the gases. Each trace gas is assigned a value by O'Dell et al., (1997). Soluble gases, such as SO_2, have an r_m value of ~0.0 s/cm. Less soluble gases, such as NO_2, have a value of 500 s/cm (Wesley, 1989; O'Dell et al., 1997).

3.4.3.3 Cuticle resistance (r_{cut})

This is the second pathway of the vegetation layer through which trace gases are deposited. Gases can enter vegetation directly through the cuticle or react at the surface of the cuticle (Zunckel, 1998). This type of deposition is mainly controlled by pollutant reactivity. The r_{cut} used in the current study for both SO_2 and NO_2 was 3 000 s/m, as estimated by Padro et al., (1991). This is the default value in the inferential model.

3.4.3.4 Ground resistance

Ground resistance is the third pathway whereby the deposition of trace gases occurs directly to the ground, but if the area is highly vegetated or has moderate vegetation, then cuticle resistance and foliage resistance account for the total canopy resistance. The ground resistance used in this study was 500 s/m for SO_2 and 300 s/m for NO_2 (Wesley, 1989).

3.4.3.5 Leaf area index

Leaf area index (LAI) links all the resistances of R_c and can be defined as the ratio of leaf surface area divided by the ground surface area. As stated in Brook et al., (1999), it is crucial to define seasonal categories when using this model, because some parameters change with the seasons. For each season, the model also requires the LAI value of the vegetation, as well as a percentage of the area covered by that specific vegetation. Table 3.12 below displays the LAI used in this study.

Table 3.12: Description of seasons, LAI and assumptions made when classifying the seasons.

Season	Month	LAI	Assumption	Reference
Summer	December, January, February	1	Plants are actively growing, highly photosynthetic. Higher rainfall.	Zunckel, 1998; Zunckel et al., 1999 Zunckel et al.,1996 Held and Mphepya,2000
Autumn	March, April, May	0.5	Plants are beginning to grow less actively and to be less photosynthetic. The rainfall starts to decline.	Scorgie and Kornelius, 2009
Winter	June, July, August	0.01	Plants are not actively growing and are not photosynthesising. There is lower rainfall. The canopy is assumed to be dormant.	Zunckel et al., 1998 Zunckel et al., 1999 Zunckel et al., 1996 Held and Mphepya, 2000
Spring	September, October, November	0.5	Plants are moderately active and photosynthetic. Spring rainfall.	Scorgie and Kornelius, 2009

The inferential model needs vegetation data to determine the deposition velocity of the abovementioned pollutants. Geographic information systems (GIS) were utilised in this study to select dominant vegetation types in the study area. The vegetation data for this study were obtained from the CSIR's Ecosystems Earth Observation Research Group. The vegetation data were digitised by the South African National Biodiversity Institute (SANBI) at a scale of 1:1 000 000. SANBI obtained the original data from Mucina and Rutherford (2006).

A study area of 10 km x 10 km (Figure 3.12) was delineated around the sampling site, and Limpopo sweet Bushveld was found to be the dominant vegetation. The size of the location was chosen and assumed to have vegetation representative of the study area. Similarly, Erisman and Draaijers (1995) used a 10 x 10 km study area when they modelled the dry deposition of trace gases using an inferential model. It is assumed that the point data can be up-scaled to a 10x10km area which in this case happens to have a constant vegetation type.

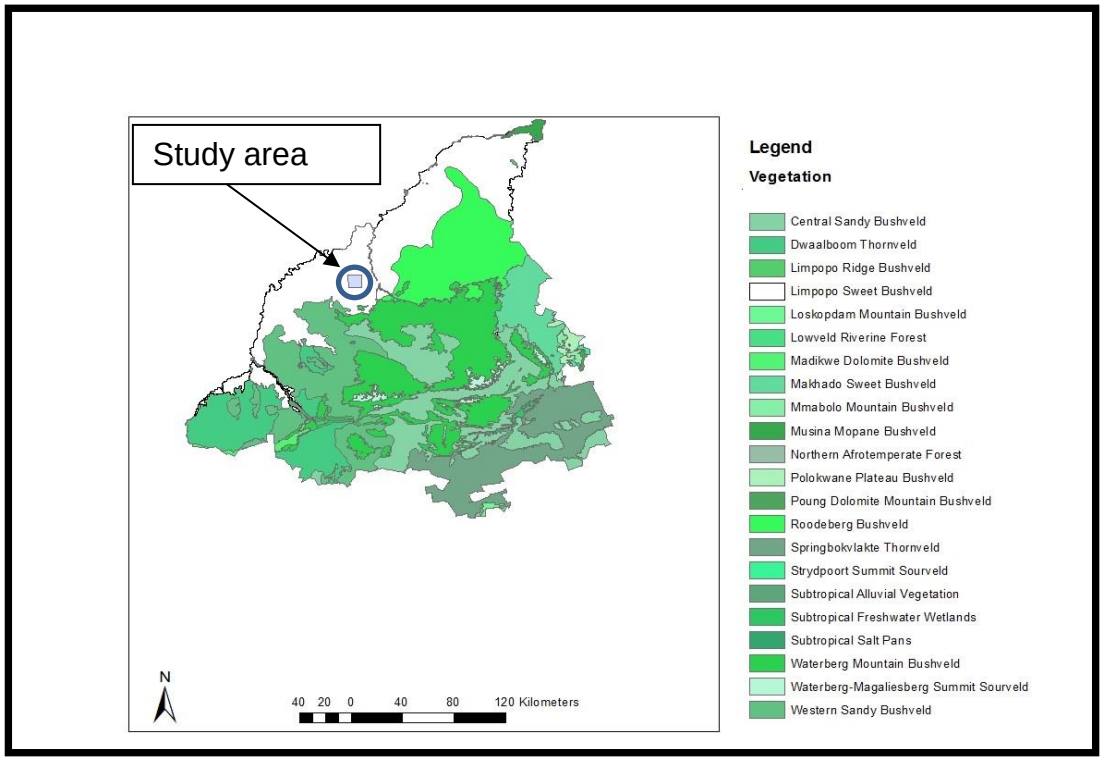


Figure 3.12: Vegetation of the Waterberg District Municipality and 10 x 10 km delineated study area (in blue circle).

3.5 Uncertainty of the inferential model

The measured and modelled deposition parameters are subjected to a number of uncertainties. (Erisman and Draaijers, 1995; Zimmermann, et al., 2006). In this study the error propagation method was applied to calculate the uncertainty of using the inferential model when calculating annual deposition velocity. This method is has been used in several studies in other countries (Heij and Schneider, 1991; Schwartz, and Slinn, 1992; Hidy, 1994; Hill, 2007). This technique was for example utilised by Erisman and Draaijers (1995), to calculate uncertainty of the deposition velocity in the Netherlands. The uncertainty of calculating V_d and flux using an inferential model in this study is described in Equation 9 (NIST/SEMATECH, 2013). This uncertainty was calculated by propagating the standard deviation of the concentrations and fluxes for each pollutant (i.e. SO_2 and NO_x (as NO_2)).

$$SD\_Vd = Vd\sqrt{\left(\frac{SD\_conc}{conc}\right)^2 + \left(\frac{SD\_flux}{flux}\right)^2} \quad (9)$$

Where, Vd is the standard deviation of deposition velocity, SD_conc is the standard deviation of the concentration, $conc$ is the mean concentration, SD_flux is the standard deviation of the deposition flux and $flux$ is the mean flux.

3.6 Hysplit Model data

This study also obtained reanalysis data from the National Center for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR). These data were downloaded from the NOAA's Air Resources Laboratory (ARL) archives. These data cover the globe from 1948 to the present and have a spatial resolution of about 2.5 x 2.5 degrees latitude-longitude (Draxler and Rolph, 2014). These archived data are reprocessed and made available in a format that is compatible with the Hysplit Model. (More details on this model can be obtained from ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis/.)

3.6.1 Cluster analysis using the Hysplit Model

Kulshresthra and Kumar (2014) stated that air masses play a role in importing and exporting depositing pollutants in nearby areas. Natural and man-made sources of air pollution from a regional level can be identified using cluster analysis of back trajectories (Katragkou et al., 2009; Xia et al., 2007). A similar approach was used in this study to understand the origin of the air masses, which could have elevated the concentrations of SO_2 and NO_x in Marapong. This method is used to aggregate similar data sets (trajectories) called clusters (Steiner et al., 2010).

This approach has been used for NO_x in countries, such as Switzerland, Germany, Australia and Slovenia, in order to understand the regional transportation of air masses in these countries (Kaiser, et al., 2007; Lawler et al, 2009; Lee et al, 2009; Baker, 2010; Liu et al., 2013b; Riuttanen et al., 2013). Other studies have applied similar approaches to understand the origin of back trajectories of air masses responsible for SO_2 concentrations in other parts of the world (Aalto et al, 2002; Tu et al., 2004; Engler et al., 2007; Francis, 2011; Afif et al, 2008; Liu, 2013; Riuttanen et al., 2013). The lifetime of NO_x is between one and two days (Liang et al., 1998; Riuttanen et al., 2013), and SO_2 can persist in the atmosphere for up to two days (Riuttanen et al., 2013). Due to the short lifetime of these pollutants, few studies have been done to relate them to long-distance transport. The lifetimes of these pollutants have not been determined in South Africa. Therefore, lifetime values of SO_2 and NO_x used in this study (i.e. 1-2 and 2, respectively) were based on those in the literature (Seinfeld and Pandis, 1998; Kaiser et al., 2007; Afif et al., 2008; Hains et al., 2008). An assumption was made that these lifetimes would be representative of NO_x and SO_2 lifetimes in South Africa. As a result of the short lifetime of NO_x in the atmosphere, the trajectories were computed for both SO_2 and NO_x over 24 hours. A similar approach was used by Kaiser et al., (2007). The analysis study assumes that the “chemical composition changes at the same rate along transport paths, the variability in the measured trace gas concentrations can be explained in terms of the trajectory origin and emission influences along the route” (Pochanart et al., 2001).

In this study, the Hysplit Model of the NOAA’s ARL was utilised to perform a trajectory analysis to determine the direction of the air mass affecting the Marapong

air quality monitoring station on a seasonal basis. This model is utilised for computing simple air parcel trajectories, as well as complex dispersion and deposition simulations (Stohl, 1996; Draxler and Hess, 1997; Draxler and Rolph, 2014). This model's calculation procedure is a hybrid between a Langrangian approach, which computes the trajectories of air parcels and follows them as they move through the model domain, and a Eulerian approach, which calculates the pollutant's fate and transportation everywhere in the modelling domain using a fixed coordinate system. This model makes use of algorithms, dispersion equations, updated stability, graphic user interfaces, as well as an option to take modules for chemical transformation into account.

When performing cluster analysis, it is necessary to decide how many clusters are needed to adequately describe the data. In the current study, six clusters were selected. The criteria for this decision depend on the analysis goal. Rather, only a specific number of clusters, which can reveal the meaningful structure in the data, will be chosen. In this procedure, individual trajectories were averaged to produce cluster means trajectories. For each cluster, cluster mean plots of all individual trajectories belonging to that cluster were produced. A limitation of this model is that trajectory analysis is used as an indication of the general airflow rather than the exact pathway of an air parcel due to the low spatial resolution of the input data.

The PC version of the model was used when doing the analysis. In this study, an attempt was made to describe the back trajectories reaching the Marapong station during different seasons for the period 2008–2012. Model parameters used for the model run when clustering are presented in Table 3.13. The height of 500 m was used because it is within the boundary layer where pollutant concentrations are assumed to be the highest (Butler et al., 2003).

Table 3.13: Hysplit Model parameters.

Model parameter	Setting
Meteorological dataset	NCEP/NCAR 2.5 degree latitude-longitude
Trajectory direction	Backward
Total run time (trajectory duration)	24 hours
Starting location	Marapong (-23.656023° 27.627999°)
Start time	12 UTC (14:00 SAST)
Start height 1	500 m

3.7 Statistical analysis

Linear correlation analysis and linear least squared regression of meteorological data were calculated using Microsoft (MS) Excel. Ambient concentration data were averaged into seasonal and annual statistics using MS Excel, and a similar procedure was applied for the deposition velocities and flux. StataIC 10 statistical software was also used to calculate analysis of variance (ANOVA) to test for the statistically significant differences (p-value) of seasonal ambient concentrations and deposition flux, as well as annual dry deposition flux. Tukey's Honestly Significant Difference (HSD) test was used to compare the differences in seasonal and annual averages of ambient concentrations and deposition flux. The Hysplit Model was also used to cluster seasonal back trajectories.

CHAPTER 4: RESULTS

This chapter provides information on the sensitivity results, uncertainty of dry deposition velocity, diurnal cycles of ambient concentrations, seasonal ambient concentrations, dry deposition velocity and flux, as well as annual concentrations and deposition flux.

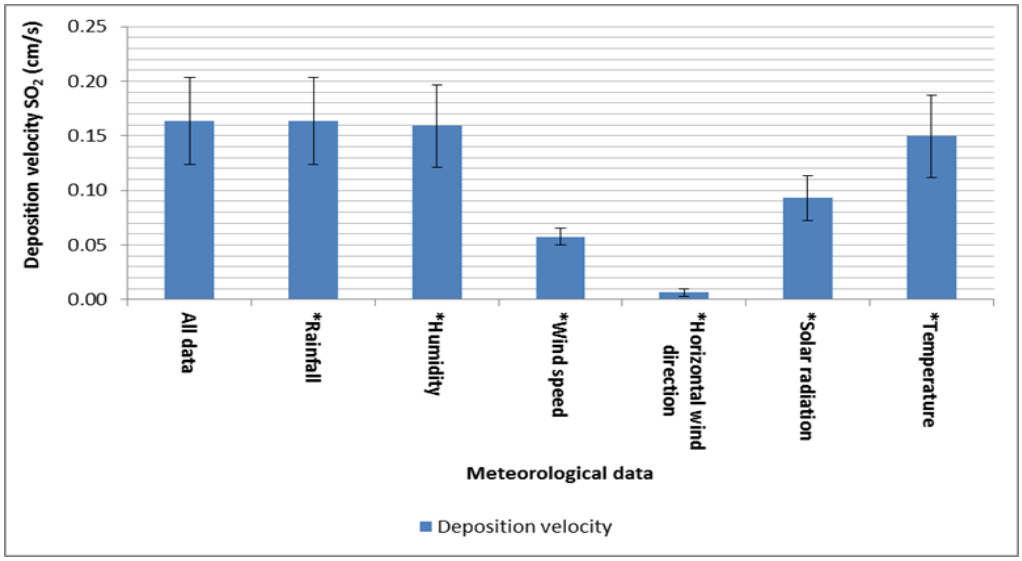
4.1 Sensitivity results of meteorological parameters

In this study, the deposition velocities of SO_2 and NO_2 were estimated. NO_x was estimated as NO_2 because NO deposition is negligible (Erisman and Draaijers, 1995). Sensitivity analysis of each meteorological parameter was conducted to understand how each meteorological parameter affects deposition velocity. The same analysis has been done before in Mpumalanga. This analysis was repeated in this study for Lephalale because the climatic conditions may be a little different from those in the Mpumalanga Highveld. In order to assess the sensitivity of the inferential model to each meteorological parameter, the meteorological data for 2008 were used to obtain baseline/reference measures of the deposition velocity of SO_2 and NO_2. Subsequently, the model was run six times with one meteorological parameter set to zero each time. In so doing, the deposition velocities of SO_2 and NO_2 were generated and comparison with the baseline case was possible. Wind direction sensitivity was not assessed because it has no effect on deposition velocity; rather it is used to calculate the important factor called standard deviation of horizontal wind direction.

This procedure was applied by Turner et al., (1995) and Mphepya (2002) in the Highveld industrial area in Mpumalanga. Figure 4.1a and Figure 4.1b below depict meteorological data versus deposition velocity to show by how much the deposition velocity of SO_2 and NO_2 will be reduced when each meteorological parameter is set to zero and when all meteorological variables are not set to zero. Figure 4.1a and Figure 4.1b clearly show that the standard deviations of horizontal wind direction (σ), wind speed and solar radiation play significant roles in determining the deposition velocity of trace gases. The SO_2 V_d experienced the largest reduction when wind

speed (65%) and horizontal wind direction (96%) were set to zero (Table 4.1). Similarly, NO_2 V_d also had a higher percentage reduction when horizontal wind direction (93%) and wind speed (55%) were set to zero (Table 4.1).

a) SO_2



a) NO_2

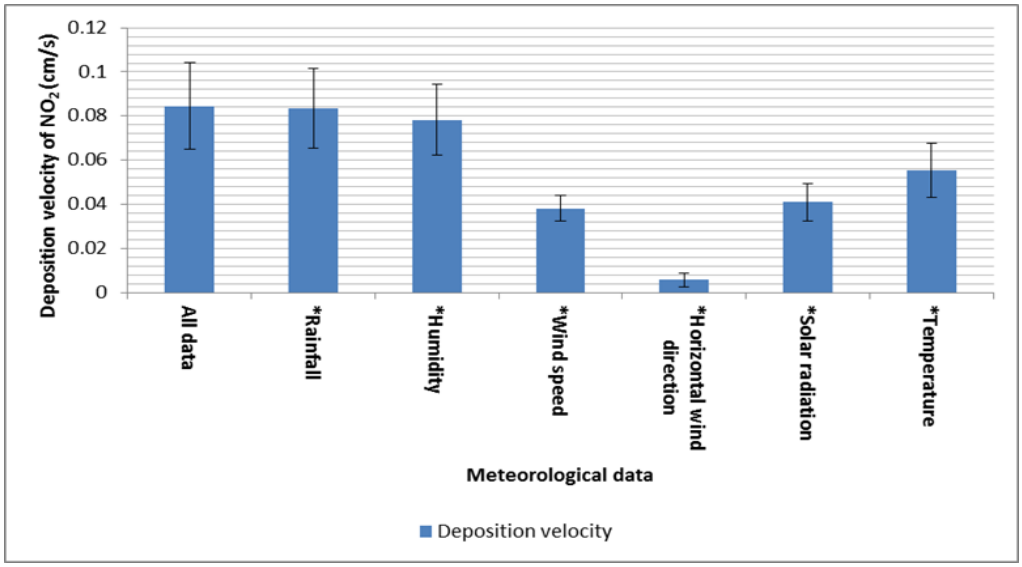


Figure 4.1: Sensitivity results of mean annual dry deposition velocity (in cm/s) of SO_2 and NO_2 in 2008.
* means this variable was set to zero during the model run.

Table 4.1: Percentage reduction of SO_2 and NO_2 deposition velocity compared to the baseline when certain meteorological data are set to zero.

Percentage reduction of each parameter	Rainfall	Humidity	Wind speed	σ	Radiation	Temperature
SO_2	3%	3%	65%	96%	43%	9%
NO_2	1%	7%	55%	93%	51%	34%

4.2 Uncertainty of dry deposition velocity using the inferential model

The uncertainty of the deposition velocity of SO_2 and NO_2, using the inferential model, was estimated using propagation of error as explained in the methodology section. Therefore, Table 4.2 below shows the percentage of uncertainty of SO_2 and NO_2 deposition velocity in 2008. SO_2 has an uncertainty of 28.8% in annual dry deposition velocity. This is within the magnitude of uncertainty of SO_2 dry deposition velocity of ±30% found by Hicks et al., (1989), Wang et al., (2003) and Meyers et al., (1991). Uncertainty of NO_2 dry deposition velocity using an inferential model is not shown in literature; only uncertainty of NO_2 dry deposition flux is shown. However, for modelling the dry deposition of NO_2, it is commonly assumed that its limiting solubility and fairly large oxidative ability result in deposition velocities similar to those of O_3 (Wesely et al., 1982; Gravenhorst and Bottger, 1983). Therefore, based on this consideration in the current study, the calculated uncertainty of NO_2 dry deposition velocity is compared to that of O_3. In this study, uncertainty of 21.3% was calculated for NO_2 deposition velocity. This is within the magnitude of ±25% uncertainty of O_3 found by Clarke et al., (1997).

These uncertainties in an inferential model are as a result of the parameterisation of dry deposition velocity (Fowler et al., 2013). The uncertainties of SO_2 dry deposition velocity could be as a result of cuticle resistance, as well as canopy aerodynamic resistance (Schwede et al., 2011). Zhang et al., (2003) also did sensitivity studies of SO_2 using an inferential model. That study attributed the uncertainties of SO_2 dry deposition velocity to cuticle resistance. However, with regard to NO_2, mesophyllic

resistance could have resulted in uncertainties because a leaf is a sink for NO_2 (Ganzeveld and Lelieveld, 1995). Other general factors that can result in uncertainties of NO_2 and SO_2 deposition velocities using an inferential model include vegetation, LAI, meteorology, as well as other surface resistance parameterisations (Nowlan et al., 2014).

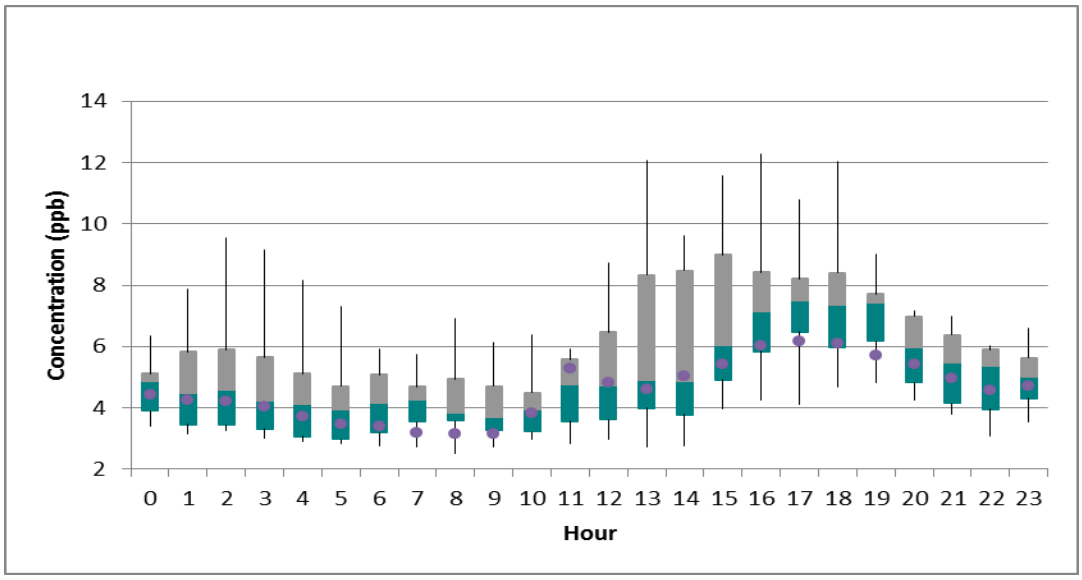
Table 4.2: The percentage of uncertainty of SO_2 and NO_2 deposition velocity in 2008.

Pollutant	Uncertainty (%)
SO_2	28.8%
NO_2	21.3%

4.3 Diurnal variations of hourly mean SO_2 and NO_x concentrations

Figure 4.2a and Figure 4.2b display diurnal cycles of mean hourly concentrations at Marapong for the period 2008–2012. The mean diurnal concentration of SO_2 peaked at 11:00 with a concentration of 4.81 ppb. Another peak was experienced at 17:00, with a concentration of 5.70 ppb. The average hourly concentrations of SO_2 for the period 2008–2012 are below the one-hour NAAQS of 134 ppb. The mean and the median of SO_2 concentration fell below 6 ppb between 0:00 and 14:00, and between 20:00 and 23:00, with a minimum concentration of 2.67 ppb at 09:00. At 13:00 and 14:00, the data are highly variable in comparison to the other times. Furthermore, diurnally, the NO_x concentrations (Figure 4.2b) peaked in the morning at 07:00 and 11:00, while in the evening, a peak was recorded at 19:00 with a value of 16.70 ppb. Again, the mean and median of NO_x concentrations were also below 20 ppb for the period 0:00-06:00 and 12:00-16:00, with a minimum of 6.34 ppb. However, NO_x also shows high data variability at 06:00, 08:00, 11:00, 19:00 and 20:00, compared to the other times. SO_2 and NO_x concentrations have distinct diurnal variations. The differences in mean and median show that there is large data variability, with most of the data being below the median (Figure 4.2a and Figure 4.2b).

a) SO_2



b) NO_x

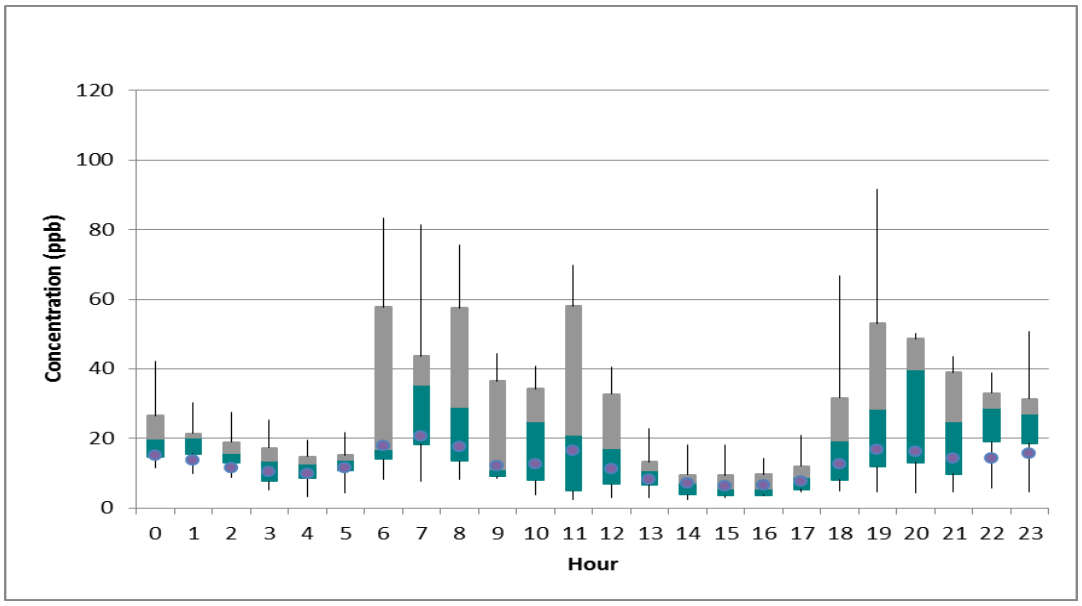


Figure 4.2: Diurnal cycles of hourly averages of a) SO_2 and b) NO_x measured at Marapong for the period 2008–2012 (the top and bottom of each box represent the 25th and 75th percentiles; the vertical line inside the box is the 50th percentile (the median); the vertical lines in the upper and lower part denote the 5th and 95th percentiles; and the purple circle represents the average.

4.4 Diurnal variations of mean hourly concentrations of NOx, NO_2 and NO

Figure 4.3 depicts diurnal cycles of mean hourly measured concentrations of NO_x, NO_2 and NO. NO and NO_2 show a similar trend, with both of them peaking in the morning at 07:00 (Figure 4.3). Two more peaks were recorded at 12:00 and 19:00 respectively (Figure 4.3). However, the diurnal concentrations of NO and NO_2 follow the same pattern as NO_x concentrations, with peaks at 07:00, 12:00 and 19:00. NO_2 is below the hourly NAAQS of 106 ppb for the entire period 2008–2012. This means that Marapong is in compliance with the 1-hr NO_2 NAAQS.

