Atmospheric SO_2 and NO_2 flux measurements at a savannah-grassland-agriculture landscape in South Africa

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List of abbreviations

EBIC:	Eastern Bushveld Igneous Complex
GAW	Global Atmosphere Watch
IPCC:	Intergovernmental Panel on Climate Change
IGAC:	International Global Atmospheric Chemistry
PM:	Particular Matter
NO_2:	Nitrogen Dioxide
NWU:	North – West University
SO_2:	Sulphur Dioxide
QCL:	Quantum Cascade Laser
UH:	University of Helsinki
WBIC:	Western Bushveld Igneous Complex
WHO:	World Health Organization

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ABSTRACT

Deposition measurements of SO_2 and NO_2 in South Africa are mainly limited to passive sampling where a constant deposition velocity is assumed for a specific land use category. Gaseous deposition velocities in South Africa are a major uncertainty as no direct deposition velocity for SO_2 and NO_2 have been measured. Considering that South Africa houses one of the most diversified trade and industry sectors within Africa – which include mining, agriculture and fisheries, vehicle manufacturing, food processing and energy production – the impact of pollutant species is an increasing concern for environmental health.

In an effort to reduce the uncertainties associated with deposition derived from passive sampling measurements and modelled deposition velocities for South African DEBITS sites, SO_2 and NO_2 flux measurements were performed at Welgegund measuring station for a one-year period with a quantum cascade laser (QCL) instrument. SO_2 and NO_2 monthly concentrations determined from passive samplers were correlated with the SO_2 and NO_2 flux measurements. It is anticipated that the active monitoring of SO_2 and NO_2 fluxes will significantly reduce the uncertainties associated with depositions derived from modelled deposition velocities. This type of study is also the first for South Africa where dry deposition velocities for relevant atmospheric gaseous species were directly measured with active online instrumentation.

SO_2- and NO_2 fluxes were determined with a fast-response QCL instrument for one year at Welgegund. SO_2 fluxes and deposition velocities determined in this study was in the same order of magnitude compared to SO_2 fluxes and deposition velocities calculated with inferential models in South Africa, with a mean flux and deposition value for the sampling period of .-0.01 $\mu g.m^{-2}.s^{-1}$ and 0.16 cm. s^{-1} respectively. Welgegund can be considered a net sink of atmospheric SO_2, as a net downward flux is observed for atmospheric SO_2.Inferential models indicated distinct seasonal patterns, which was not observed from micrometeorological measurements with net SO_2 fluxes remaining relatively similar throughout the year. In addition, marginal diurnal patterns were determined with relatively higher SO_2 concentrations corresponding to break-up of inversion layers.

NO_2 fluxes and deposition velocities determined in this study were compared between two studies in South Africa in which an inferential model (Mpepya, 2002, Phala, 2015) was used to calculate NO_2 fluxes and – deposition velocities. NO_2 deposition fluxes calculated from modelled deposition velocities generally overestimate N deposition for these regions, since N upward fluxes are not considered in inferential models. The mean flux and deposition velocities value for the sampling period was 0.005 $\mu g.m^{-2}.s^{-1}$ and - 0.16 cm. s^{-1} respectively. Welgegund can be considered to be a net NO_2 emitter, as a net upward flux for atmospheric NO_2 was observed. Distinct seasonal patterns were observed for NO_2 fluxes with highest NO_2 fluxes corresponding to the warm and wet months due to increased temperature, soil temperature, precipitation and biogenic activity.

Keywords: NO_2, SO_2, air quality, deposition velocity, flux

Chapter 1

Background and objectives

The following chapter considers the relevance of the current study and provides the motivation thereof in terms of background information which considers atmospheric processes, deposition and environmental impacts (Par 1.1). Chapter 1 also presents the objectives set for this study (Par. 1.2).

1.1. Background and motivation

Atmosphere–biosphere interactions are important considerations for the assessment of biogeochemical cycles and atmospheric composition relevant to the modulation of atmospheric species. Within these considerations, it becomes essential to evaluate the wet and dry- deposition of chemical species from atmosphere to earth and the influence thereof on concentrations of atmospheric gases and aerosols. Atmospheric deposition – and the chemical composition of deposition – is a product of several interactions between physical and chemical processes which take place in the atmosphere. This includes the following; emissions and source strengths; transport processes and dynamics of the atmosphere; atmospheric chemical reactions; and removal processes. A comprehensive study of deposition processes are thus necessary for identifying