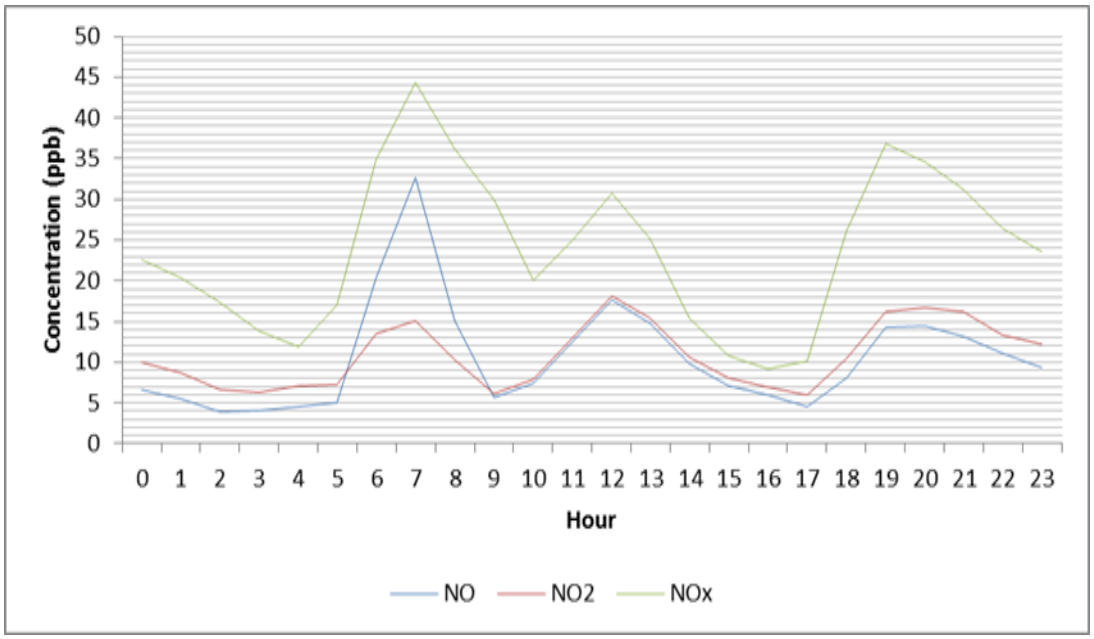


Figure 4.3: Diurnal cycles of mean hourly concentrations of NO_x, NO_2 and NO measured at the Marapong monitoring site from 2008–2012.

4.5 Diurnal seasonal mean concentrations of SO_2 and NO_x

Figure 4.4 displays seasonal diurnal cycles of SO_2 for the period 2008–2012. The concentrations of SO_2 peaked at 15:00 in summer (4.03 ppb), autumn (5.97 ppb), winter (7.17 ppb) and spring (4.02 ppb). Other peaks of SO_2 were observed in winter at 09:00 (4.55 ppb), while autumn had peaks at 13:00 (5.124 ppb), as well as at 19:00 (5.42 ppb). Additionally, spring peaks were observed at 05:00 and 11:00, with concentrations of 2.59 and 2.07 ppb, respectively.

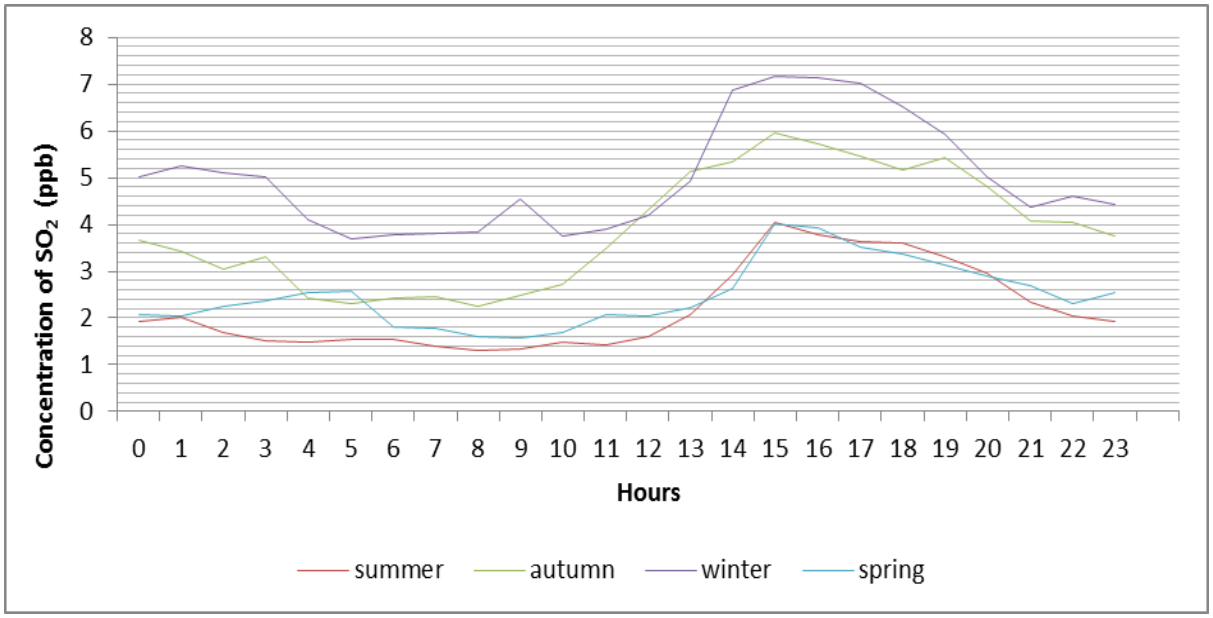


Figure 4.4: Seasonal diurnal cycle of SO_2 for the period 2008–2012.

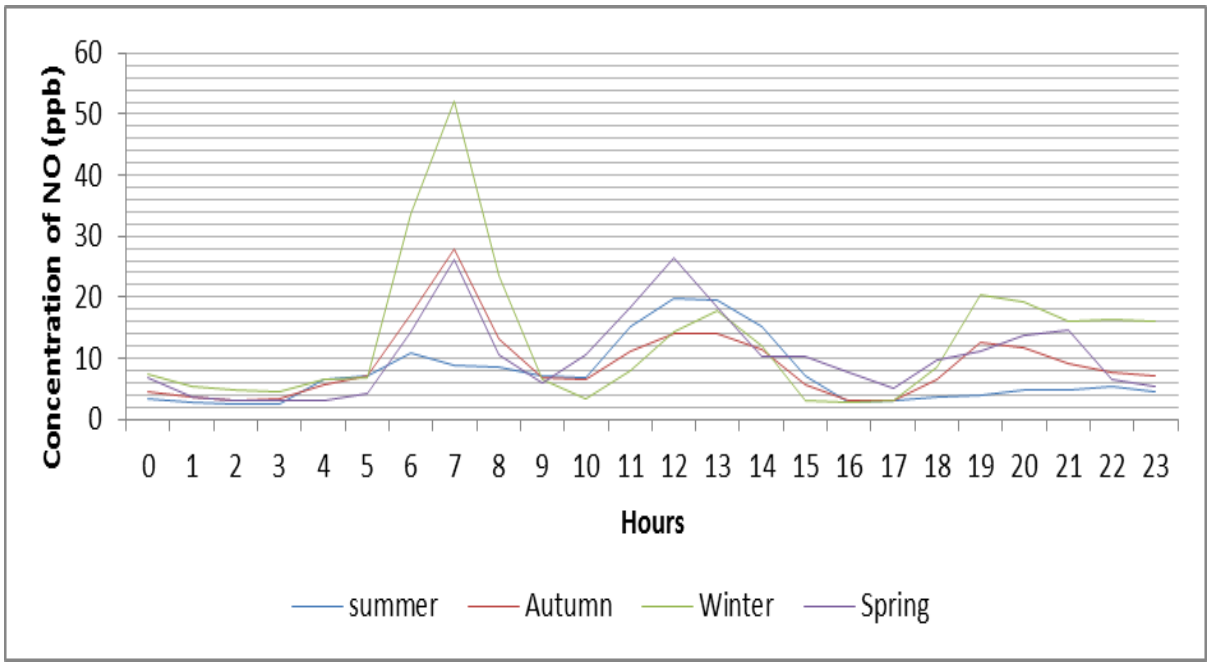
Figure 4.5a, b and c depict the seasonal diurnal cycles of NO, NO_2 and NO_x for the period 2008–2012. NO peaked at 07:00 in autumn (27.84 ppb), winter (52.04 ppb) and spring (26.25 ppb), while it peaked at 06:00 in summer (8.71 ppb) (Figure 4.5a). Other peaks of NO were observed at 13:00 for summer (15.91 ppb), autumn (13.96 ppb) and winter (17.68). In spring it peaked at 12:00 (18.21 ppb) and in autumn (12.49 ppb) and winter (20.36 ppb) it peaked at 19:00. In spring, it peaked at 12:00 (26.50 ppb).

In Figure 4.5b, NO_2 peaked at 07:00 for autumn (10.66 ppb), winter (21.17 ppb) and spring (20.32 ppb). The peak in summer was at 06:00 (9.98 ppb). Other peaks were observed at 12:00 in summer (19.51 ppb), autumn (28.37ppb), winter (13.51 ppb) and spring (26.64 ppb), while late evening peaks were observed at 19:00 for autumn (16.99 ppb) and winter (18.78 ppb). Other late peaks were observed at 21:00 in spring (17.37 ppb) and autumn (18.85 ppb), as well as at 20:00 in summer (7.79 ppb).

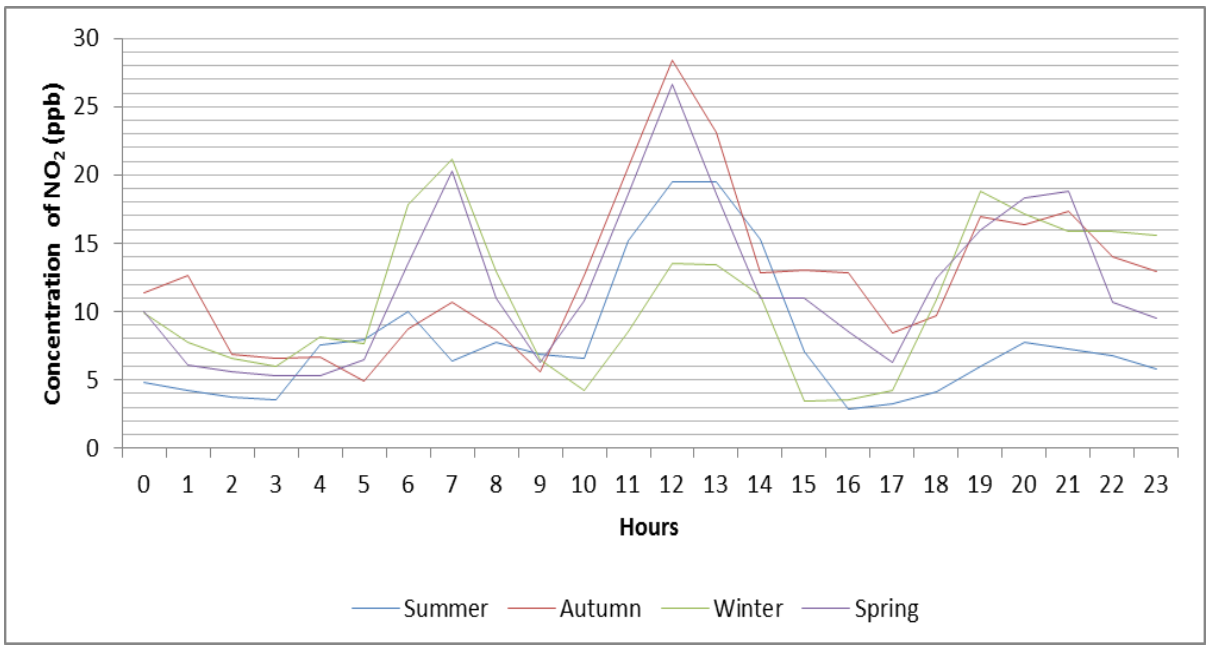
NO_x concentrations peaked at 07:00 for summer (11.60 ppb), autumn (18.74 ppb), winter (48.99 ppb) and spring (25.63 ppb) (Figure 4.5c). Similarly, other peaks were recorded at 10:00 for summer (6.55 ppb), autumn (17.11 ppb), winter (32.26 ppb) and spring (11.62 ppb). NO, NO_2 and NO_x concentrations all peaked at 07:00, which

shows that NO and NO_2 are responsible for the formation of NO_x (NO and NO_2), but at 10:00, there is a decrease of NO and NO_2, with an increase in NO_x, which could mean that NO_x might have been transported to the Marapong station.

a) NO



b) NO_2



c) NO_x

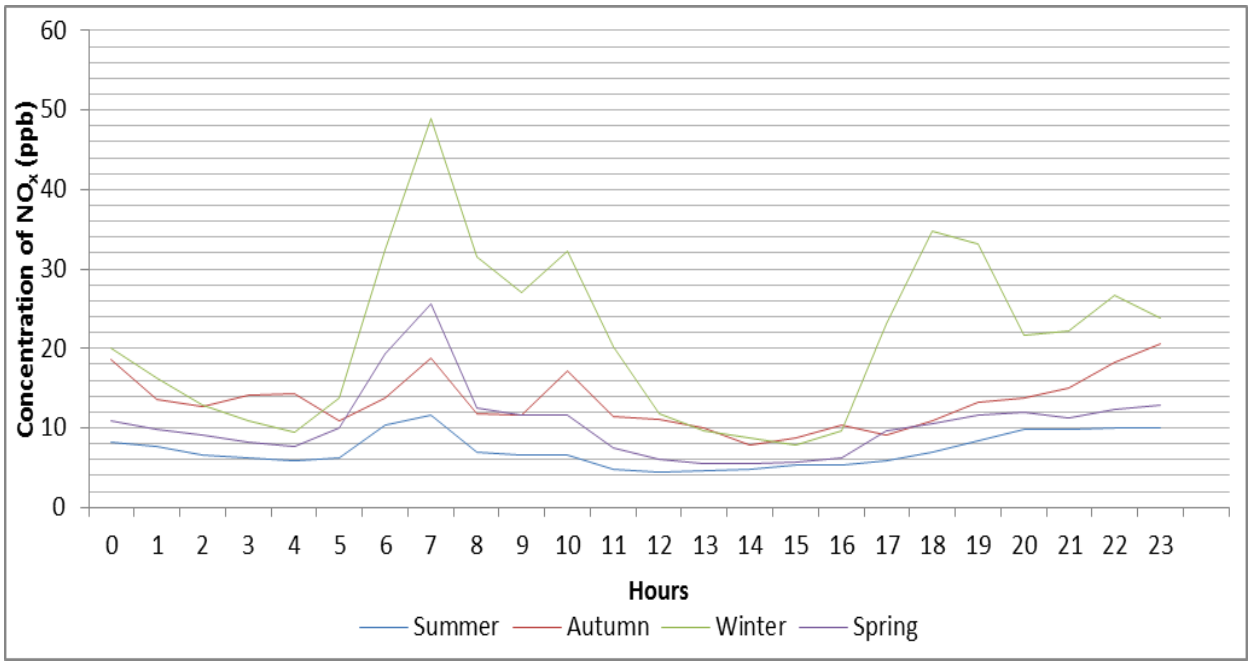
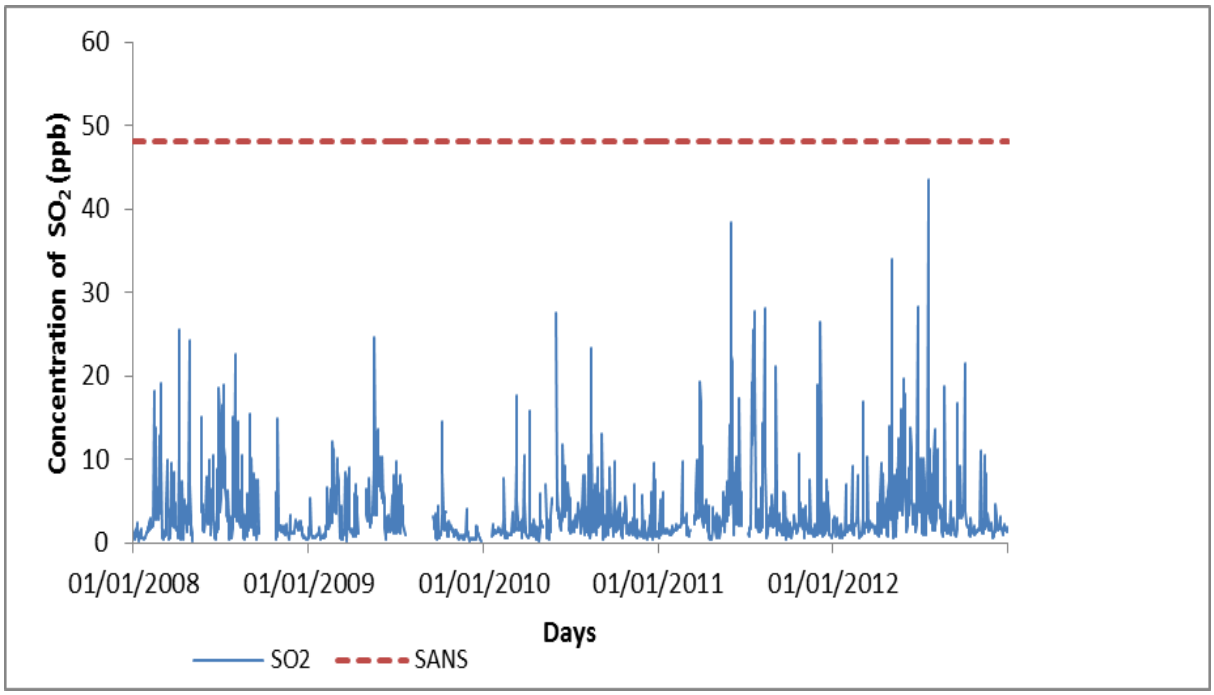


Figure 4.5: Seasonal diurnal cycles of NO, NO_2 and NO_x for the period 2008–2012.

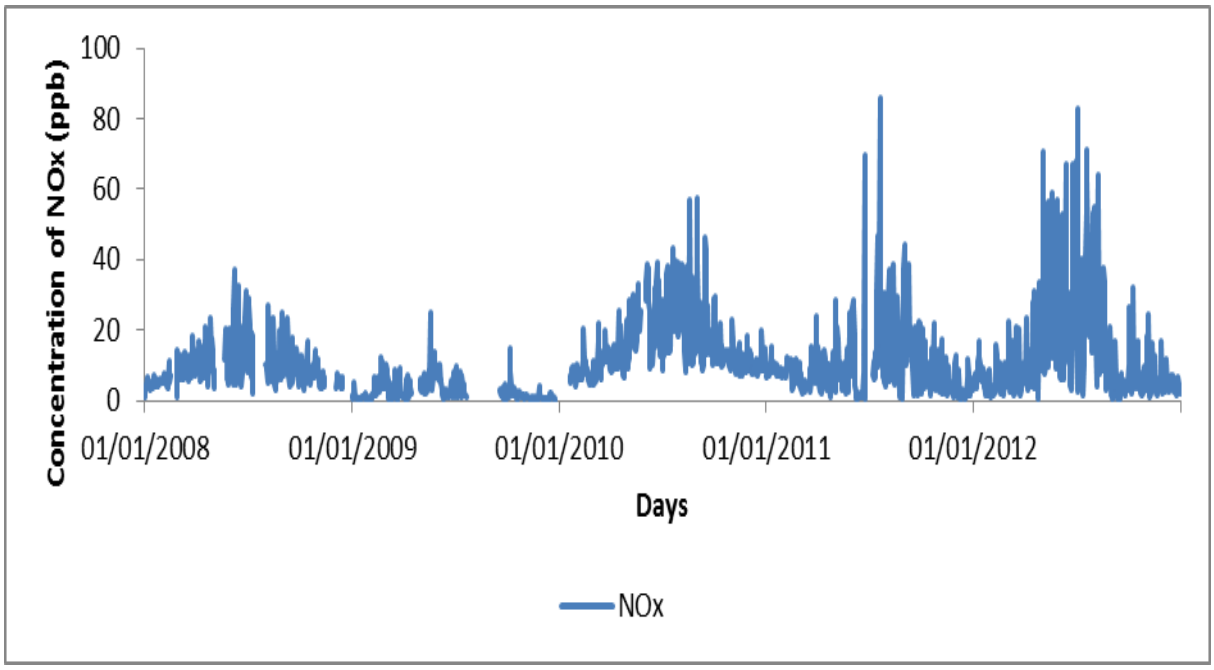
4.6 Daily mean concentrations of SO_2, NO_x and NO_2

Figure 4.6a depicts recorded daily mean concentrations of SO_2 at the Marapong station for the period 2008–2012, together with the current NAAQS of 48 ppb for SO_2 (red line). There are no exceedances of the SO_2 NAAQS for the entire period of 2008-2012. Figure 4.6b and Figure 4.6c depict recorded daily mean concentrations of NO_x and NO_2 at the Marapong station for the period 2008–2012. In South Africa, there is no NAAQS for NO_x concentrations. The mean daily concentrations of NO_x (Figure 4.6b) show an increase in these concentrations for the period 2008–2012, with 2012 having the highest daily concentration of 89.98 ppb. Furthermore, there is no daily NAAQS for NO_2 in South Africa (there are only 1-hour and annual NO_2 standards). The daily mean concentrations of NO_2 also show an increase for the period 2008–2012 (Figure 4.6c). These time series graphs also show data gaps. This was a result of power cuts and faulty analysers at the Marapong station during this period

a) SO_2


60
50
40
30
20
10
0
Concentration of SO2 (ppb)
01/01/2008
01/01/2009
01/01/2010
01/01/2011
01/01/2012
Days
SO2
SANS

b) NO_x


100
80
60
40
20
0
Concentration of NOx (ppb)
01/01/2008
01/01/2009
01/01/2010
01/01/2011
01/01/2012
Days
NOx

c) NO_2

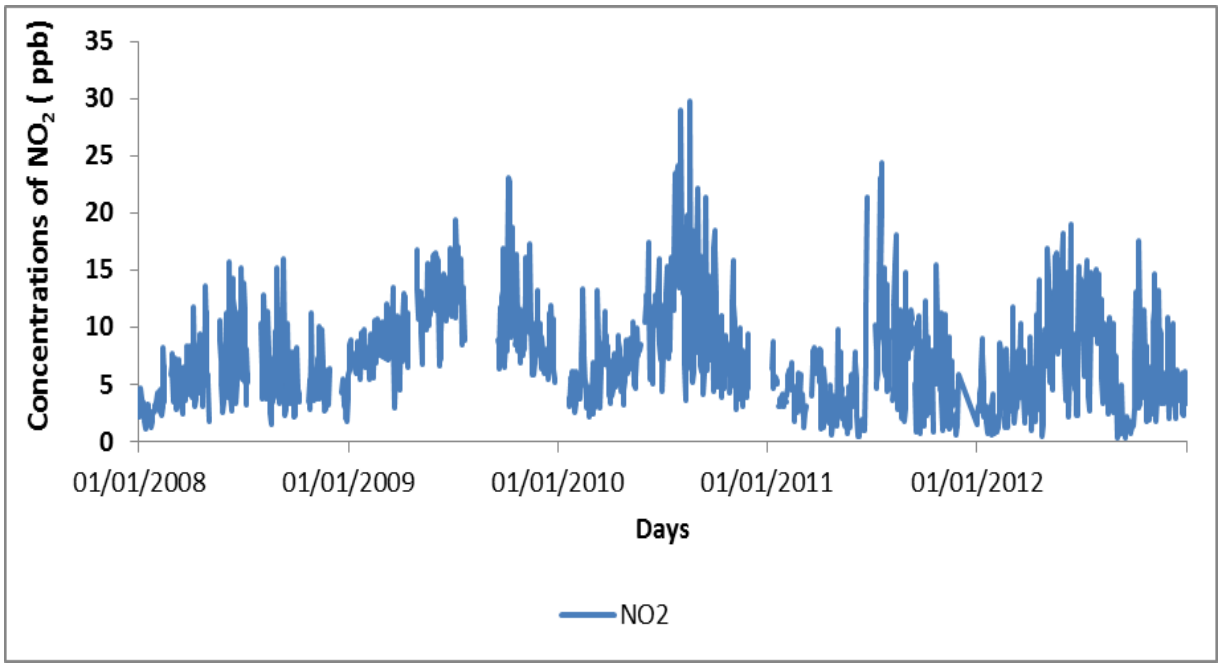


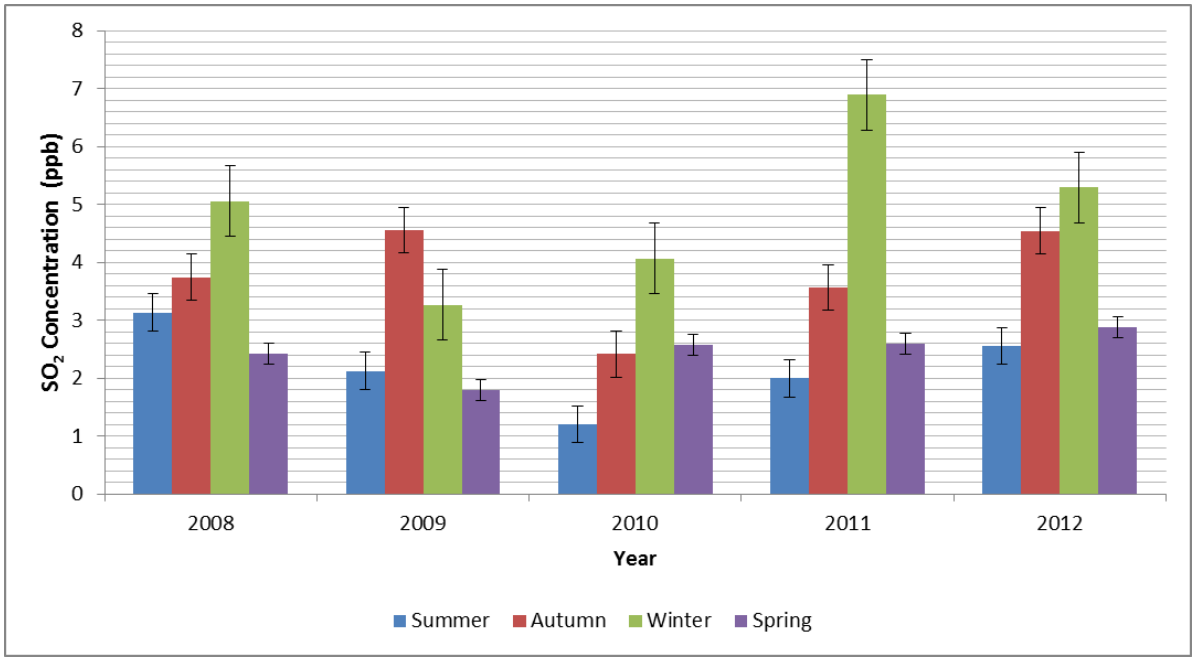
Figure 4.6: Daily averages of a) SO_2, b) NO_x and c) NO_2 concentrations measured at Marapong for the period 2008–2012 (the dotted red line indicates the one-hour NAAQS for SO_2).

4.7 Seasonal mean concentrations of SO_2, NO_2 and NO_x

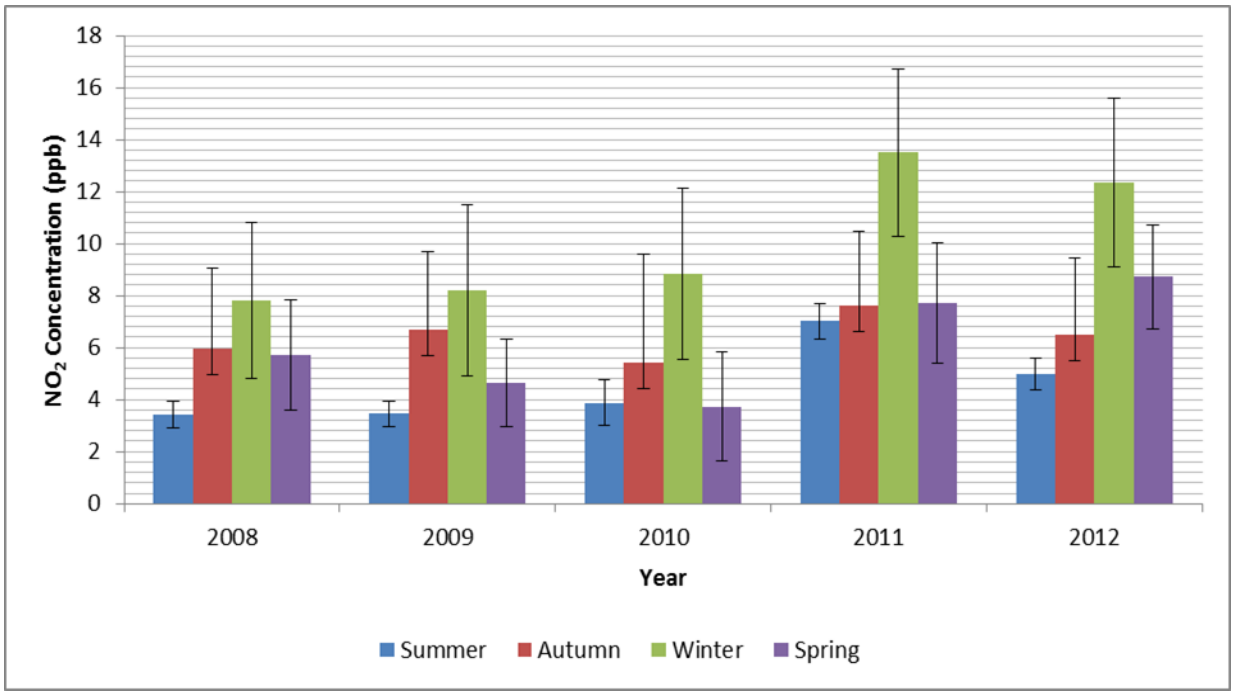
Figure 4.7a and Figure 4.7b display the seasonal averages of SO_2, NO_2 and NO_x ambient mass concentration at Marapong station for the period 2008–2012. The bars represent the seasonal averages and the vertical lines with whiskers are standard deviations (one standard deviation up and one standard deviation down). The seasonal results of SO_2 for the period 2008–2012 show that this pollutant had the lowest ambient concentrations during summer (1.20 to 3.14 ppb) and the highest ambient concentrations in winter (3.27 to 6.89 ppb) for all the years, except in 2009 when there was a concentration of 4.56 ppb in autumn (Figure 4.7a). When comparing all the seasons, there is less data variability (small standard deviation) across the seasons compared to winter, which has a slightly higher variability. In Table 4.3, there is a statistically significant difference ($p < 0.05$) between the seasonal means of SO_2 concentrations for the period 2008–2012, with a p-value of 0.0020.

NO_2 also peaked in winter for the entire period 2008–2012 with concentrations ranging between 7.81 and 13.50 ppb (Figure 4.7b). However, lower concentrations were observed in summer, ranging from 3.42 to 7.02 ppb. In general, the winter data for the entire period show high variability (large standard deviation) compared to the other seasons. A statistically significant difference in seasonal means is observed across the seasons with a p-value of 0.0010 (Table 4.3). Furthermore, the concentrations of NO_x also peaked in winter for the entire period, with a maximum concentration of 26.86 ppb observed in 2012. The data show high variability in winter (Figure 4.7c). However, summer concentrations were low, ranging between 5.70 ppb and 9.46 ppb, with 2012 having the lowest concentration of 5.70 ppb. Autumn concentrations ranged between 8.89 and 21.93 ppb, with winter ranging between 15.48 and 28.82 ppb. Additionally, spring ranged between 9.01 and 15.65 ppb. In general, high variability of data is observed in winter, compared to the other seasons. Similarly, there is a statistically significant difference ($p < 0.05$) between the seasonal means of NO_x for the period 2008–2012 because a p-value of 0.0030 was observed (Table 4.3). In addition to the above, the observed SO_2 concentrations are lower than those of NO_x.

a) SO_2



b) NO_2



c) NO_x

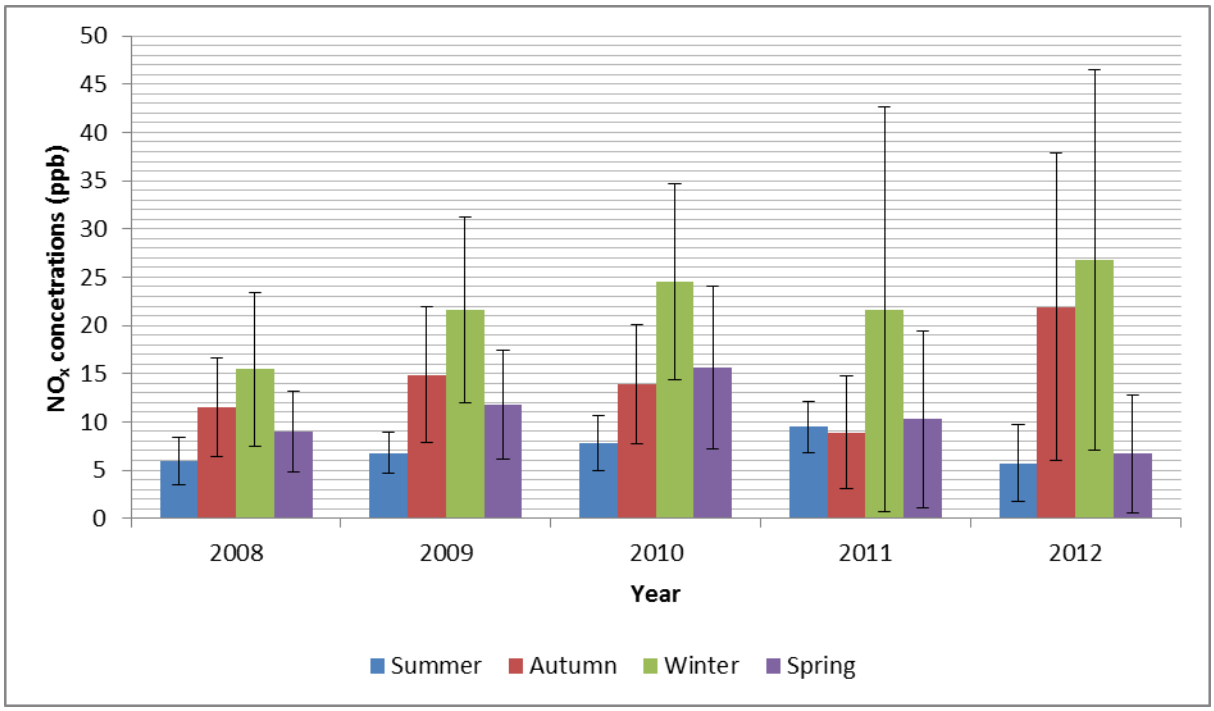


Figure 4.7: Seasonal concentrations (in ppb) and standard deviation of a) SO_2, b) NO_2 and c) NO_x for the period 2008–2012.

Table 4.3: Seasonal significant differences of SO_2, NO_2 and NOx dry deposition velocity for the period 2008–2012.

Pollutant	p-value (0.05)
SO_2	0.0020
NO_2	0.0010
NO_x	0.0030

Table 4.4 a, b and c shows the post hoc comparisons between seasonal averages of SO_2, NO_2 and NO_x ambient concentrations at Marapong for the period 2008-2012 using Tukey's HSD (Honestly significance difference) test with a value of 0.9. The seasonal statistically significant difference of ambient concentrations of SO_2, NO_2 and NO_x has no clear inter-annual trend on a seasonal scale for the entire 2008-2012 period (Table 4.4 a, b and c). However, each winter compared to the other seasons in the same year shows a statistically significant difference in SO_2, NO_2 and NO_x ambient concentrations except for SO_2 ambient concentrations in winter 2012. Interestingly, the NO_2 ambient concentrations in winter 2011 and 2012 show a statistically significant difference when compared to the other seasons across all the years. Similarly, NO_x ambient concentrations in winter 2012 show a significant difference with all the other seasons annually even though it was an exception for winter 2011 compared to winter 2009. On the other hand, the 2011 winter of SO_2 ambient concentrations indicate a statistically significant difference compared to the other seasons across the years.

Table 4.4a: Post hoc comparisons between seasonal averages of SO_2 ambient concentrations for the period 2008-2012 (HSD = 0.9). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.9.

	Year	2008	2008	2008	2008	2009	2009	2009	2009	2010	2010	2010	2010	2011	2011	2011	2011	2012	2012	2012
Year	Seasons	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA
2008	MAM	0.6																		
2008	JJA	1.9	1.3																	
2008	SON	0.7	1.3	2.6																
2009	DJF	1.0	1.6	2.9	0.3															
2009	MAM	1.4	0.8	0.5	2.1	2.4														
2009	JJA	0.1	0.5	1.8	0.9	1.1	1.3													
2009	SON	1.3	2.0	3.3	0.6	0.3	2.8	1.5												
2010	DJF	1.9	2.5	3.9	1.2	0.9	3.4	2.1	0.6											
2010	MAM	0.7	1.3	2.6	0.0	0.3	2.1	0.9	0.6	1.2										
2010	JJA	0.9	0.3	1.0	1.6	1.9	0.5	0.8	2.3	2.9	1.7									
2010	SON	0.6	1.2	2.5	0.2	0.4	2.0	0.7	0.8	1.4	0.2	1.5								
2011	DJF	1.1	1.7	3.1	0.4	0.1	2.6	1.3	0.2	0.8	0.4	2.1	0.6							
2011	MAM	0.4	0.2	1.5	1.1	1.4	1.0	0.3	1.8	2.4	1.2	0.5	1.0	1.6						
2011	JJA	3.8	3.1	1.8	4.5	4.8	2.3	3.6	5.1	5.7	4.5	2.8	4.3	4.9	3.3					
2011	SON	0.5	1.2	2.5	0.2	0.5	2.0	0.7	0.8	1.4	0.2	1.5	0.0	0.6	1.0	4.3				
2012	DJF	0.6	1.2	2.5	0.1	0.4	2.0	0.7	0.8	1.4	0.1	1.5	0.0	0.6	1.0	4.3	0.0			
2012	MAM	1.4	0.8	0.5	2.1	2.4	0.0	1.3	2.8	3.3	2.1	0.5	2.0	2.5	1.0	2.3	2.0	2.0		
2012	JJA	2.2	1.5	0.2	2.9	3.2	0.7	2.0	3.5	4.1	2.9	1.2	2.7	3.3	1.7	1.6	2.7	2.7	0.7	
2012	SON	0.3	0.9	2.2	0.5	0.8	1.7	0.4	1.1	1.7	0.5	1.2	0.3	0.9	0.7	4.0	0.3	0.3	1.7	2.4

DJF-Summer, MAM-Autumn, JJA, winter and SON-Spring

Table 4.4b: Post hoc comparisons between seasonal averages of NO_2 ambient concentrations for the period 2008-2012 (HSD = 0.9). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.9.

	Year	2008	2008	2008	2008	2009	2009	2009	2009	2010	2010	2010	2010	2011	2011	2011	2011	2012	2012	2012
Year	Seasons	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA
2008	MAM	2.5																		
2008	JJA	4.4	1.8																	
2008	SON	2.3	0.2	2.1																
2009	DJF	0.0	2.5	4.4	2.3															
2009	MAM	3.3	0.7	1.1	1.0	3.2														
2009	JJA	4.8	2.2	0.4	2.5	4.8	1.5													
2009	SON	1.2	1.3	3.1	1.1	1.2	2.0	3.5												
2010	DJF	0.5	2.1	3.9	1.8	0.4	2.8	4.3	0.8											
2010	MAM	2.0	0.5	2.4	0.3	2.0	1.3	2.8	0.8	1.5										
2010	JJA	5.4	2.9	1.0	3.1	5.4	2.2	0.6	4.2	5.0	3.4									
2010	SON	0.3	2.2	4.1	2.0	0.3	3.0	4.5	0.9	0.2	1.7	5.1								
2011	DJF	3.6	1.1	0.8	1.3	3.6	0.3	1.2	2.4	3.1	1.6	1.8	3.3							
2011	MAM	4.2	1.7	0.2	1.9	4.2	0.9	0.6	3.0	3.7	2.2	1.2	3.9	0.6						
2011	JJA	10.1	7.5	5.7	7.8	10.0	6.8	5.3	8.8	9.6	8.1	4.7	9.8	6.5	5.9					
2011	SON	4.3	1.8	0.1	2.0	4.3	1.0	0.5	3.1	3.8	2.3	1.1	4.0	0.7	0.1	5.8				
2012	DJF	1.6	1.0	2.8	0.7	1.5	1.7	3.2	0.3	1.1	0.4	3.9	1.3	2.0	2.6	8.5	2.7			
2012	MAM	3.1	0.5	1.3	0.8	3.0	0.2	1.7	1.8	2.6	1.1	2.3	2.8	0.5	1.1	7.0	1.2	1.5		
2012	JJA	8.9	6.4	4.5	6.6	8.9	5.7	4.2	7.7	8.5	6.9	3.5	8.6	5.3	4.7	1.1	4.6	7.4	5.9	
2012	SON	5.3	2.8	0.9	3.0	5.3	2.0	0.5	4.1	4.9	3.3	0.1	5.0	1.7	1.1	4.8	1.0	3.7	2.2	3.6

DJF-Summer, MAM-Autumn, JJA, winter and SON-Spring

Table 4.4c: Post hoc comparisons between seasonal averages of NO_x ambient concentrations for the period 2008-2012 (HSD = 0.9). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.9.

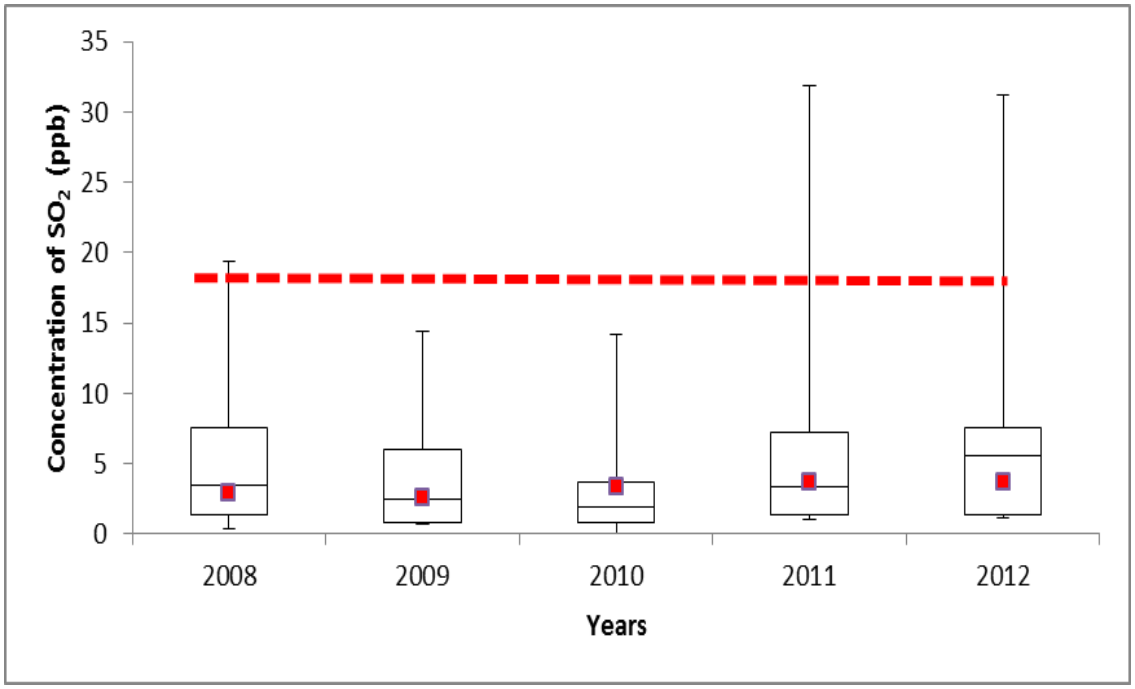
	Year	2008	2008	2008	2008	2009	2009	2009	2009	2010	2010	2010	2010	2011	2011	2011	2011	2012	2012	2012
Year	Seasons	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA
2008	MAM	5.6																		
2008	JJA	9.5	4.0																	
2008	SON	3.1	2.5	6.5																
2009	DJF	0.8	4.7	8.7	2.2															
2009	MAM	9.0	3.4	0.6	5.9	8.1														
2009	JJA	15.6	10.0	6.1	12.5	14.8	6.7													
2009	SON	5.8	0.3	3.7	2.8	5.0	3.1	9.8												
2010	DJF	1.8	3.7	7.7	1.2	1.0	7.1	13.8	4.0											
2010	MAM	7.9	2.3	1.6	4.8	7.1	1.0	7.7	2.1	6.1										
2010	JJA	18.6	13.1	9.1	15.6	17.8	9.7	3.0	12.8	16.8	10.7									
2010	SON	9.7	4.1	0.2	6.6	8.9	0.8	5.9	3.9	7.9	1.8	8.9								
2011	DJF	3.5	2.0	6.0	0.4	2.7	5.4	12.1	2.3	1.7	4.4	15.1	6.2							
2011	MAM	2.9	2.6	6.6	0.1	2.1	6.0	12.7	2.9	1.1	5.0	15.7	6.8	0.6						
2011	JJA	15.7	10.2	6.2	12.7	14.9	6.8	0.1	9.9	13.9	7.8	2.9	6.0	12.2	12.8					
2011	SON	4.3	1.2	5.2	1.3	3.5	4.6	11.3	1.5	2.5	3.6	14.3	5.4	0.8	1.4	11.4				
2012	DJF	0.2	5.8	9.8	3.3	1.1	9.2	15.9	6.1	2.1	8.1	18.9	10.0	3.8	3.2	16.0	4.6			
2012	MAM	16.0	10.4	6.5	12.9	15.2	7.0	0.4	10.2	14.1	8.1	2.7	6.3	12.5	13.0	0.3	11.7	16.2		
2012	JJA	20.9	15.3	11.3	17.8	20.0	11.9	5.3	15.0	19.0	13.0	2.2	11.2	17.4	17.9	5.2	16.5	21.1	4.9	
2012	SON	0.7	4.8	8.8	2.3	0.1	8.2	14.9	5.1	1.1	7.2	17.9	9.0	2.8	2.2	15.0	3.6	1.0	15.2	20.1

DJF-Summer, MAM-Autumn, JJA, winter and SON-Spring

4.8 Annual hourly averages of SO_2 and NO_x concentrations

Figure 4.8 represents the annual average SO_2 and NO_x concentrations recorded at Marapong station for the period 2008–2012. In general, the results indicate that SO_2 and NO_x concentrations peaked in 2011 and 2012, with averages of 3.7 ppb and 15.5 ppb respectively. For the entire period, the lowest SO_2 (0.1 ppb) and NO_x (0.3 ppb) were recorded in 2010. The median and hourly averages of SO_2 are below 10 ppb with 2008 and the period 2010–2012 showing high variability of data, except for 2009 and 2010. The annual hourly averages of SO_2 are not significantly different across the years. The ambient concentrations in Marapong are complying with the annual NAAQS because all the mean concentrations are below 19 ppb. The mean and median of NO_x concentrations were below 20 ppb for the entire period except for 2010 and 2012. Furthermore, NO_x annual mean concentrations do not show a significant difference.

a) SO_2



b) NO_x

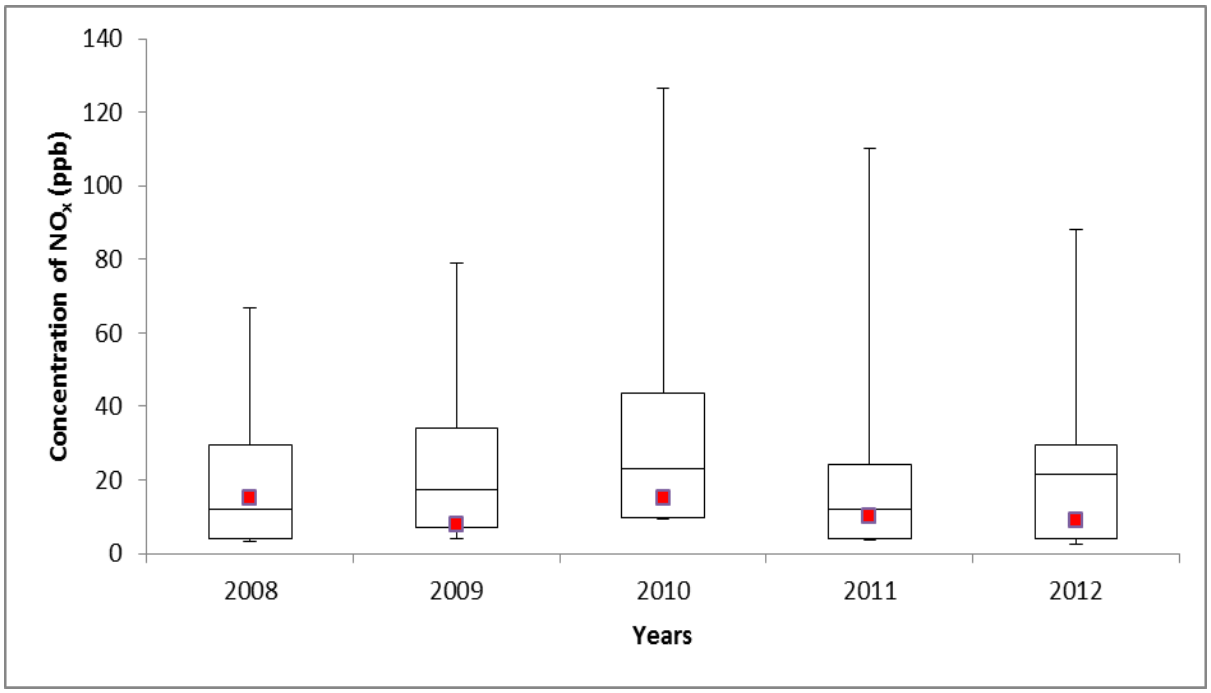


Figure 4.8: Annual hourly average of SO_2 and NO_x concentrations for the period 2008–2013 (the top and bottom of each box represent the 25th and 75th percentiles; the horizontal line inside the box is the 50th percentile (the median); the vertical lines in the upper and lower part denote minimum and maximum and the red square represents the average; the red dotted line is the annual NAAQS of SO_2.

4.9 Seasonal averaged dry deposition velocity of SO_2 and NO_2

At the Marapong sampling site, there were no humidity data for 2009, 2011 or 2012. Therefore, the 2008 and 2010 humidity data from Marapong were used during the estimation of dry deposition velocity for these years. Both years had all the meteorological data required for inferential modelling, while 2008 was used as an example to test the sensitivity of each meteorological variable. Table 4.5a and Table 4.5b display the seasonal dry deposition velocities and standard deviation of SO_2 and NO_2 for the period 2008–2012. During summer, deposition velocities of SO_2 for the period 2008–2012 varied from 0.17 to 0.23 cm/s, while winter had deposition velocities ranging from 0.09 to 0.15 cm/s (Table 4.5a). Spring deposition velocities ranged from 0.15 to 0.21 cm/s, while autumn had velocities between 0.10 and 0.19 cm/s. In summer, the highest mean deposition velocity of 0.23 ±0.10 cm/s was observed in 2012. Similarly, spring had the highest deposition velocity of 0.21 ±0.03

cm/s in 2012. The other two seasons, winter (0.15 ±0.04 cm/s) and autumn (0.19 ±0.03 cm/s), also recorded the highest deposition velocities in 2012.

Table 4.5b displays the seasonal deposition velocities and standard deviation of NO_2 for the period 2008–2012. In summer, deposition velocities of NO_2 were between 0.10 and 0.15 cm/s, while the deposition velocities in autumn ranged between 0.06 and 0.10 cm/s. Winter varied from 0.05 to 0.09 cm/s and spring ranged between 0.08 and 0.12 cm/s. The deposition velocities of NO_2 were also high in the summer of 2012, similar to those of SO_2. In general, the deposition velocity of NO_2 was the highest in summer, with a deposition velocity of 0.15 ±0.02 cm/s. The winter of 2009 had the lowest deposition velocity (0.05 ±0.004 cm/s). In addition to the above, the SO_2 deposition velocities are higher than those of NO_2. Using the 2008 and 2010 humidity data to estimate deposition velocities of SO_2 and NO_2 in 2009, 2011 and 2012, the results overlap (Table 4.5b); hence the results for each year show a negligible difference.

Table 4.5a: Seasonal average dry deposition velocities (cm/s) and standard deviation of SO_2 and NO_2 for the period 2008–2012.

a) SO_2

Season	2008	2009 (using 2008 humidity data)	2009 (using 2010 humidity data)	2010	2011 (using 2008 humidity data)	2011 (using 2010 humidity data)	2012 (using 2008 humidity data)	2012 (using 2010 humidity data)
Summer	0.19 ±0.05	0.17 ±0.10	0.17 ±0.09	0.19 ±0.08	0.18 ±0.010	0.17 ±0.12	0.23 ±0.10	0.23 ±0.10
Autumn	0.15 ±0.01	0.10 ±0.01	0.10 ±0.02	0.14 ±0.02	0.16 ±0.09	0.18 ±0.10	0.19 ±0.03	0.19 ±0.03
Winter	0.13 ±0.06	0.09 ±0.005	0.09 ±0.03	0.12 ±0.06	0.14 ±0.06	0.14 ±0.04	0.15 ±0.04	0.15 ±0.03
Spring	0.18 ±0.08	0.15 ±0.10	0.1 5±0.09	0.16 ±0.07	0.17 ±0.08	0.17 ±0.07	0.21 ±0.03	0.21 ±0.03

b) NO_2

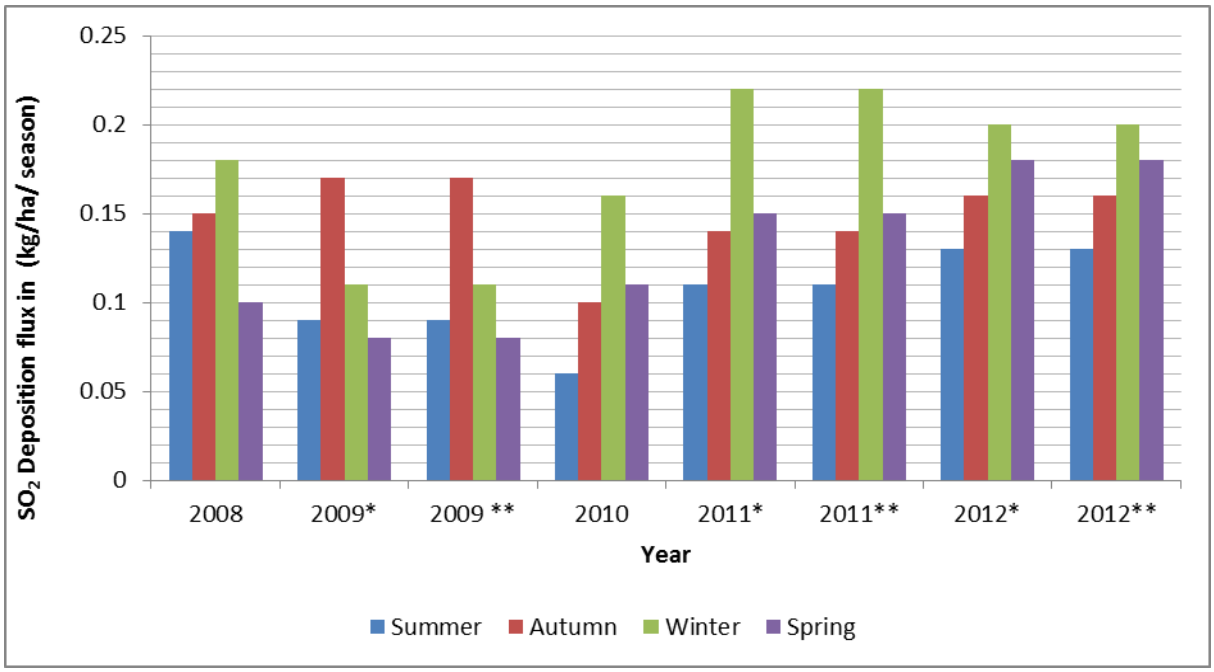
Season	2008	2009 (using 2008 humidity data)	2009 (using 2010 humidity data)	2010	2011 (using 2008 humidity data)	2011 (using 2010 humidity data)	2012 (using 2008 humidity data)	2012 (using 2010 humidity data)
Summer	0.12 ±0.002	0.10 ±0.003	0.10 ±0.003	0.11 ±0.003	0.13 ±0.03	0.13 ±0.03	0.15 ±0.02	0.15 ±0.02
Autumn	0.08 ±0.003	0.06 ±0.001	0.06 ±0.002	0.08 ±0.003	0.09 ±0.003	0.09 ±0.002	0.10 ±0.05	0.10 ±0.05
Winter	0.07 ±0.001	0.05 ±0.005	0.05 ±0.004	0.07 ±0.04	0.06 ±0.01	0.08 ±0.02	0.09 ±0.02	0.09 ±0.02
Spring	0.09 ±0.02	0.08 ±0.002	0.08 ±0.002	0.09 ±0.02	0.10 ±0.02	0.10 ±0.02	0.12 ±0.08	0.12 ±0.09

4.10 Seasonal dry deposition flux of SO_2 and NO_x (as NO_2)

In this study NO_x dry deposition flux was estimated as NO_2 because NO deposition is negligible. Figure 4.9a and 4.9b show the seasonal dry deposition flux of SO_2 (as S) and NO_2 (as N) for the period 2008–2012. Summer dry deposition flux of SO_2 ranged between 0.06 and 0.14 kg S ha^{-1} per season, while autumn calculated deposition flux between 0.10 and 0.17 kg S ha^{-1} per season. Winter had deposition flux ranging between 0.11 and 0.22 kg S ha^{-1} per season, with spring having values between 0.08 and 0.18 kg S ha^{-1} per season. Seasonal dry deposition flux of SO_2 varies for the entire period with winter recording the highest deposition flux (0.18 to 0.22 kg S ha^{-1} per season), except in 2009, when it peaked in autumn (0.17 kg S ha^{-1} per season). There is a significant difference between these seasons (Table 4.6), and the deposition flux of 2009, 2011 and 2012 overlap when using 2008 and 2010 humidity data.

The dry deposition flux of NO_2 (as N) (Figure.4.9b) in summer ranged between 0.14 and 0.23 kg N ha^{-1} per season, with autumn ranging between 0.20 and 0.27 kg N ha^{-1} per season. Winter had values ranging between 0.26 and 0.33 kg N ha^{-1} per season, while spring ranged between 0.19 and 0.23 kg N ha^{-1} per season. The results of deposition flux using the 2008 and 2010 humidity data for 2009, 2011 and 2012 show overlapping results (Figure 4.9b). There is a statistically significant difference between all the seasons across the years (Table 4.6) and the deposition flux of 2009, 2011 and 2012 overlap when using 2008 and 2010 humidity data.

a) SO_2 (as S)



b) NO_2 (N)

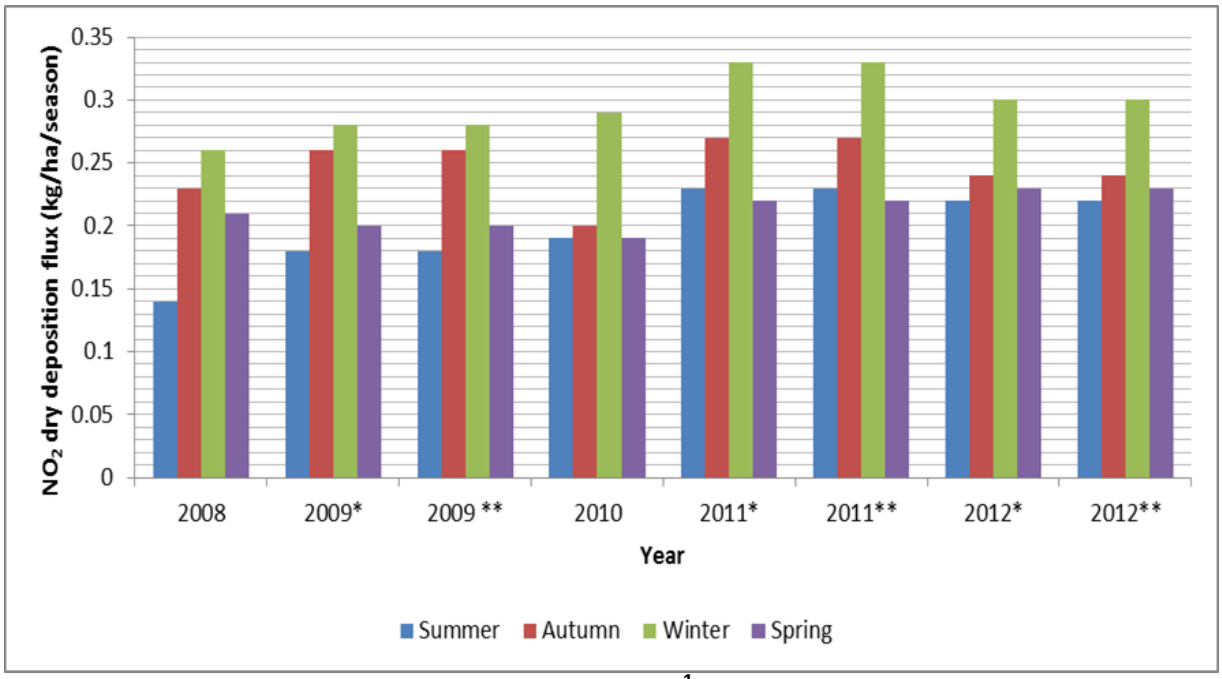


Figure 4.9: Seasonal dry deposition flux (kg.ha^{-1} per three-month period (season) of SO_2 (as S) and NO_2 (as N) for the period 2008–2012.

* means 2008 humidity data was used when calculating flux. ** means 2010 humidity data was used when calculating flux.

Table 4.6: Seasonal significant differences in SO_2 (as S) and NO_2 (as N) deposition flux for the period 2008–2012.

Pollutant	p-value (0.05)
SO_2	0.0004
NO_x (as NO_2)	0.0001

Table 4.7 a and b presents the post hoc comparisons of seasonal deposition flux of SO_2 and NO_x (as NO_2) for the period 2008-2012 using the Tukey's HSD test with a value of 0.03. Like SO_2, NO_2 and NO_x concentrations these dry deposition fluxes of SO_2 and NO_x (as NO_2) show no statistical significant difference trend. The SO_2 winter deposition flux is also statistically significant difference in the winter of each year in comparison to the other seasons in the same year, except in winter 2008, winter 2009 and winter 2012. One other thing which is interesting is that winter 2011 is statistically significantly different from the other seasons across the years. When comparing NO_x (as NO_2) seasonal flux for each winter with other seasons within the same year, it also shows a statistical significant difference from these seasons apart from winter 2008 and 2009. One other thing which is interesting is that seasonal dry deposition flux of NO_x (as NO_2) winter 2011 is statistically significantly different from the other seasons across the years.

Table 4.7a: Post hoc comparisons between seasonal averages of SO_2 dry deposition flux for the period 2008-2012 (HSD =0.03). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.03.

	Year	2008	2008	2008	2008	2009	2009	2009	2009	2010	2010	2010	2010	2011	2011	2011	2011	2012	2012	2012
Year	Seasons	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA
2008	MAM	0.01																		
2008	JJA	0.04	0.03																	
2008	SON	0.04	0.05	0.08																
2009	DJF	0.05	0.06	0.09	0.01															
2009	MAM	0.03	0.02	0.01	0.07	0.08														
2009	JJA	0.03	0.04	0.07	0.01	0.02	0.06													
2009	SON	0.06	0.07	0.1	0.02	0.01	0.09	0.03												
2010	DJF	0.08	0.09	0.12	0.04	0.03	0.11	0.05	0.02											
2010	MAM	0.04	0.05	0.08	0	0.01	0.07	0.01	0.02	0.04										
2010	JJA	0.02	0.01	0.02	0.06	0.07	0.01	0.05	0.08	0.1	0.06									
2010	SON	0.03	0.04	0.07	0.01	0.02	0.06	0	0.03	0.05	0.01	0.05								
2011	DJF	0.03	0.04	0.07	0.01	0.02	0.06	0	0.03	0.05	0.01	0.05	0							
2011	MAM	0	0.01	0.04	0.04	0.05	0.03	0.03	0.06	0.08	0.04	0.02	0.03	0.03						
2011	JJA	0.08	0.07	0.04	0.12	0.13	0.05	0.11	0.14	0.16	0.12	0.06	0.11	0.11	0.08					
2011	SON	0.01	0	0.03	0.05	0.06	0.02	0.04	0.07	0.09	0.05	0.01	0.04	0.04	0.01	0.07				
2012	DJF	0.01	0.02	0.05	0.03	0.04	0.04	0.02	0.05	0.07	0.03	0.03	0.02	0.02	0.01	0.09	0.02			
2012	MAM	0.02	0.01	0.02	0.06	0.07	0.01	0.05	0.08	0.1	0.06	0	0.05	0.05	0.02	0.06	0.01	0.03		
2012	JJA	0.06	0.05	0.02	0.1	0.11	0.03	0.09	0.12	0.14	0.1	0.04	0.09	0.09	0.06	0.02	0.05	0.07	0.04	
2012	SON	0.04	0.03	0	0.08	0.09	0.01	0.07	0.1	0.12	0.08	0.02	0.07	0.07	0.04	0.04	0.03	0.05	0.02	0.02

DJF-Summer, MAM-Autumn, JJA, winter and SON-Spring

Table 4.7b: Post hoc comparisons between seasonal averages of NO_x (as NO_2) dry deposition flux for the period 2008-2012 (HSD =0.03). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.03.

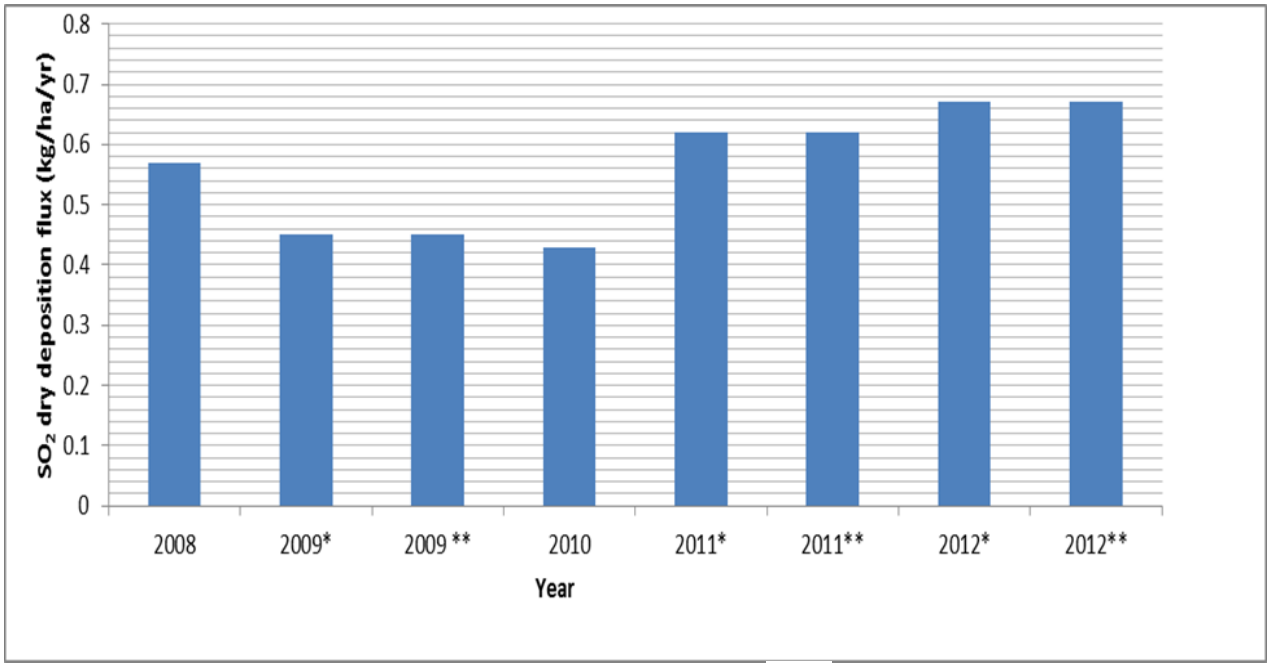
	Year	2008	2008	2008	2008	2009	2009	2009	2009	2010	2010	2010	2010	2011	2011	2011	2011	2012	2012	2012
Year	Seasons	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON	DJF	MAM	JJA
2008	MAM	0.09																		
2008	JJA	0.12	0.03																	
2008	SON	0.07	0.02	0.05																
2009	DJF	0.04	0.05	0.08	0.03															
2009	MAM	0.12	0.03	0	0.05	0.08														
2009	JJA	0.14	0.05	0.02	0.07	0.1	0.02													
2009	SON	0.06	0.03	0.06	0.01	0.02	0.06	0.08												
2010	DJF	0.05	0.04	0.07	0.02	0.01	0.07	0.09	0.01											
2010	MAM	0.06	0.03	0.06	0.01	0.02	0.06	0.08	0	0.01										
2010	JJA	0.15	0.06	0.03	0.08	0.11	0.03	0.01	0.09	0.1	0.09									
2010	SON	0.05	0.04	0.07	0.02	0.01	0.07	0.09	0.01	0	0.01	0.1								
2011	DJF	0.09	0	0.03	0.02	0.05	0.03	0.05	0.03	0.04	0.03	0.06	0.04							
2011	MAM	0.13	0.04	0.01	0.06	0.09	0.01	0.01	0.07	0.08	0.07	0.02	0.08	0.04						
2011	JJA	0.19	0.1	0.07	0.12	0.15	0.07	0.05	0.13	0.14	0.13	0.04	0.14	0.1	0.06					
2011	SON	0.08	0.01	0.04	0.01	0.04	0.04	0.06	0.02	0.03	0.02	0.07	0.03	0.01	0.05	0.11				
2012	DJF	0.08	0.01	0.04	0.01	0.04	0.04	0.06	0.02	0.03	0.02	0.07	0.03	0.01	0.05	0.11	0			
2012	MAM	0.1	0.01	0.02	0.03	0.06	0.02	0.04	0.04	0.05	0.04	0.05	0.05	0.01	0.03	0.09	0.02	0.02		
2012	JJA	0.16	0.07	0.04	0.09	0.12	0.04	0.02	0.1	0.11	0.1	0.01	0.11	0.07	0.03	0.03	0.08	0.08	0.06	
2012	SON	0.09	0	0.03	0.02	0.05	0.03	0.05	0.03	0.04	0.03	0.06	0.04	0	0.04	0.1	0.01	0.01	0.01	0.07

DJF-Summer, MAM-Autumn, JJA, winter and SON-Spring

4.11 Total annual dry deposition flux of SO_2 and NO_x (as NO_2)

Figure 4.10a and Figure 4.10b below represent the annual dry deposition flux of SO_2 (as S) and NO_2 (as N) for the period 2008–2012. The annual dry deposition flux of SO_2 ranged between 0.43 and 0.67 kg S ha^{-1} yr^{-1} (Figure 4.10a). The highest dry deposition flux of 0.67 kg S ha^{-1} yr^{-1} was observed in 2012, with 2010 having the lowest (0.43 kg S ha^{-1} yr^{-1}). For NO_2 (as N), the lowest dry deposition flux of 0.84 kg N ha^{-1} yr^{-1} was observed in 2008, and the highest was observed in 2011 (1.05 kg N ha^{-1} yr^{-1}) (Figure 10.4b). The NO_2 (as N), dry deposition flux of the entire period varied between 0.84 and 1.05 kg N ha^{-1} yr^{-1}. There is a statistical significant difference between these dry deposition fluxes (Table 4.8)

a) SO_2 (as S)



b) NO_2 (as N)

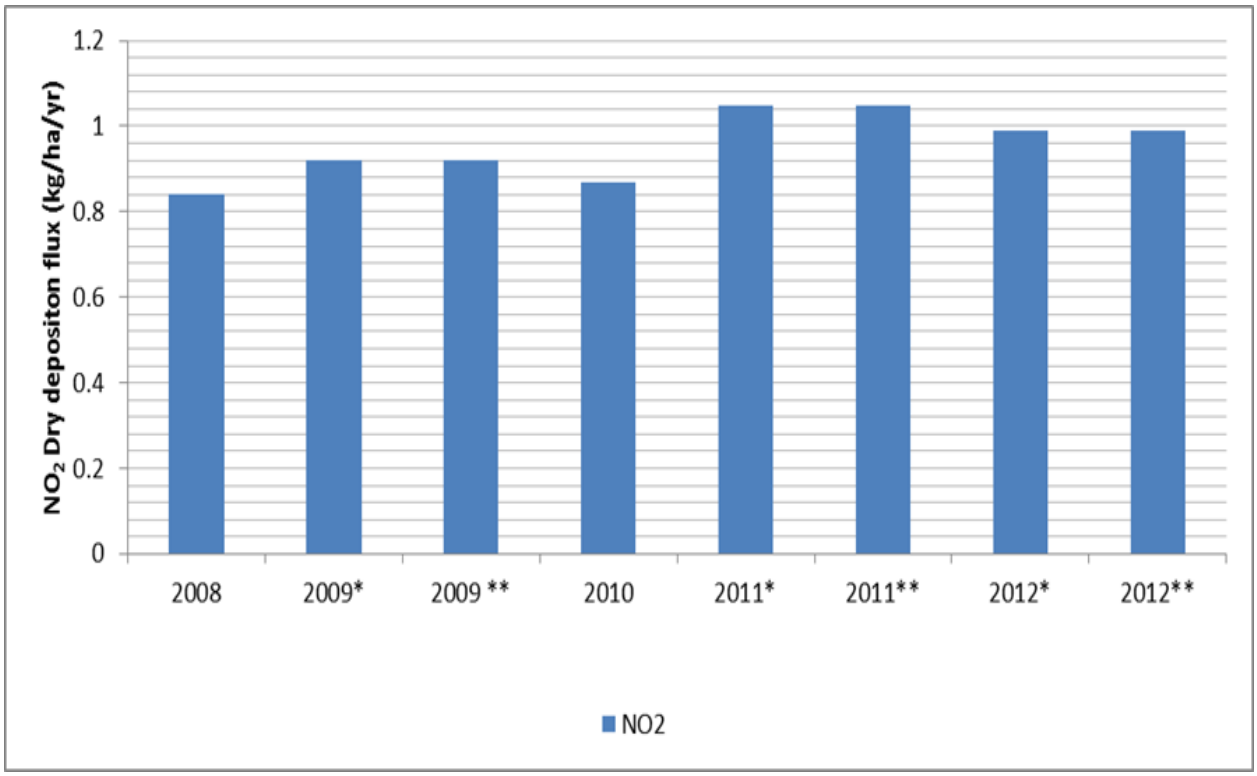


Figure 4.10: Annual dry deposition flux (in kg/ha/year) of a) SO_2 (as S) and b) NO_2 (as N) for the period 2008–2012.
* means 2008 humidity data was used when calculating flux. ** means 2010 humidity data was used when calculating flux**.**

Table 4.8 Annual statistical significance of SO_2 (s) and NO_2 (as N) dry deposition flux for the period 2008-2012

Pollutant	p-value (0.05)
SO_2 (as S)	0.004
NO_2 (as N)	0.003

Table 4.9a indicates the post hoc comparisons between annual dry deposition fluxes of SO_2 (as S) and NO_2 (as N) at Marapong for the period 2008-2012 using the Tukey's HSD test. The results indicate that the mean SO_2 (as S) annual dry deposition fluxes in 2008 are significantly different from those in 2009 and 2010, whereas 2009 annual dry deposition fluxes of SO_2 (as S) are significantly different from 2011 and 2012. There is also a significant difference in 2010 annual SO_2 (as S) dry deposition flux from 2011 and 2012, while 2011 has no significant difference with 2012.

The annual dry deposition fluxes of NO_2 (as N) in 2008 vary significantly from those in 2011 and 2012 (Table 4.9b). There is also a significant difference between the NO_2 (as N) annual deposition fluxes in 2009 with those of 2011, while 2010 vary significantly with 2011 and 2012, plus 2011 shows no significant difference from 2012.

Table 4.9a: Post hoc comparisons between annual SO_2 (as S) dry deposition flux for the period 2008-2012 (HSD=0.10). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.10.

Year	2008	2009	2010	2011
2009	0.12			
2010	0.14	0.02		
2011	0.05	0.17	0.19	
2012	0.10	0.22	0.24	0.05

Table 4.9b: Post hoc comparisons between annual NO_2 (as N) dry deposition flux for the period 2008-2012 (HSD = 0.10). The values that are highlighted are those where a significant difference was not found. Their mean differences are above 0.010.

Year	2008	2009	2010	2011
2009	0.08			
2010	0.03	0.05		
2011	0.21	0.13	0.18	
2012	0.15	0.07	0.12	0.06

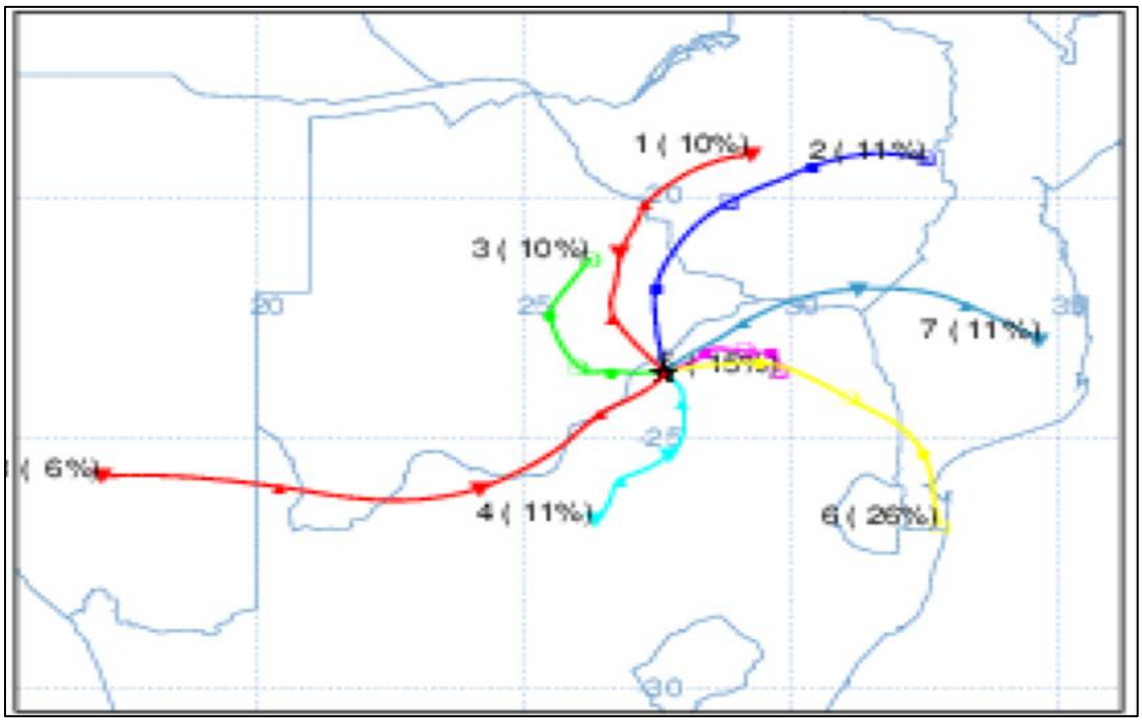
4.12 Seasonal back trajectories

Back trajectory cluster analysis was utilised to determine the direction of air masses reaching the Marapong station for the period 2008–2012. Figure 4.11a, Figure 4.11b, Figure 4.11c and Figure 4.11d depict seasonal back trajectories grouped according to the categories of summer, autumn, winter and spring for the period 2008–2012. The back trajectories of summer (31%) for the period 2008–2012 originated north of the station. Other trajectories originated east and southeast of the station (52%) and 17% of back trajectories were from the southwest. In autumn, 61% of trajectories are from the east and southeast of the station, with 31% from the north.

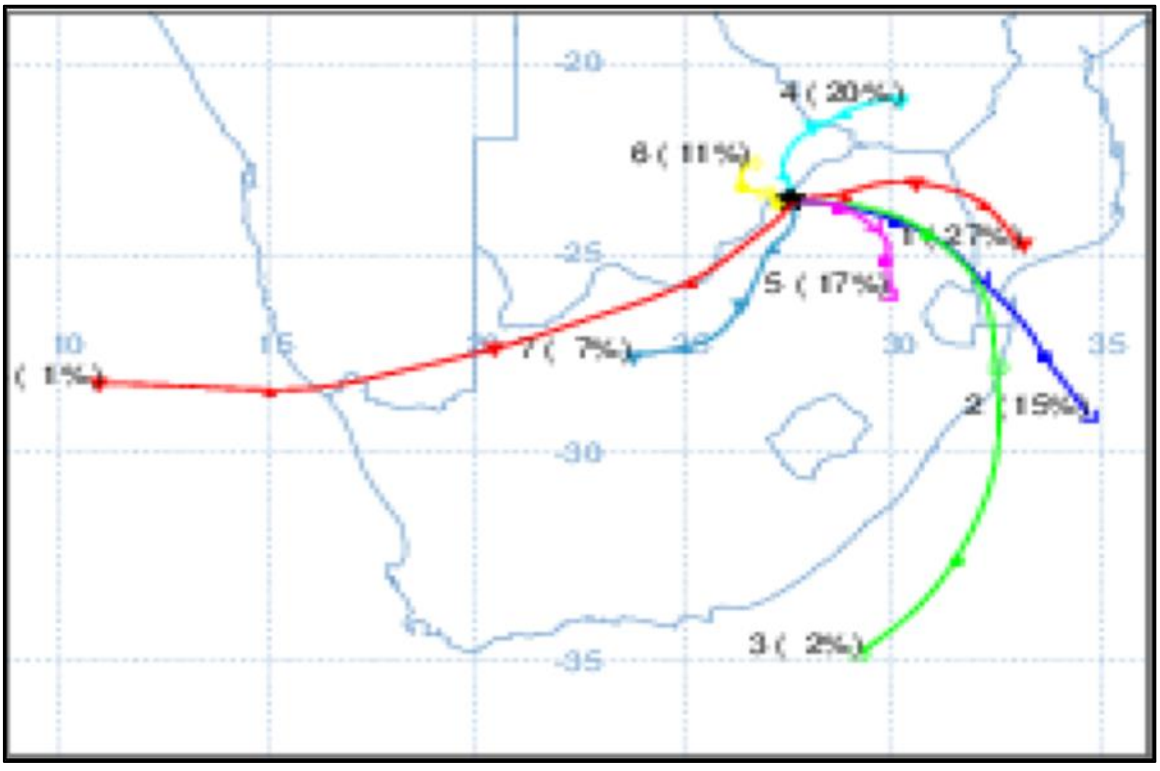
In winter, the dominant wind direction is from the east and southeast (53%), while 35% of back trajectories were observed from the north. The remaining 12% was from

the west and southwest of the station. During spring, 53% of the back trajectories were from the east and southeast of the station. The other 29% of back trajectories were from the north of the station, with 4% from the southwest. Additionally, 14% were observed from the northwest of the station. In general, most (above 52%) of the air masses originate east and southeast of the station.

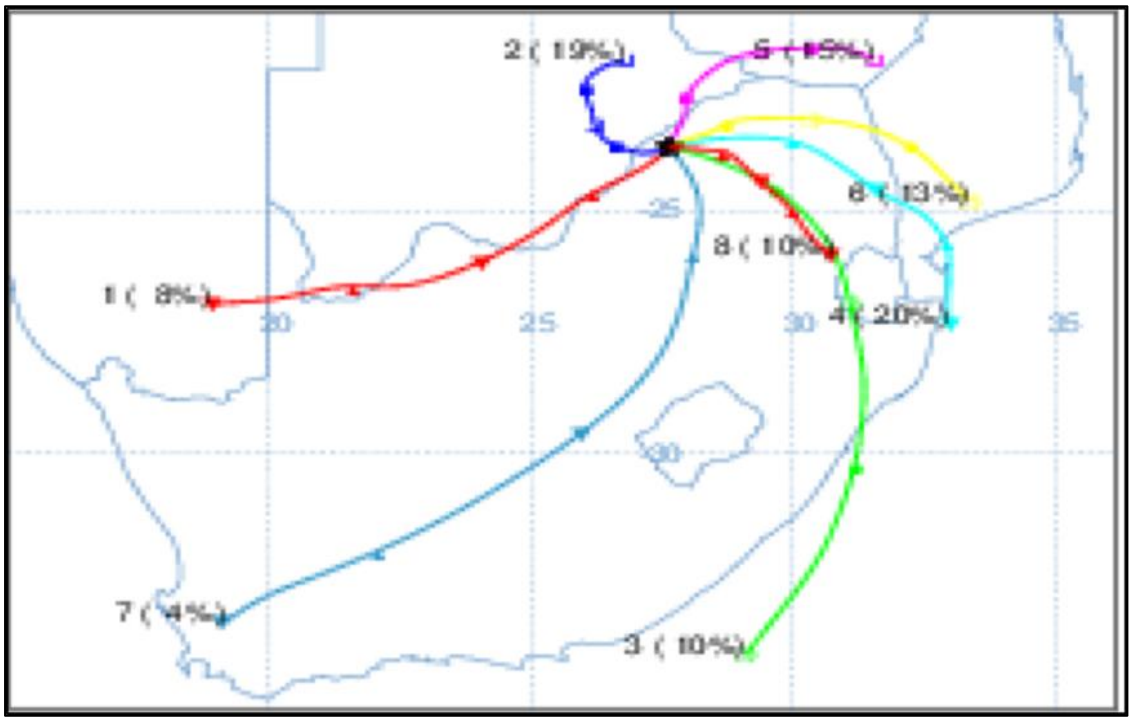
a) Summer



b) Autumn



c) Winter



d) Spring

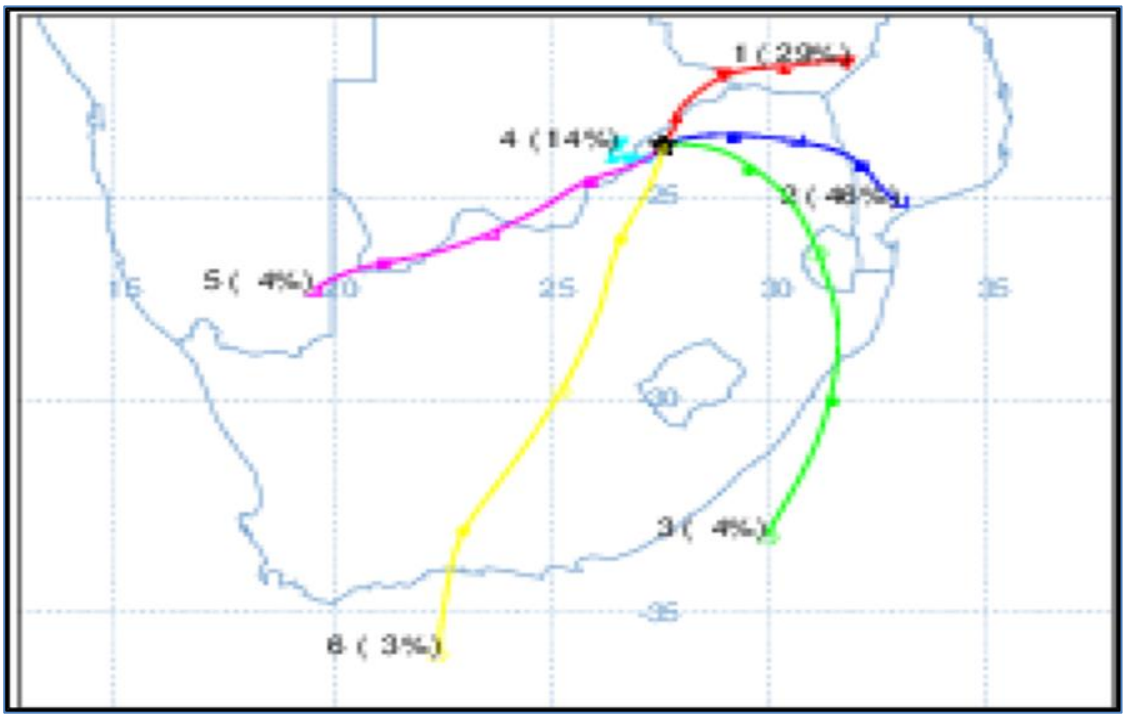


Figure 4.11: Seasonal back trajectories reaching Marapong power station for the period 2008–2012 (the number in brackets is the percentage of trajectories from that specific direction, while the number outside the brackets is the cluster number).

CHAPTER 5: DISCUSSION

This chapter provides a discussion of the results.

5.1 Diurnal and seasonal averages of ambient concentrations

5.1.1 Diurnal variation of SO_2 and NO_x

In general, the diurnal cycle of SO_2 concentrations peaked at 11:00 at a concentration of 4.81 ppb. This peak is most likely associated with an industrial signature. This finding is corroborated by a study done by Singleton (2010), where peaks between 10:00 and 16:00 were attributed to industrial emissions. The 17:00 peak of 5.70 ppb can be attributed to traffic because this is the time for peak traffic as people are travelling home after work. Muthige (2013) obtained similar results, where peaks at 17:00 were attributed to vehicle emissions. The diurnal concentrations of NO, NO_2 and NO_x peaked in the morning at 07:00 and 12:00, while in the evening, a peak was recorded at 19:00. The morning and evening peaks are most likely associated with domestic fuel burning for cooking and heating. Two studies at Marikana (North West) discovered that peaks between 06:00 and 07:00, and between 18:00 and 20:00 are the result of domestic fuel burning for cooking and heating (Beukes et al., 2012; Venter et al., 2012).

5.1.2 Seasonal diurnal variation and seasonal averages

Diurnal seasonal averages of SO_2 concentrations peaked at 15:00, irrespective of the season. These peaks are not related to domestic fuel burning for cooking and heating or traffic, but probably display an industrial signature. Muthige (2013) looked at the seasonal diurnal variation of SO_2 for the period 2005–2006 at Grootstryd station, Lephalale and found peaks of SO_2 at a similar time in Grootstryd. These were attributed to an industrial signature (i.e. Matimba power station). Other peaks of SO_2 in the current study were observed in autumn at 13:00. These peaks are most likely associated with the industrial signature as well, because there is generally not

much traffic or domestic fuel burning at this time (Keir et al., 2007). This was also confirmed by Singleton (2010), who reported that diurnal cycles of SO_2 at Zwartwater station in Lephalale for the period 2000–2002 peaked at 13:00. This was attributed to an industrial signature (i.e. Matimba power station). The morning winter peak at 09:00 can be associated with the breakup of the inversion layers in the morning (Beukes et al., 2012; Venter et al., 2012). These inversion layers form at night and break up in the morning as a result of an increase in turbulence (Garstang et al., 1996; Tyson et al., 1996; Rao et al., 2003; Wenig et al, 2003; Collet et al., 2010; Song et al., 2011).

In general, for the entire period 2008–2012, and for all the seasons, NO and NO_2 concentrations peaked at 07:00 and 12:00. Similarly, NO_x also peaked at 07:00. The peaks that were recorded between 06:00 and 08:00, and between 18:00 and 20:00 are most likely associated with domestic fuel burning (for cooking and heating), as well as vehicle emissions (Venter et al., 2012). Therefore, the 07:00 peaks in this study could be associated with domestic fuel burning and vehicle emissions. A possible source of these peaks may be Mandela Road, approximately 3 km from Marapong station, which experiences high traffic volumes (IDP, 2013). Lourens et al., (2012) similarly found high concentrations of NO and NO_2 between 07:00 and 10:00 in the Highveld Priority Area, and attributed them to vehicle emissions. The 12:00 peak of NO and NO_2 is likely to be associated with an industrial signature because by this time there is not much traffic or domestic fuel burning, and the nocturnal surface inversion has already dissipated (Collet et al., 2010). The evening peak may be as a result of inversion layers because the present study results compares well to a study by Al-Jeelani (2014), where the high concentrations of NO_x in the evening were attributed to a descending boundary layer that usually remains low until the morning, resulting in reduced mixing of pollutants.

A seasonal mean variation of SO_2, NO_2 and NO_x concentrations has been observed for the period 2008–2012. Winter has the highest concentrations of SO_2 (3.69 to 7.17 ppb), NO_2 (17.81 to 13.50 ppb) and NO_x (7.84 to 48.99 ppb) for the entire period in comparison to the other seasons. These high concentrations can be attributed to inversion layers that develop as a result of atmospheric stability during winter. This had been confirmed by a study done in Marikana, North West, where

high peaks of measured SO_2, NO_2, and NO_x trace gases were recorded in winter. These high concentrations were associated with inversion layers (Beukes et al., 2012; Venter et al., 2012). Domestic fuel burning for heating and cooking is another factor that is associated with high concentrations of these pollutants in winter, because low income households make use of coal and other fuels to heat their homes during this time (Collet et al., 2010). Biomass burning may contribute to increased NO_x concentrations during the dry winter season, which is when most of the biomass burning in South Africa occurs as shown by studies done in the Mpumalanga Highveld Priority Area by Collet et al., (2010) and Laasko et al., (2012). Pollutants from biomass burning in areas like Sekhukhune District and Bojanala local municipality can therefore affect the air quality of Lephalale Local Municipality during winter (Walton and Ngcukana, 2009).

5.2 Daily averages of NO_x and SO_2

The daily mean concentration records of SO_2 and NO_x for the period 2008–2012 show higher maximum daily mean NO_x concentrations (89.75 ppb) compared with SO_2 (48.44 ppb) and NO_2 (29.82 ppb). The SO_2 concentrations at the Marapong station are below the national standard and no exceedances were recorded. Therefore, this study can safely conclude that Marapong ambient air quality concentrations of SO_2 are complying with 24-hour NAAQS. A similar study that was conducted in Marapong for the period 2007–2010 also recorded daily concentrations of SO_2 below the NAAQS and thus had no exceedances (Muthige, 2013). The SO_2 maximum daily concentration of 42 ppb reported by Muthige (2013) was recorded in 2007, and is lower than the maximum found in the current study (48.44 ppb in 2012). A maximum NO_x concentration, of 58.8 ppb was observed in the 2007-2010 study, while the current study obtained a maximum of 85.97 ppb in 2012. Another study in Marikana (in North West) also found no SO_2 exceedances over the study period, even though the study area was close to the industrial area of Rustenburg (Beukes et al., 2012).

5.3 Annual averages of NO_x and SO_2

The annual average SO_2 for the period 2008–2012 varied across the years, with the highest annual SO_2 average of 3.7 ppb recorded in 2011. The spread (variability) of the data was far greater during 2011 and 2012 compared to the other years. The maximum annual average SO_2 was 3.7 ppb, which is low compared to the maximum SO_2 annual average of 16.3 ppb for the Highveld Priority Area for the 1999–2008 period (Mugabo, 2011). The annual average concentrations of NO_x varied between 10.2 and 15.7 ppb, with the highest average concentration (15.7 ppb) in 2012 and the lowest (10.2 ppb) in 2008. These concentrations are higher than those obtained for Elandsfontein station in Mpumalanga for the period 2003-2008, which ranged between 5-15 ppb (Mdluli, 2008). No trend was observed for SO_2, although there was a noticeable trend for NO_x for the 2008–2012 period. The addition of industries such as Medupi, the expansion of Grootegeluk mine and road developments close to the Marapong site may have contributed to the slightly higher average concentrations of NO_x and SO_2 in 2010–2012 (Walton and Ngcukane, 2009; IDP, 2013; Muthige, 2013).

5.4 Dry deposition velocity of SO_2 and NO_x (NO_2)

The dry deposition velocity of SO_2 shows variation across the seasons. In general, these deposition velocities are higher during summer (0.17 to 0.23 cm/s) for the entire period, compared to the other seasons (0.09 to 0.21cm/s), with the lowest deposition velocities (0.09 to 0.15 cm/s) recorded in winter. The higher deposition velocities in summer can be attributed to higher solar radiation and turbulence, which are at their peak during summer. This is supported by sensitivity results of meteorological data to deposition velocity. If solar radiation and horizontal wind direction (horizontal wind direction is the turbulence proxy) are omitted, deposition velocity is reduced by 43% and 96% respectively. Other studies conducted over the Highveld Priority Area of Mpumalanga found similarly higher deposition velocities during summer due to an increase in solar radiation and turbulence (Zunckel et al., 1996; Zunckel, 1998; Zunckel et al., 1999; Mphepya and Held, 1999; Mphepya, 2002; Held and Mphepya, 2000). In contrast, 2012 had the highest dry deposition

velocity in winter compared to all other seasons for the period 2008–2012. The high 2012 deposition velocity may be attributed to variation in meteorology across the years. This may be due to the high solar radiation average of 360 W/m^2 obtained in summer 2012, compared to 349 to 352 W/m^2 in the other seasons.

These studies also indicated the influence of photosynthetically active vegetation in summer on the deposition velocity of SO_2 (Zunckel et al., 1996; Zunckel, 1998; Zunckel et al., 1999; Mphepya and Held, 1999; Mphepya, 2002; Held and Mphepya, 2000). This was confirmed by Mphepya and Held (1999), who also used an inferential model to estimate the dry deposition of SO_2 in Elandsfontein and Palmer for the period 1996–1998. They found that the variation in seasonal averaged deposition velocities of SO_2 may be ascribed to photosynthetic activity of the vegetation, solar radiation and turbulence. Zunckel et al., (1999) observed seasonal variation of deposition velocities similar to this study, where the maximum deposition velocity was observed in summer and the minimum was observed in winter. They attributed this to insolation, turbulence and photosynthetically active vegetation. Deposition velocities determined in this study are within the magnitude of the SO_2 deposition velocities obtained by Zunckel et al., (1999) and Mphepya (2002) for the Highveld Priority Area using the same inferential model. The dry deposition velocities of SO_2 in Zunckel et al., (1999) varied between 0.11 and 0.28 cm/s, while Mphepya (2002) reported deposition velocities ranging between 0.10 and 0.36 cm/s.

Similarly, NO_2 deposition velocities varied seasonally (0.05 to 0.15 cm/s). They were the lowest in winter (0.05 to 0.09 cm/s) and highest in summer (0.10 to 0.15 cm/s). The results of the current study are supported by the study of Mphepya (2002) conducted in the Highveld Priority Area, estimating seasonal dry deposition velocities of NO_2 for the period 1996–1998. This has been the only study in South Africa to use an inferential model to estimate NO_2 deposition velocities. The results indicated that dry deposition velocities of NO_2 peaked in summer, with deposition velocities varying between 0.040 and 0.250 cm/s. The high deposition velocities of NO_2 in summer were attributed to solar radiation and turbulence. The seasonal deposition velocities of NO_2 in this study are within the range of the deposition velocities of NO_2 which were estimated for the Highveld Priority Area.

5.5 Deposition flux of SO_2 and NO_x (as NO_2)

5.5.1 Seasonal dry deposition flux of SO_2 and NO_x (as NO_2)

In this study, SO_2 dry deposition flux has been high in winter (0.11 to 0.22 kg S ha^{-1} per season) compared to the other seasons (ranging between 0.06 and 0.17 kg S ha^{-1} per season). This can be ascribed to the higher SO_2 concentrations observed during this season, as explained above. Similarly, Zunckel et al., (1998), Mphepya (2002), Ferguson (2009) and Held and Mphepya, (2000) attributed higher dry deposition flux of SO_2 in the Highveld Priority Area to high concentrations of SO_2. The magnitude of the seasonal dry deposition flux (0.06 to 0.22 kg S ha^{-1} per season) found in this study is within the magnitude of the SO_2 deposition flux (0.05 to 2.05 kg S ha^{-1} per season) found in the Highveld Priority Area (Held and Mphepya, 2000; Mphepya, 2002).

Similarly, NO_x (as NO_2) also showed the highest deposition flux in winter (0.26 to 0.33 kg N ha^{-1} per season) compared to other seasons (0.14 to 0.23 kg N ha^{-1} per season) for the entire period 2008–2012. These high deposition fluxes of NO_x (as NO_2) in winter were also associated with the high concentrations in winter as explained above. The seasonal deposition flux found in this study are within the magnitude of the deposition flux (0.06 to 0.410 kg N ha^{-1} per season) found in a study conducted in Mpumalanga, which included Elandsfontein, Palmer and Amersfoort (Mphepya, 2002). In general, the SO_2 deposition flux obtained in this study is lower than that found in the Highveld Priority Area. This could be due to the lower concentrations and deposition velocities obtained in the current study compared to those found in the Highveld Priority Area. The NO_2 (as N) flux is similar to that of the Highveld Priority Area which could be explained by the high concentrations of NO_2 observed in this study.

5.6 Annual dry deposition flux of SO_2 and NO_x (as NO_2)

The annual average dry deposition flux of SO_2 (as S) ranged between 0.43 and 0.67 kg S ha^{-1} yr^{-1}. These deposition fluxes are smaller than those found in Mpumalanga. Several studies on dry deposition using an inferential model have been conducted in the Mpumalanga Highveld Priority Area (Mphepya, 2002; Zunckel, 1999; Zunckel et al., 2000). These studies found dry deposition flux of SO_2 (as S) ranging between 1.59 and 9.24 kg S ha^{-1} yr^{-1} (Mphepya, 2002), 3.3 to 13.1 kg S ha^{-1} yr^{-1} (Zunckel, 1999; Zunckel et al., 2000) and 0.18 to 6.6 kg S ha^{-1} yr^{-1} (Ferguson, 2009). The lower dry deposition flux of SO_2 (as S) might be due to lower SO_2 concentrations determined for Marapong compared to those in the Highveld Priority Area. The dry deposition flux of NO_2 (as N) varied between 0.84 and 1.05 kg N ha^{-1} yr^{-1}, which is of the same order of magnitude as the dry deposition flux of NO_2 (as N) (within the range of 0.09 and >0.95 kg N ha^{-1} yr^{-1}) found on the Highveld Priority Area (Elandsfontein, Palmer and Amersfoort) for the period 1996–1998 (Mphepya, 2002). However, Collet et al., (2010) found a much higher dry deposition NO_2 (as N) flux of 6.7 to 13.1 kg N ha^{-1} yr^{-1} for the period April 2005 to March 2006 in a study conducted in the Highveld Priority Area (Elandsfontein).

Air pollution in the form of SO_2 or NO_x (as NO_2) may cause adverse effects to vegetation once concentration levels or deposition loads exceed certain limits. Currently, there are no critical loads levels of SO_2 and NO_x (as NO_2) deposition rates that have been published on savannas (i.e. Limpopo sweet Bushveld). Therefore, the current study will only compare the deposition rates found in this study to those that were found at Mpumalanga Highveld on grassland because the Limpopo sweet Bushveld (Limpopo sweet Bushveld) also consist of grasslands.

The annual dry deposition fluxes of SO_2 (as S) and NO_2 (as N) in the current study are well below those found in the Mpumalanga Highveld as explained above. Hence, such dry deposition fluxes in the current study will not cause significant threats to the grassland of Lephalale. This is corroborated by a study conducted by Van Tienhoven et al., (1995) in the Highveld where they found similar results regarding sulphur, where the rates of sulphur deposition did not exceed the critical loads levels nor cause any direct threats to the ecosystems in the region. Another study conducted

by Ferguson et al., (2010) also found that the NO_2 deposition in the Highveld region does not pose any threat to the natural ecosystems as the NO_2 deposition is well below the stipulated critical load value of 15 kg N ha^{-1} yr^{-1}. However, Josipovic et al., (2011) indicated that continued emissions of acid gases (SO_2 and NO_2) pose a risk of exceeding critical loads in sensitive soils in the Mpumalanga Highveld. The same effect must accordingly be considered possible in the Lephalale area given the addition of new industries and the lack of knowledge on critical levels or critical loads for the ecosystems of the area.

5.6 Seasonal back trajectories for the period 2008–2012

Generally, the dominant direction of back trajectory air masses during summer (52%) autumn (61%), winter (53%) and spring (53%) for the period 2008–2012 was from the east and southeast, indicating that concentrations of SO_2 and NOx can be affected by pollution sources from Mpumalanga and Gauteng. As can be seen below in Figure 5.1, east/southeast of Marapong is dominated by mines and power stations from Mpumalanga. Additionally, these back trajectories pass over Gauteng where the cities of Johannesburg and Pretoria are rich in different emission sources. The back trajectories do not show any seasonal variation because the dominant direction in all the seasons is east and southeast. Therefore, lack of seasonal pattern in back trajectories and source regions cannot alone explain the seasonal changes in ambient concentrations (SO_2 and NO_x). Hence, climatic factors or seasonal changes in combustion source intensity must be responsible.

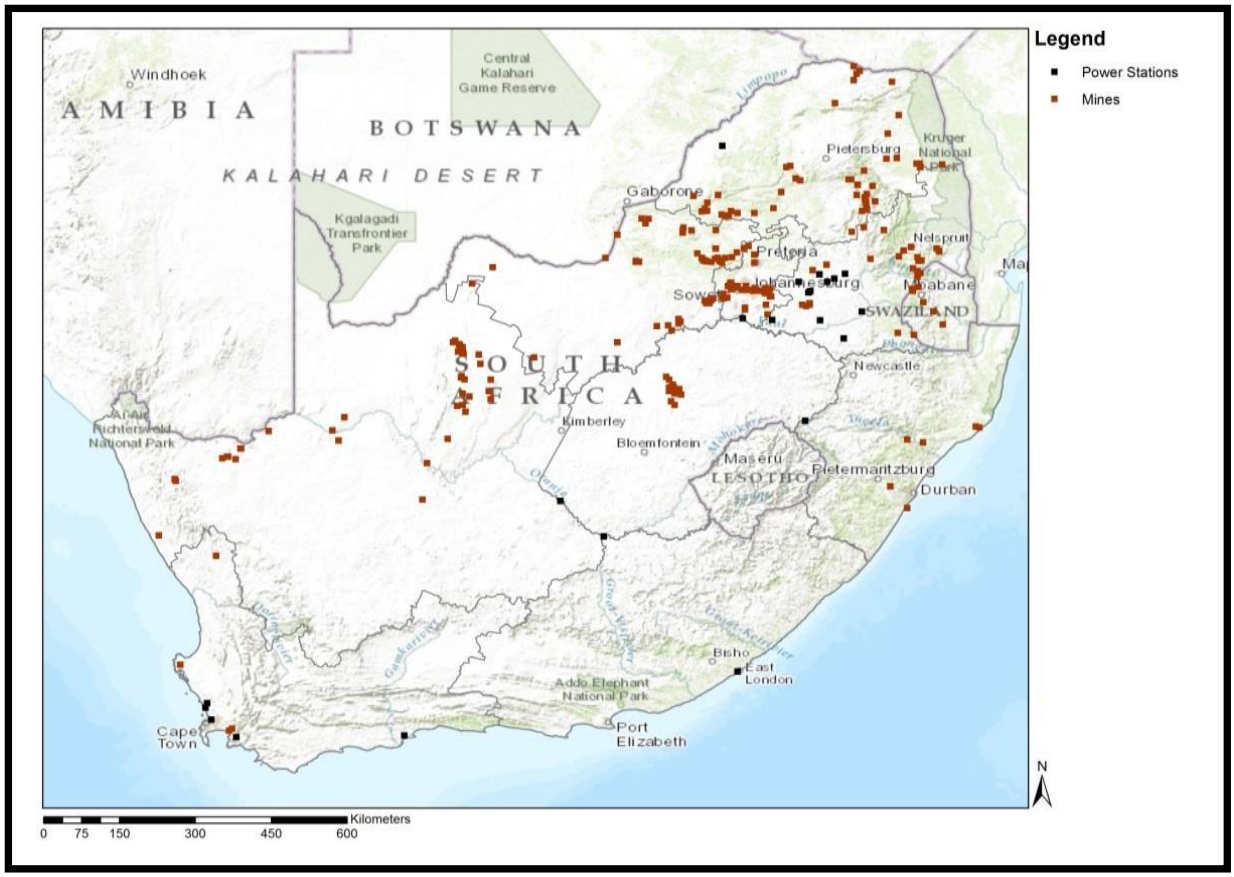


Figure 5.1: Large air pollution sources (mines and power stations) in South Africa

CHAPTER 6: CONCLUSIONS

This chapter outlines the conclusions, limitations and recommendations.

The primary aim of this project is to evaluate SO_2 and NO_x dry deposition fluxes for the period 2008–2012 in Lephalale in the Waterberg-Bojanala Priority Area. A secondary aim is to understand the regional air masses that can affect NO_x and SO_2 concentrations on a seasonal scale. The objectives of the study were stated in Chapter 1, and an evaluation of each objective is given below.

6.1 To evaluate the inter-annual variability of NO_x and SO_2 ambient concentrations for the period 2008–2012

There are inter-annual variations of mean SO_2 annual concentrations ranging between 2.6 and 7.6 ppb. NO_x also shows an inter-annual variability with annual mean concentrations ranging between 10.2 and 15.7 ppb. However, the difference in SO_2 and NO_x concentrations over the years is not significant. The results also indicate that SO_2 and NO_x concentrations peaked in 2011 and 2012, with averages of 3.7 ppb and 15.5 ppb respectively. For the entire period, the minimum concentrations of SO_2 (0.1 ppb) and NO_x (0.3 ppb) were recorded in 2010. The limitation of this objective is that there are data gaps due to power cuts and measurement errors, thus resulting in poor data resolution, therefore data completeness were used to ensure data gaps did not impact averages very much. Future research should look at O_3 and PM ambient concentrations as they are also criteria pollutants which might pose a threat to the receiving environment.

6.2 To calculate the total annual dry deposition rates of NO_x (as NO_2) and SO_2 for the period 2008–2012

The annual total dry deposition flux of SO_2 (as SO_2) ranged between 0.43 and 0.67 kg S ha^{-1} yr^{-1}. For the period 2008–2012, these dry deposition flux values are smaller than those found in previous studies in Mpumalanga. The low dry deposition flux in the current study can be attributed to low observed concentrations and modelled

deposition velocities observed in this study, compared to studies in the Highveld Priority Area. The dry deposition flux of NO_2 (as N) varied between 0.84 and 1.05 kg N ha^{-1} yr^{-1}. The deposition flux in this study is within the magnitude of the dry deposition flux of NO_2 (as N) within the range of 0.09 and >0.950 kg N ha^{-1} yr^{-1}) found in the Highveld (Elandsfontein, Palmer and Amersfoort) for the period 1996–1998 (Mphepya, 2002). The lower SO_2 (as S) dry deposition flux in the current study can be attributed to the observed lower ambient SO_2 concentrations and these are lower than those found in Mpumalanga Highveld at Elandsfontein (10.7 ppb) by Zunckel et al., (1999). The high NO_2 (as N) dry deposition flux in this study can be associated with high concentrations observed in this study.

In general, the dry deposition fluxes of SO_2 in the current study are below those which were found by previous studies in the Highveld Priority Area. However, NO_2 (as N) fluxes in the current study are comparable to those of the previous studies found in the late 1990s in the Highveld Priority Area. These results could be attributed to the concentrations of SO_2 and NO_2 in the current study, with NO_2 having recorded high concentrations while SO_2 recorded low concentrations relative to the Highveld.

6.3 To assess seasonal variations of NO_x (as NO_2) and SO_2 dry deposition rates during the period 2008–2012

There are seasonal variations of NO_2 (as N) and SO_2 (as S) across the years, with winter having the highest dry deposition flux, compared to other seasons. In this study, SO_2 (as S) dry deposition flux is high in winter (0.11 to 0.22 kg S ha^{-1} per season), compared to the other seasons (0.06 to 0.17 kg S ha^{-1} per season). Similarly, NO_2 (as N) also showed the highest deposition flux in winter (0.26 to 0.33 kg N ha^{-1} per season), compared to the other seasons (0.14 to 0.23 kg N ha^{-1} per season) for the entire period 2008–2012.

6.4 Limitations of objectives 6.2 and 6.3

- The study area did not have full meteorological data set as required by the inferential model. Hence data substitution was required. This included humidity (Lephalale) and modelled solar radiation (CCAM).
- Modelled solar radiation data from CCAM was used, which has a coarse resolution. Additionally, only one station was used to validate the model.
- NO_3 and NH_3 were not included in calculating the total dry deposition of N, so the NO_2 dry deposition is not the representative total dry deposition of N in Lephalale.
- Another limitation is that initially the study planned to estimate dry deposition rates at Lephalale in the Waterberg-Bojanala Priority Area, as it was initially believed that there were multiple monitoring stations. However, this is a single-point model and only one monitoring station had continuous data for the study period 2008–2012. The reader must interpret the results with caution because only one station was used to estimate the dry deposition rates and this may not give a good representation of the deposition rates across Lephalale.

6.5 Future work for 6.2 and 6.3

- Wet deposition studies should be conducted to calculate the total wet deposition of N and S in Lephalale.
- NO_3 and NH_3 should be included to calculate the total dry deposition flux of N in Lephalale.
- Critical loads of S and N should be studied to assess the threat that acid deposition poses to the terrestrial and aquatic ecosystems of the Limpopo sweet Bushveld.
- More monitoring is needed at the same time at different sites to get a spatial idea of the deposition in Lephalale.

6.6 To identify seasonal regional sources of air pollution for the period 2008–2012 using the Hysplit Model

Generally, the dominant direction of back trajectory air masses during summer (52%) autumn (61%), winter (53%) and spring (53%) for the period 2008–2012 was from the east and southeast, indicating that concentrations of SO_2 and NO_x can be affected by industrial pollution sources from Mpumalanga and Gauteng. This lack of seasonal pattern in back trajectories and source regions cannot alone explain the seasonal changes in ambient concentrations (SO_2 and NO_x). Hence climatic factors or seasonal changes in combustion source intensity must be responsible.

6.7 Limitation for 6.6

- A limitation of this model is that trajectory analysis is used as an indication of the general airflow, rather than the exact pathway of an air parcel, due to the low spatial resolution of the input data.

6.8 Future work for 6. 6

- Further work is required to estimate the atmospheric life time of SO_2 and NO_x from a South African point of view. This will help in understanding transport of SO_2 and NO_x based on South African meteorological conditions.

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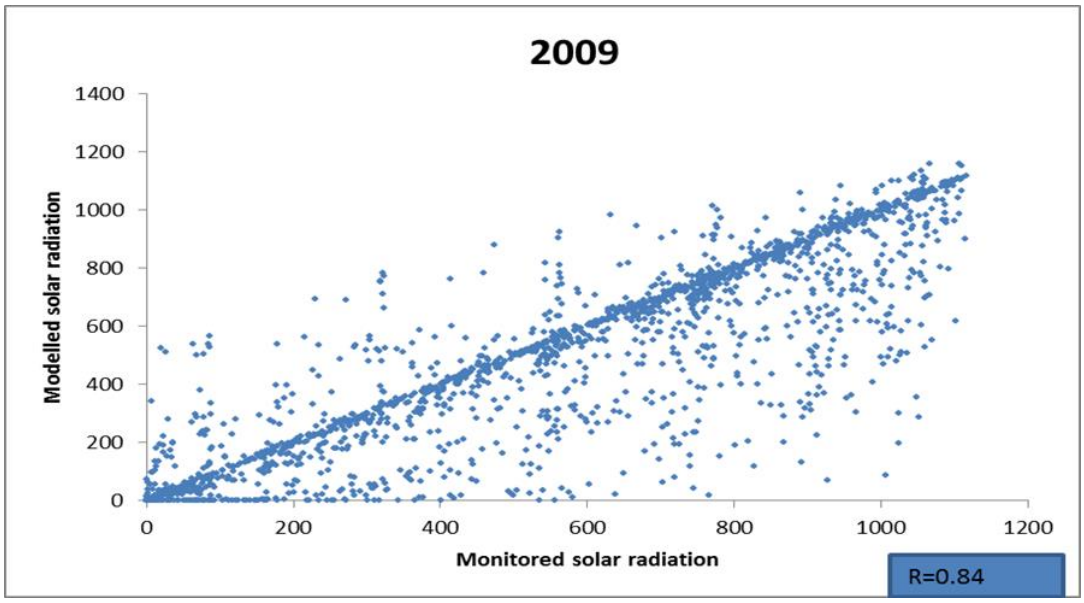
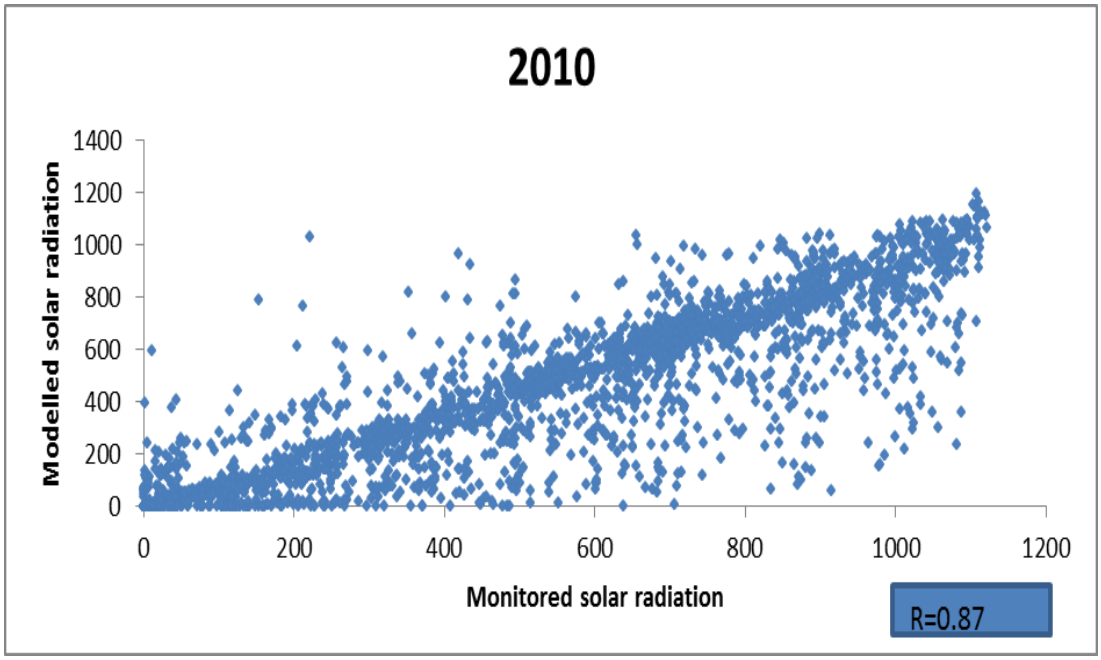
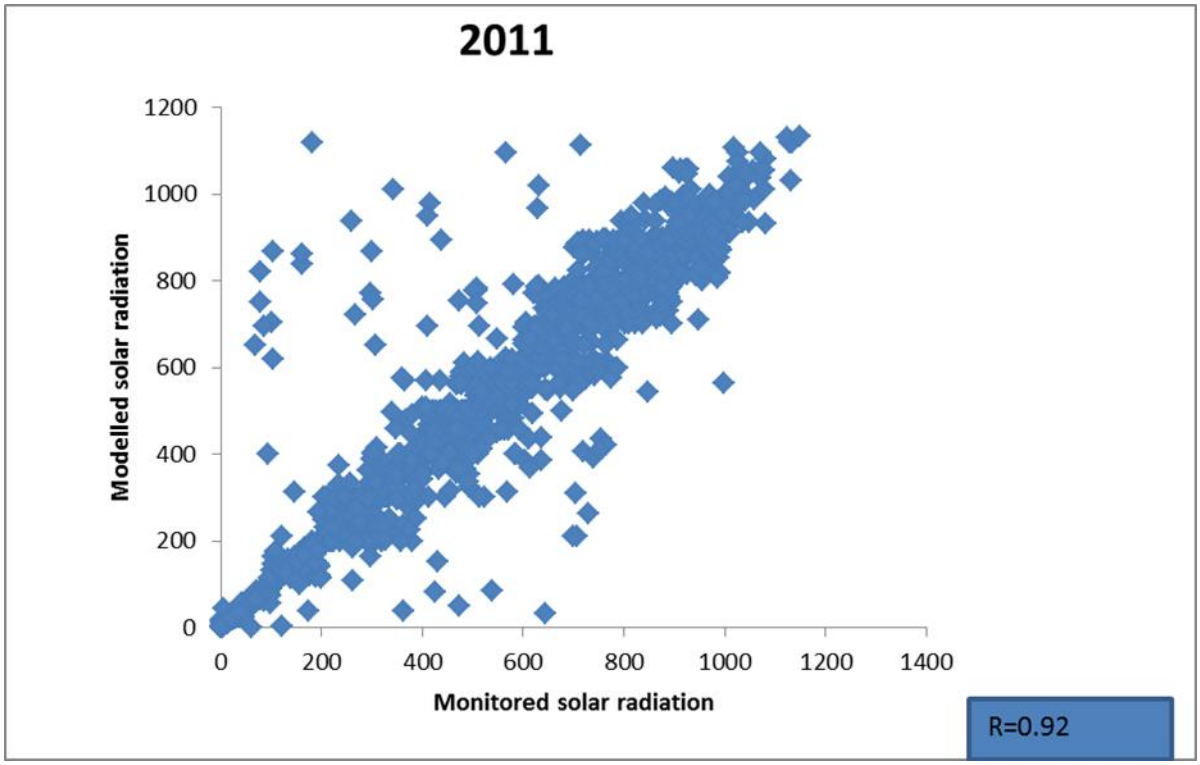
APPENDICES

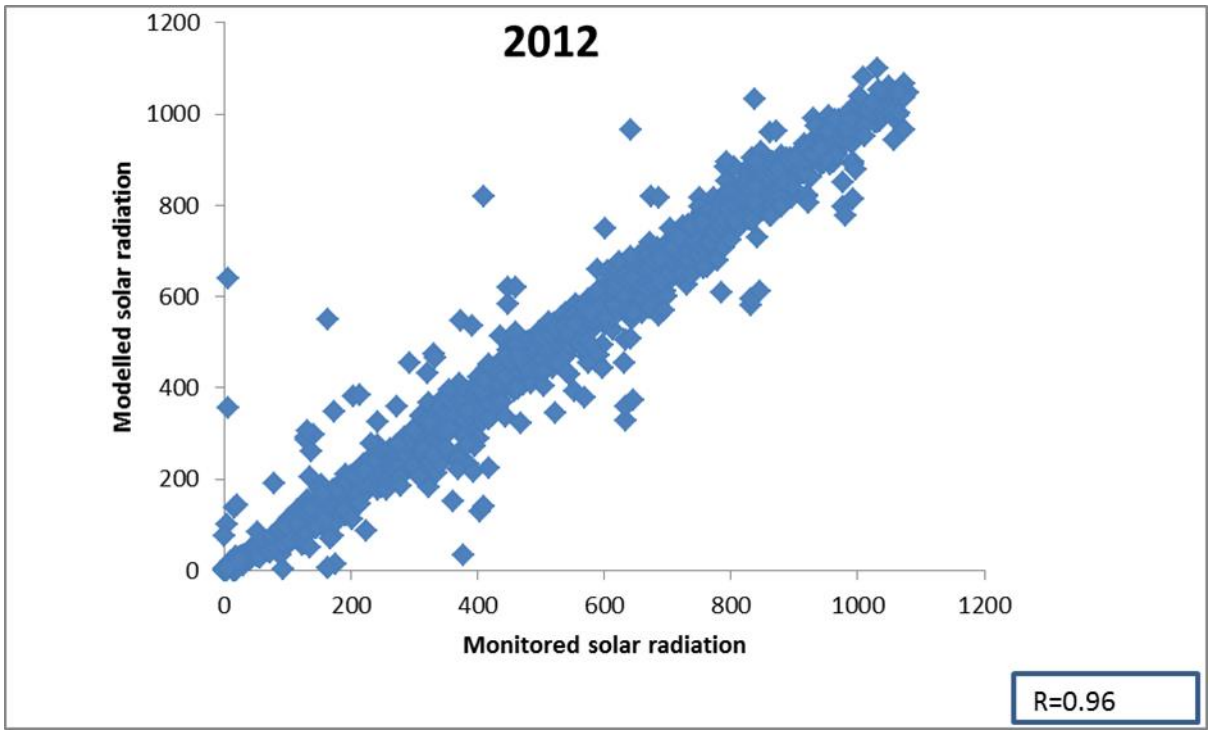
Appendix 1

Linear correlation analysis results of modelled CCAM data and monitored Werkendam solar radiation (W/m^2) data for the period 2008-2012.



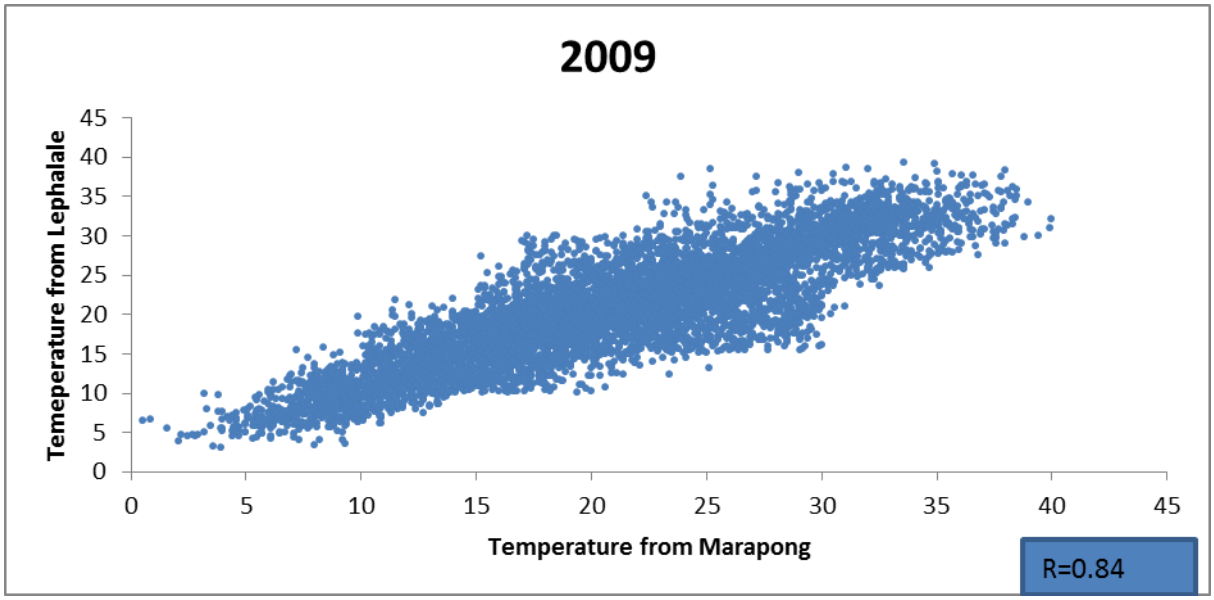


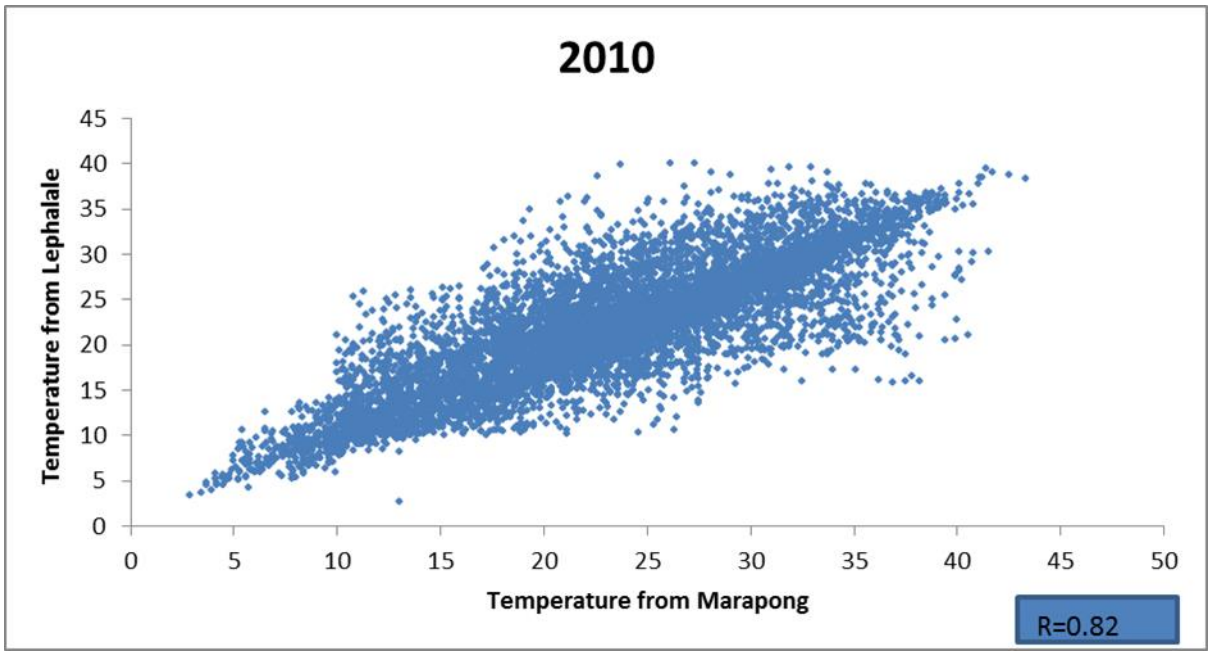

2011
Modelled solar radiation
Monitored solar radiation
0
200
400
600
800
1000
1200
1400
R=0.92

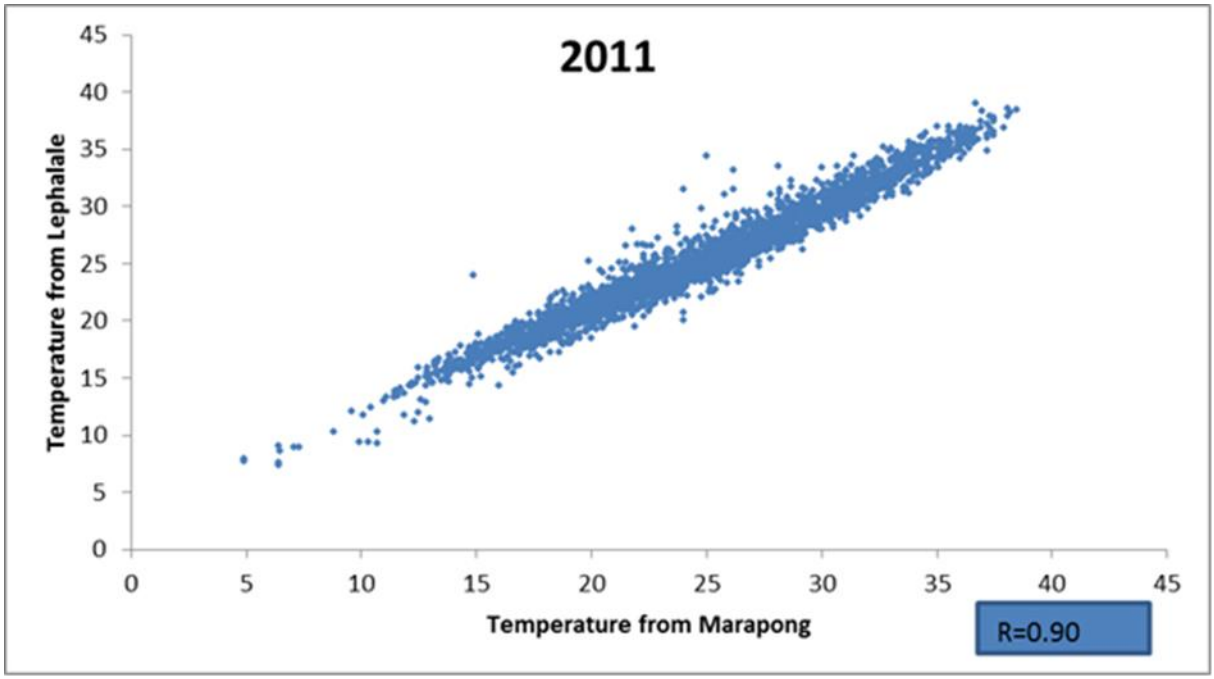

2012
Modelled solar radiation
Monitored solar radiation
0
200
400
600
800
1000
1200
R=0.96

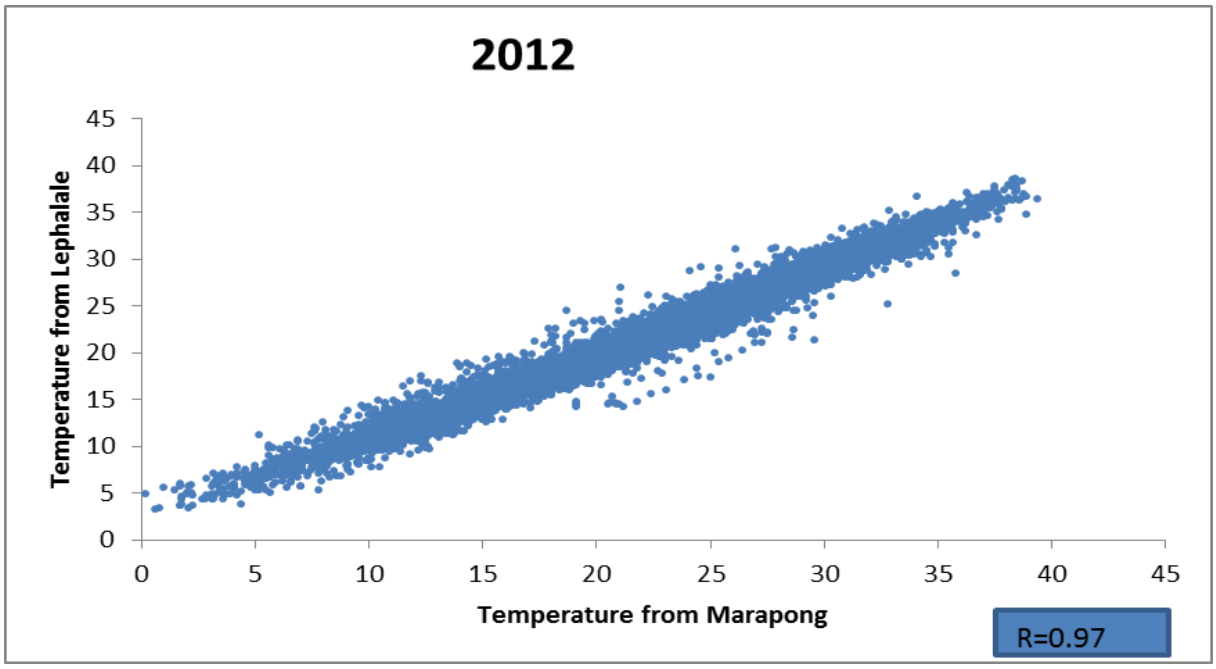
Appendix 2

Linear correlation analysis results of temperature (°C) data of Marapong versus Lephalale for the period 2009-2012.

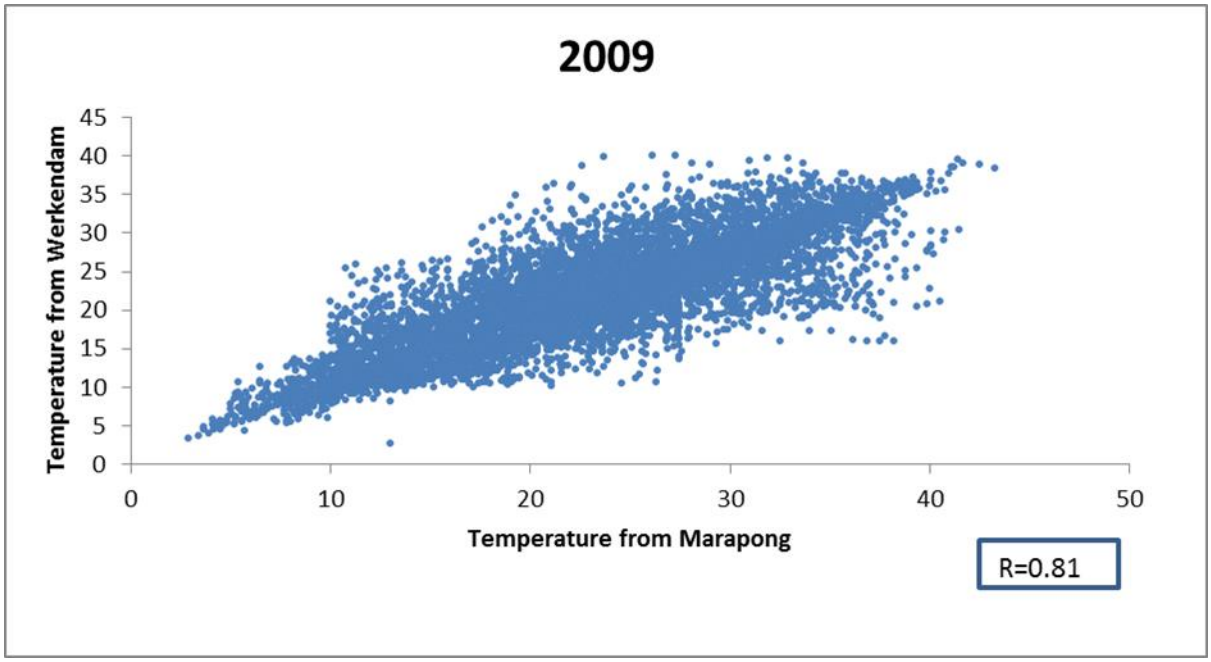


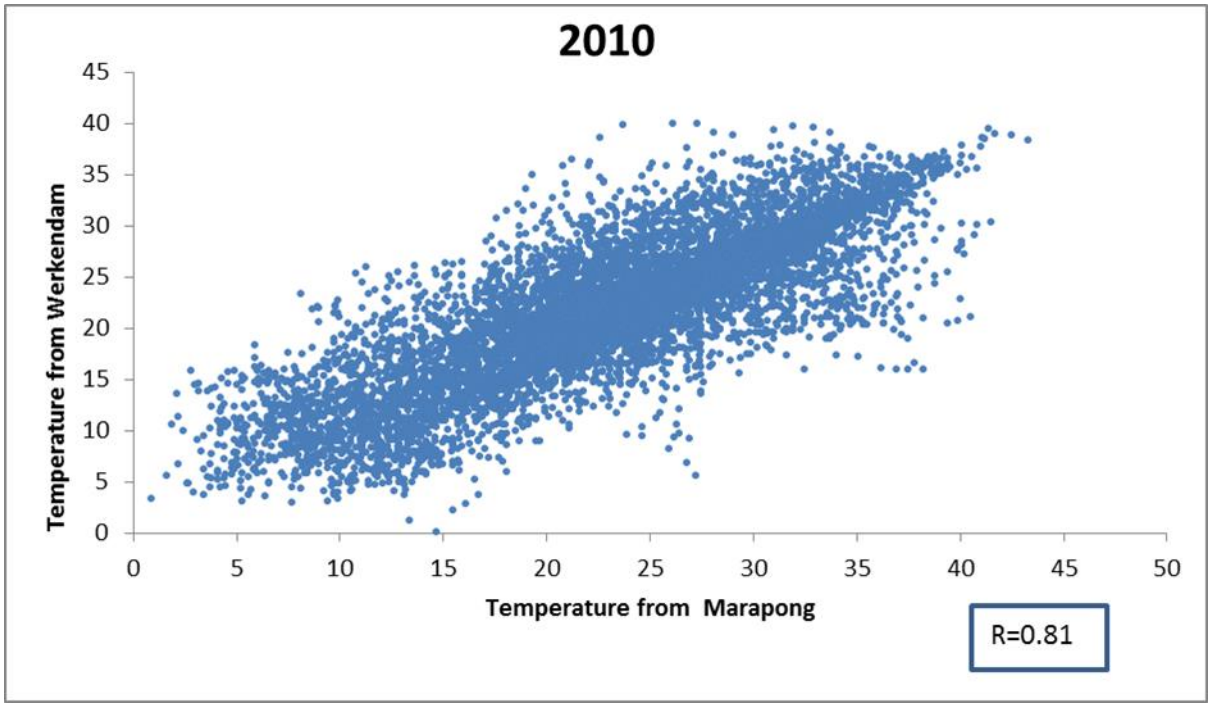


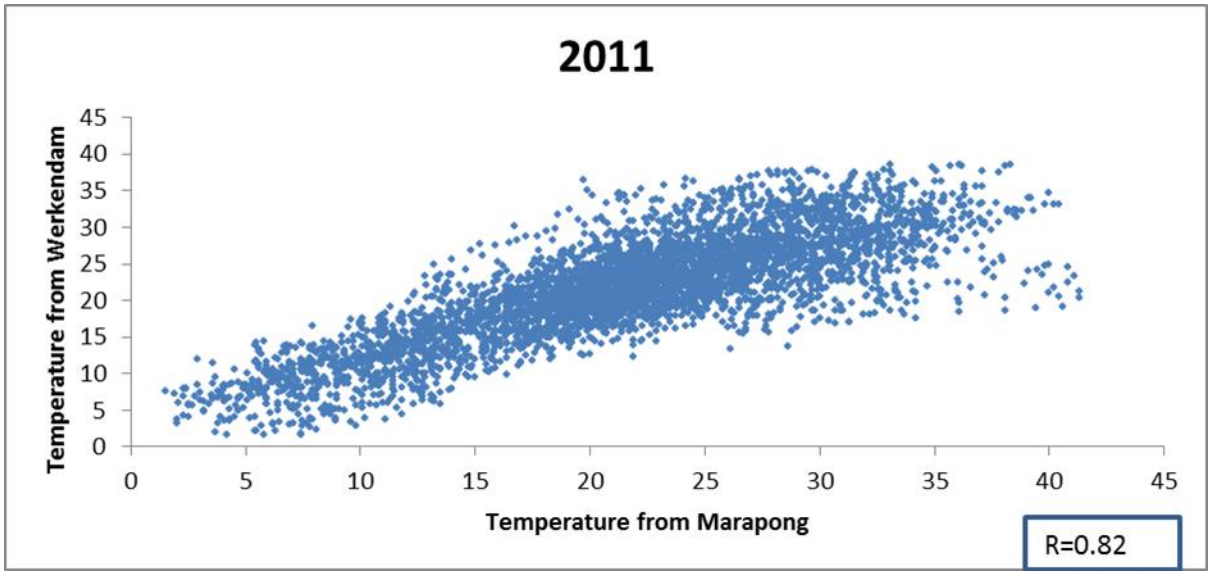

2011
Temperature from Lephalale
Temperature from Marapong
R=0.90
0
5
10
15
20
25
30
35
40
45

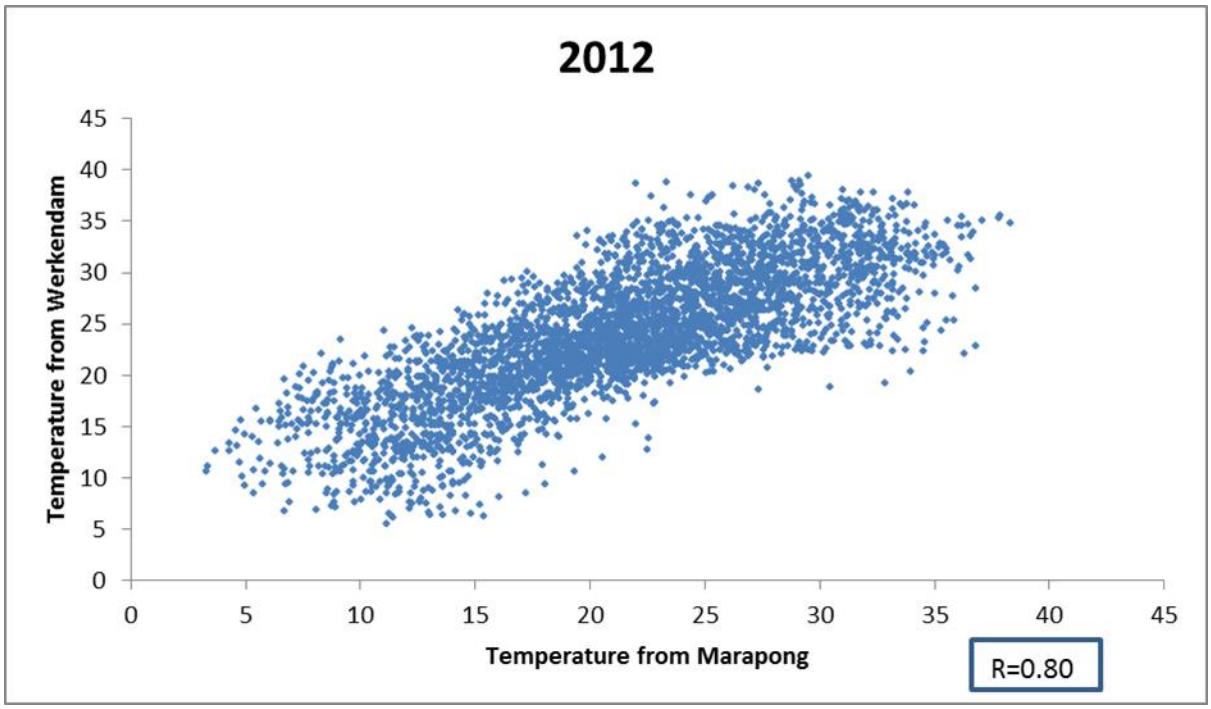

2012
Temperature from Lephalale
Temperature from Marapong
R=0.97
0
5
10
15
20
25
30
35
40
45

Linear correlation analysis results of temperature (^{o}C) data Marapong versus Werkendam for 2009-2012.



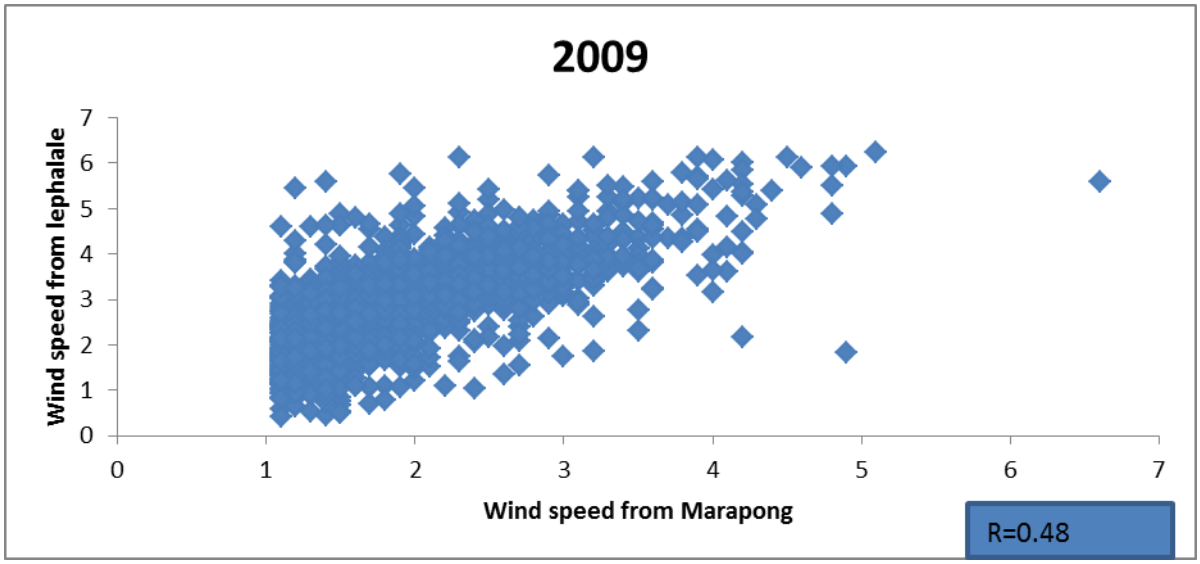


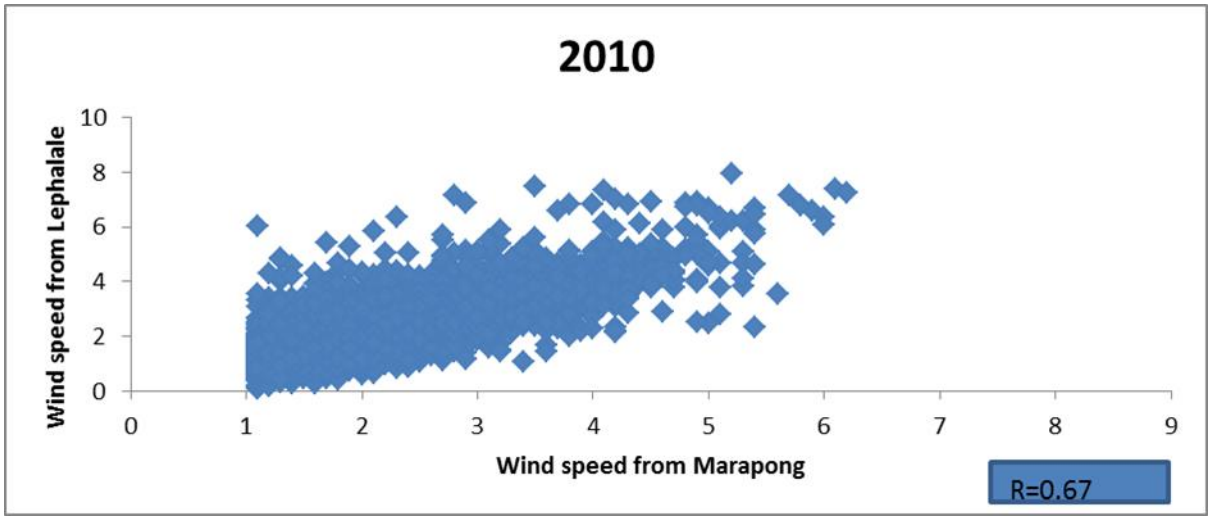

2011
Temperature from Werkendam
0
5
10
15
20
25
30
35
40
45
Temperature from Marapong
R=0.82

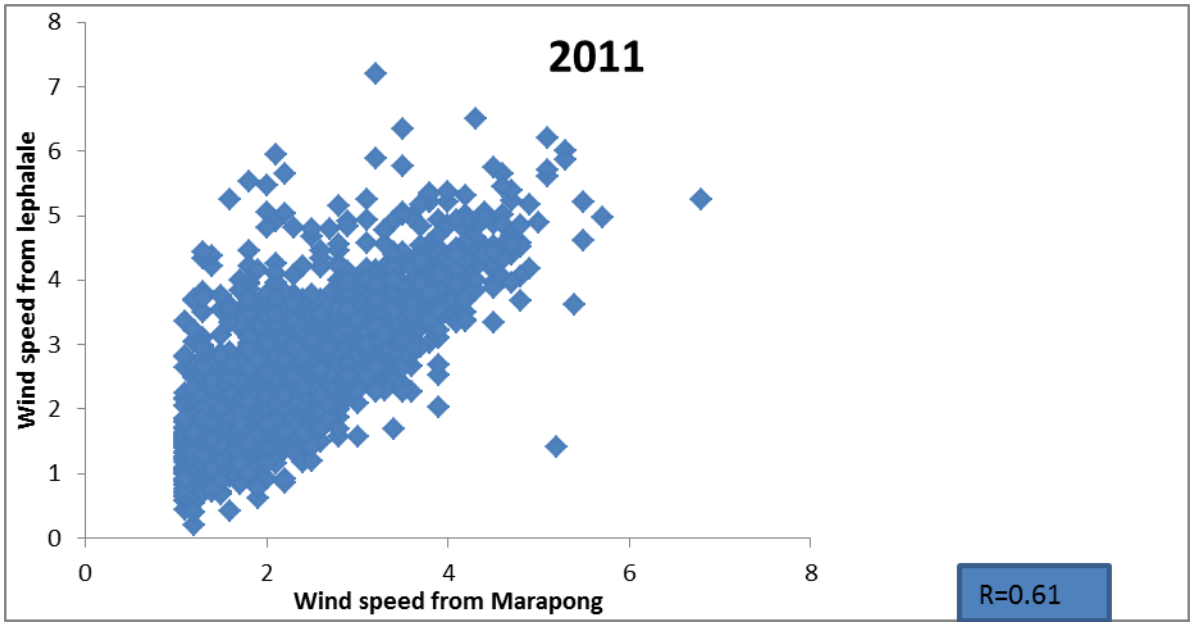

2012
Temperature from Werkendam
0
5
10
15
20
25
30
35
40
45
Temperature from Marapong
R=0.80

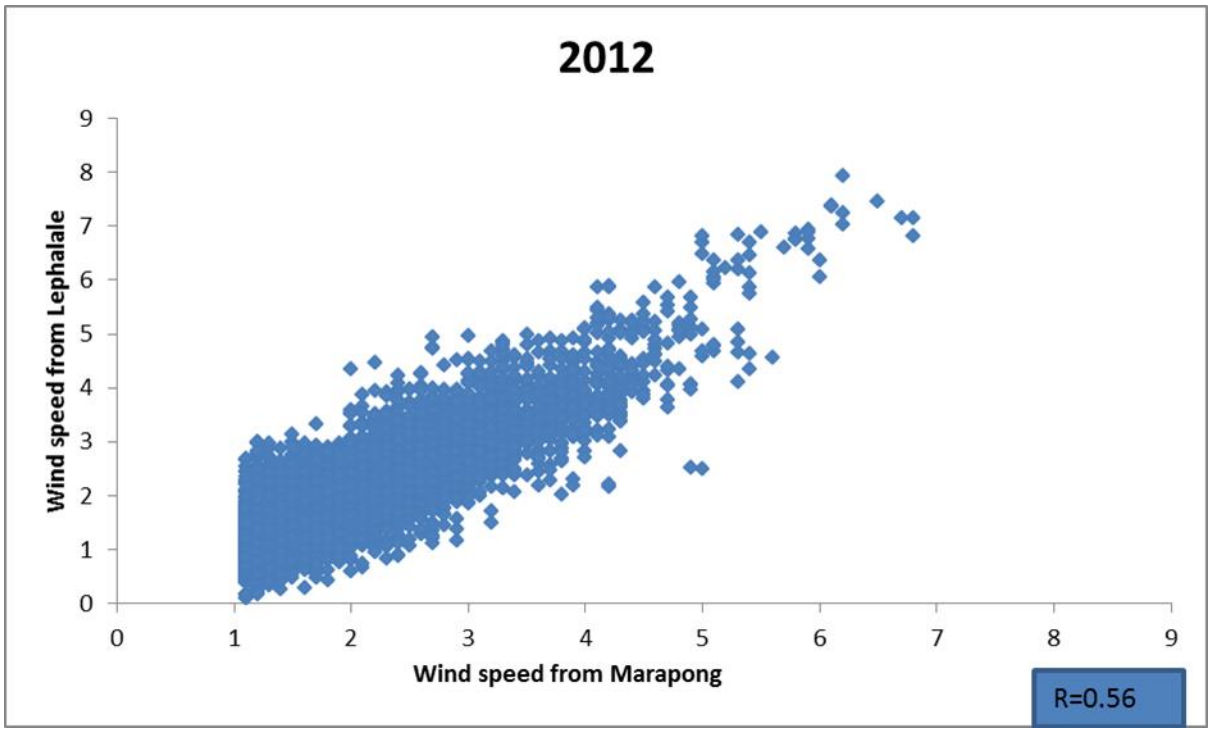
Appendix 3

Linear correlation analysis of wind speed (m/s) from Marapong versus Lephalale for the period 2009-2012

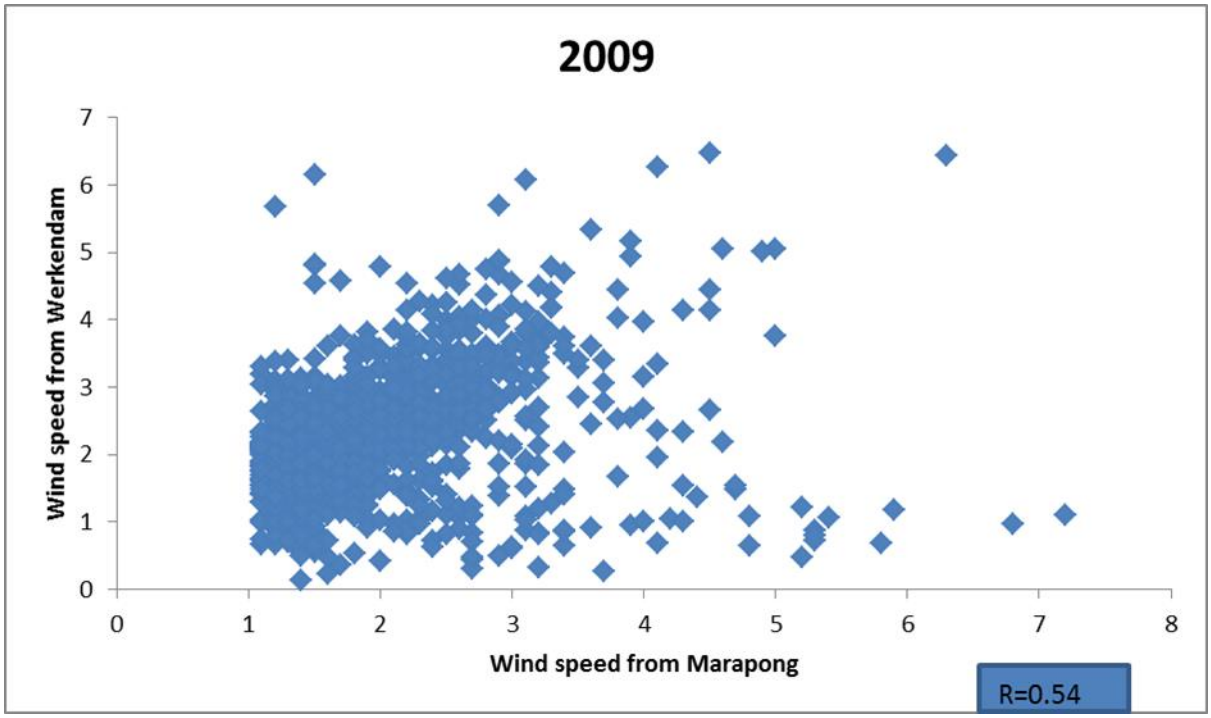


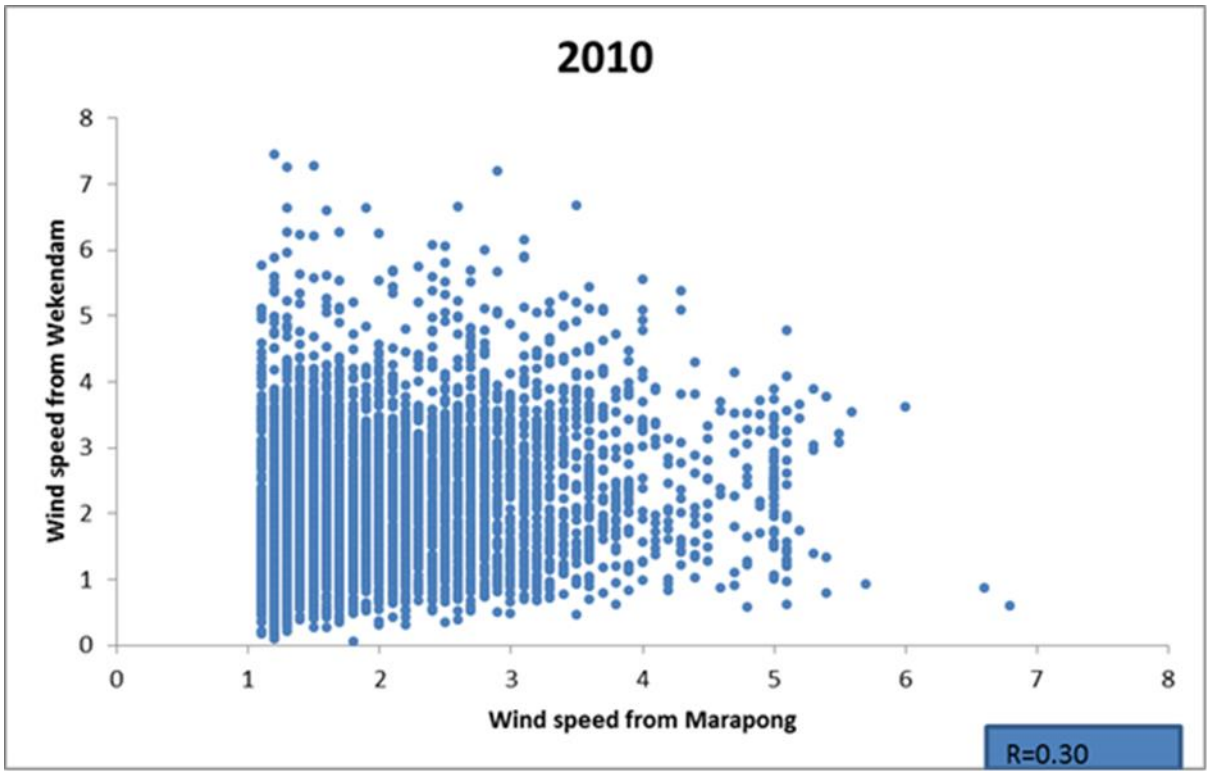


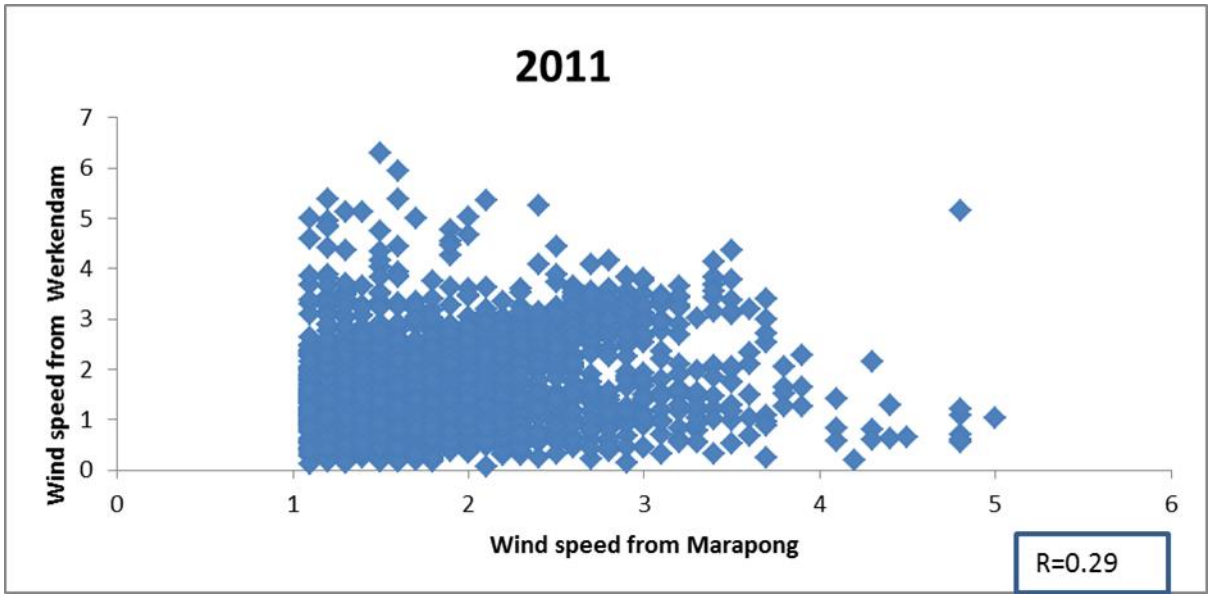

2011
Wind speed from lephalale
Wind speed from Marapong
R=0.61

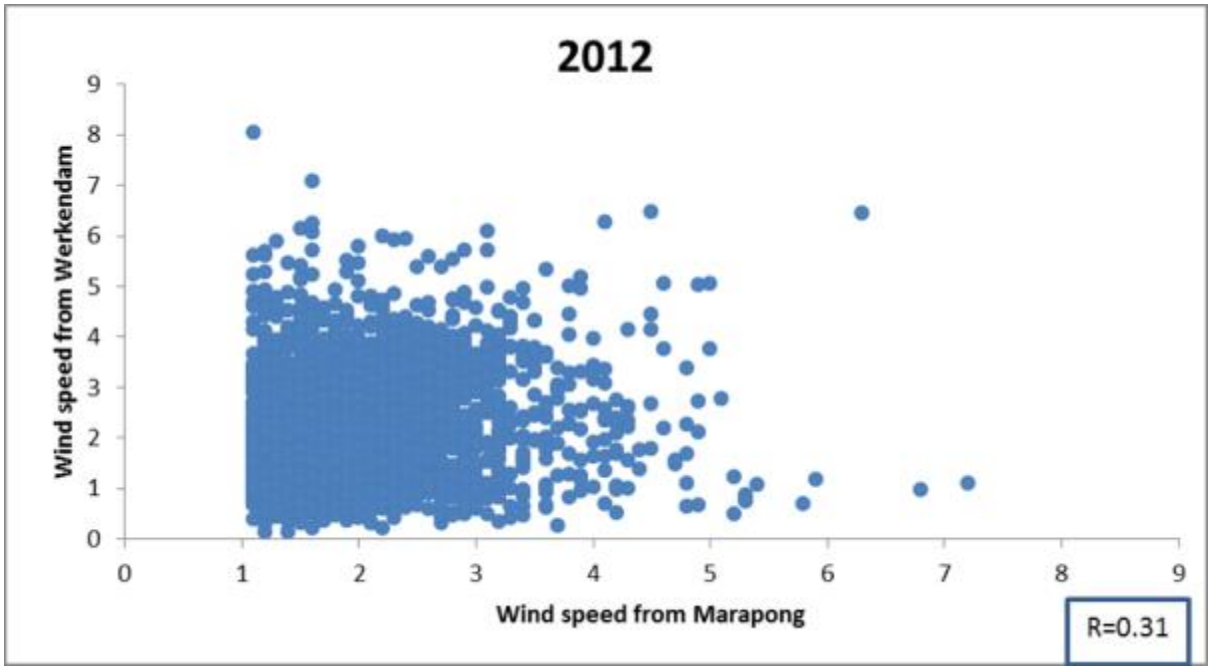

2012
Wind speed from Lephalale
Wind speed from Marapong
R=0.56

Linear correlation analysis of wind speed (m/s) from Marapong versus Werkendam for the period 2009-2012.



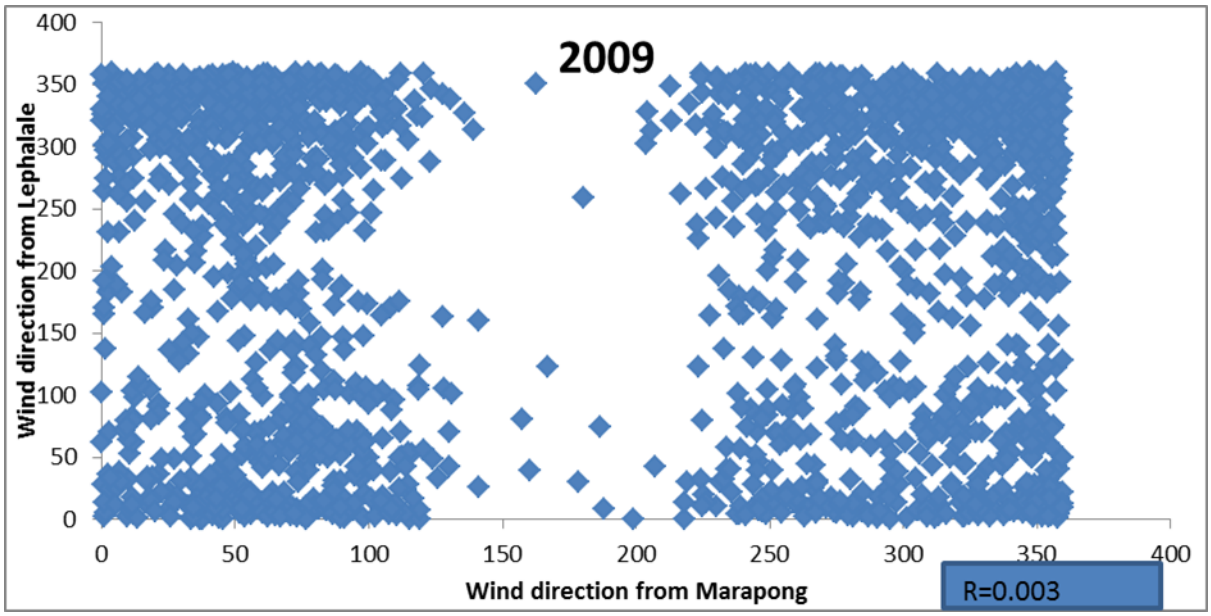


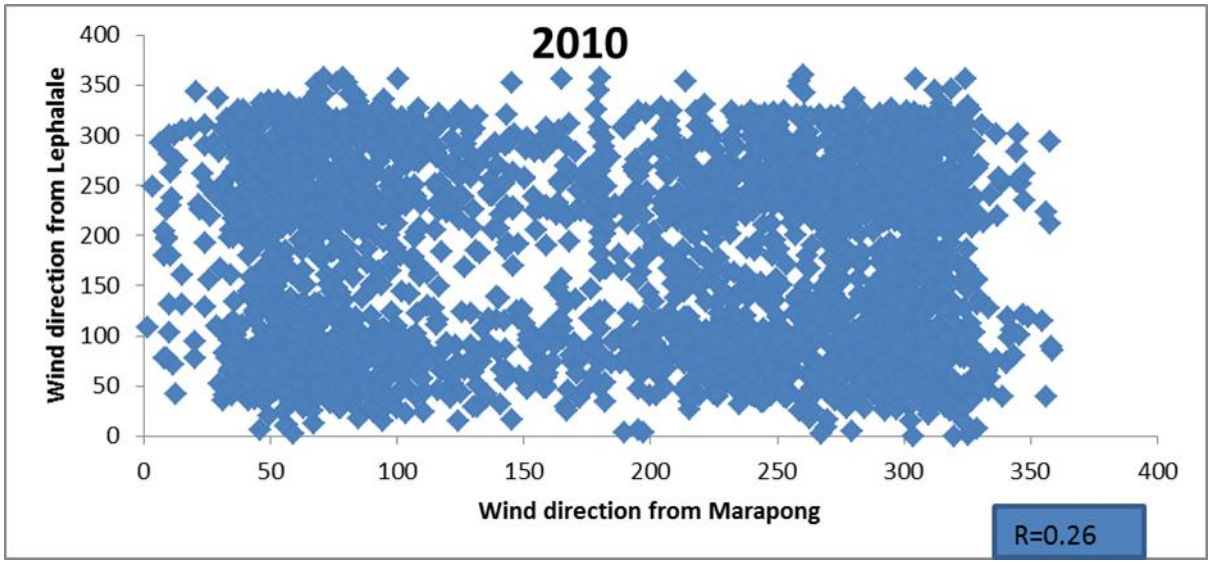

2011
Wind speed from Werkendam
Wind speed from Marapong
R=0.29

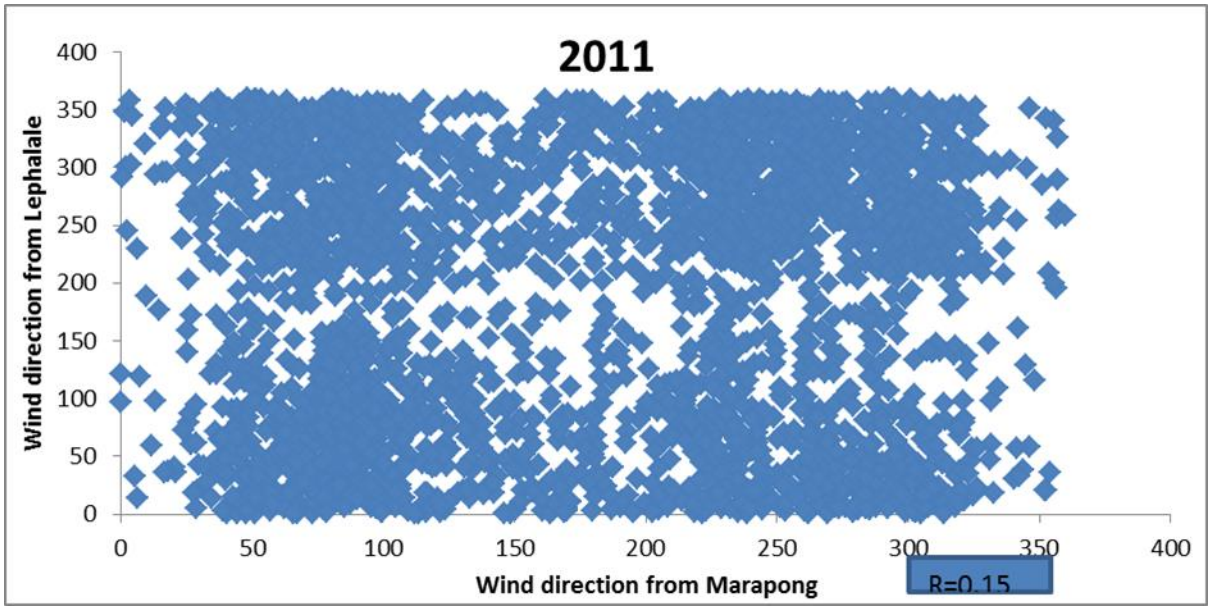

2012
Wind speed from Werkendam
Wind speed from Marapong
R=0.31

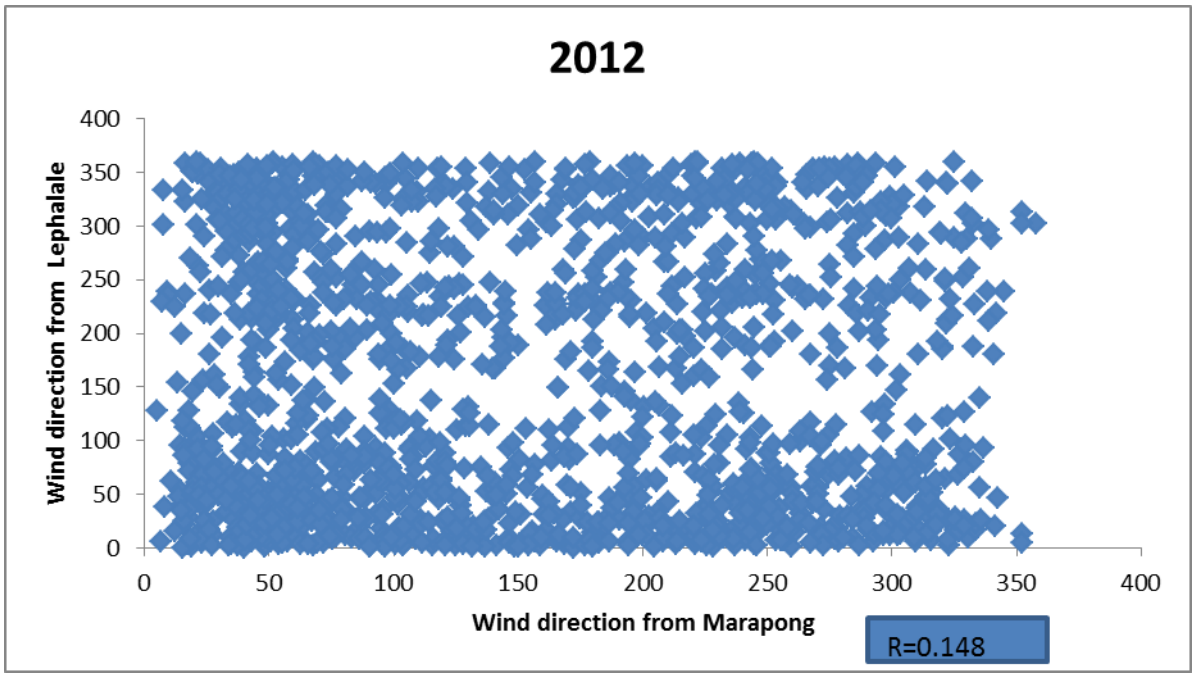
Appendix 4

Linear correlation analysis of wind direction (^{o}) Marapong versus Lephalale for the period 2009-2012

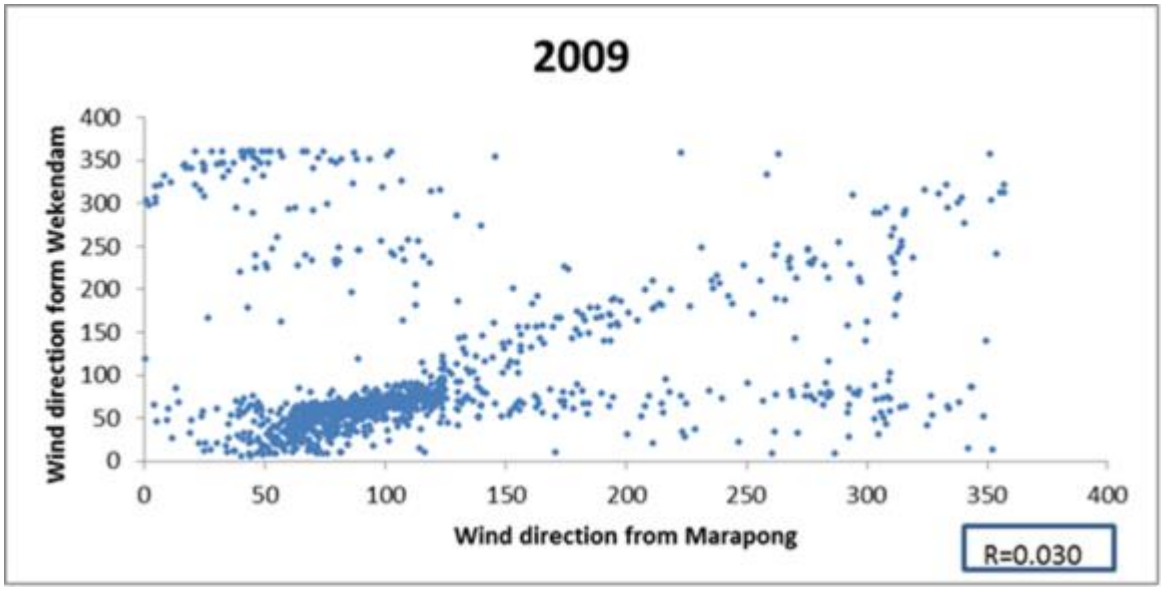


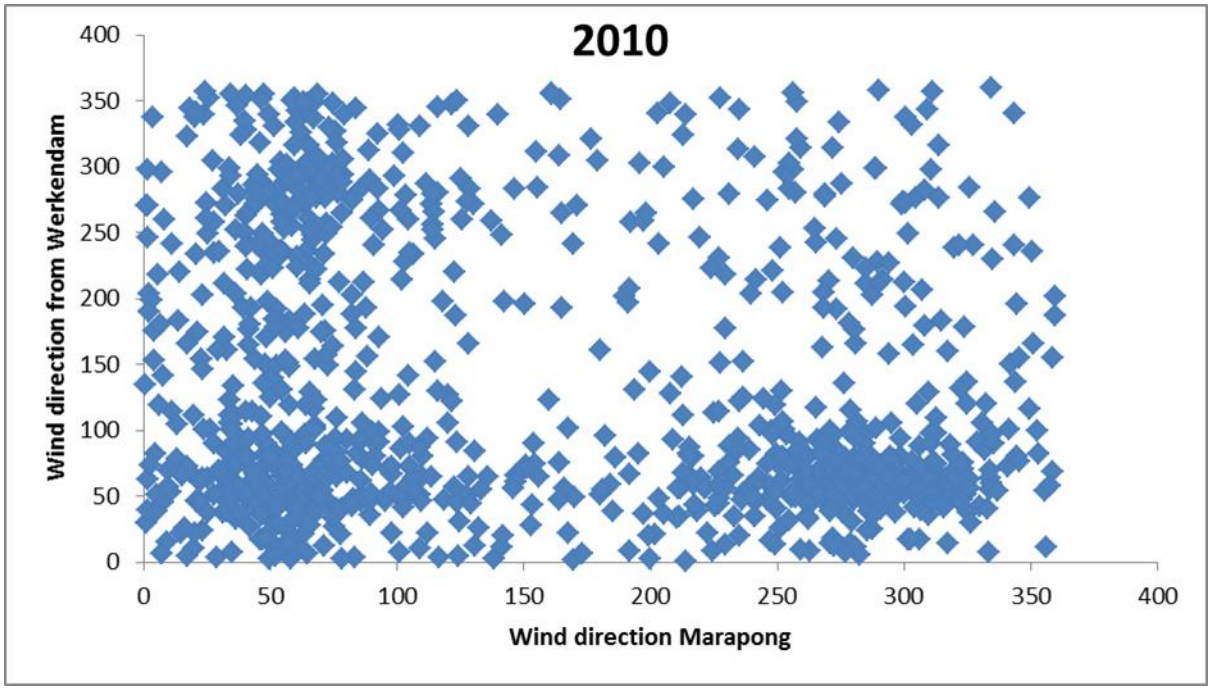


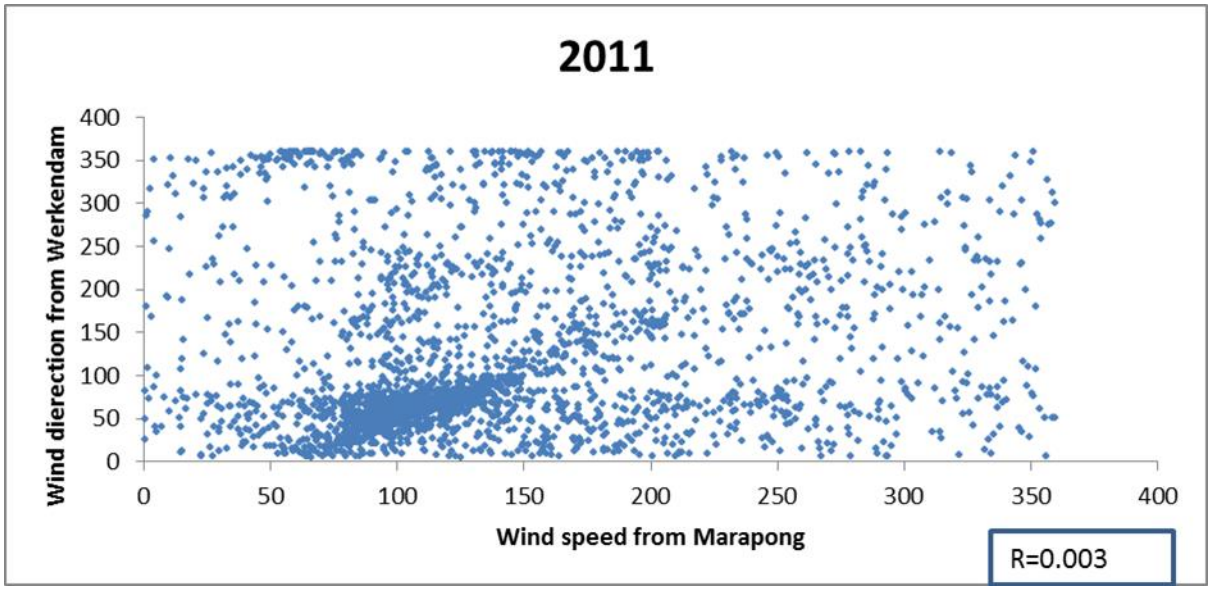

2011
Wind direction from Lephalale
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
Wind direction from Marapong
R=0.15

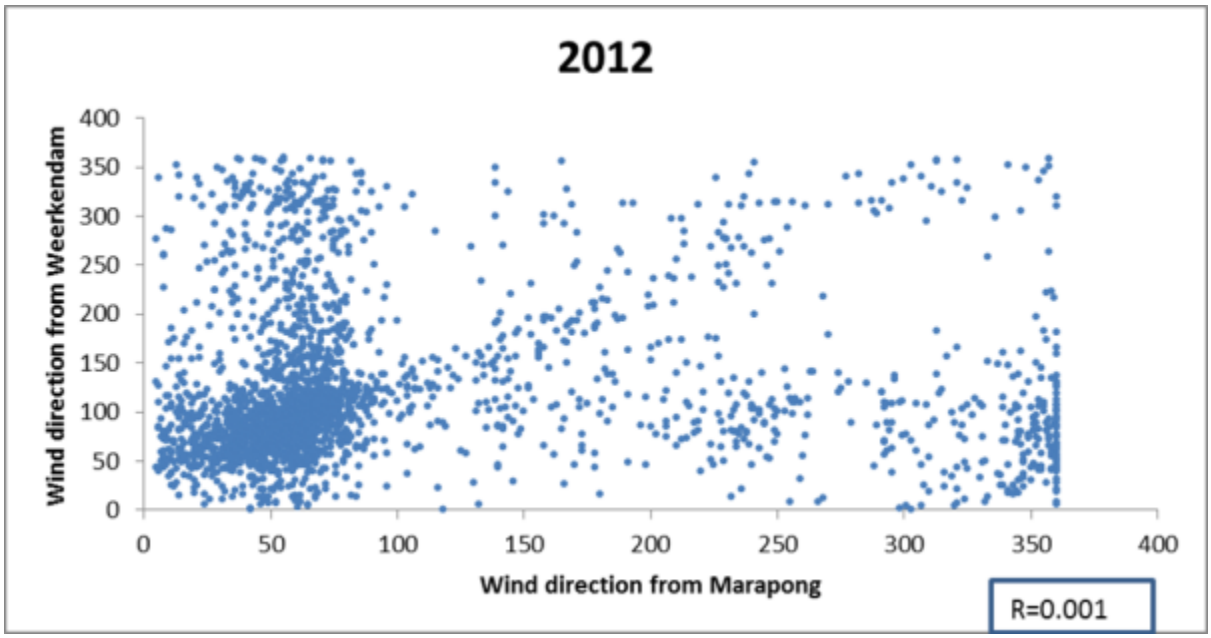

2012
Wind direction from Lephalale
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
Wind direction from Marapong
R=0.148

Linear correlation analysis wind direction (°) from Marapong versus Werkendam for the period 2009-2012.



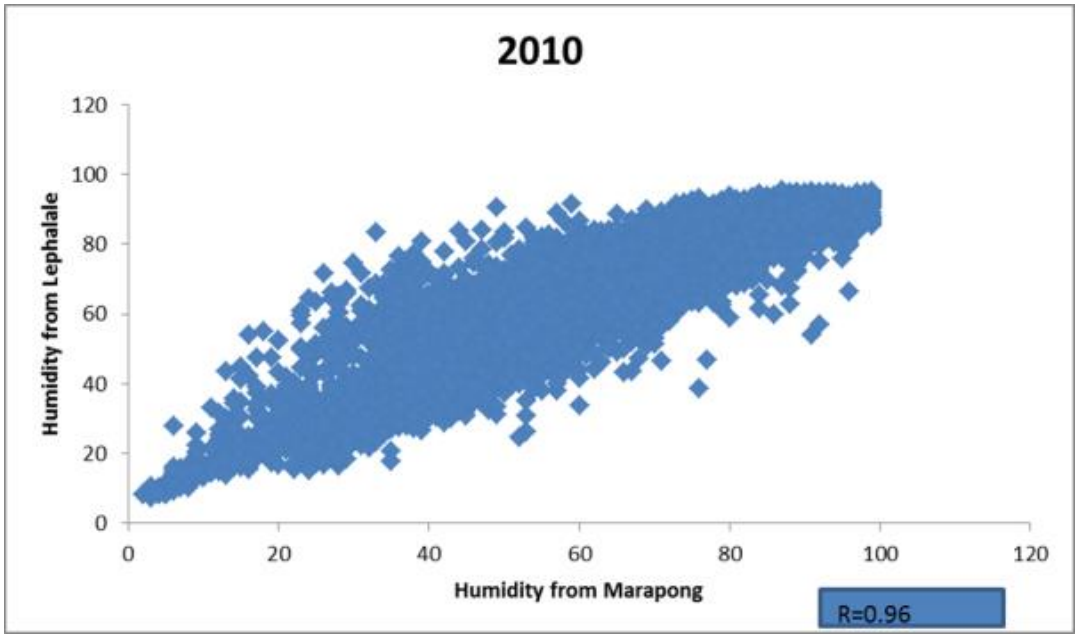



2011
Wind dierection from Werkendam
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
Wind speed from Marapong
R=0.003


2012
Wind direction from Weerkendam
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
Wind direction from Marapong
R=0.001

Appendix 5

Linear correlation analysis of humidity (%) from Marapong versus Lephalale for 2010.



Linear correlation analysis of humidity (%) from Marapong versus Werkendam for the period 2008 and 2010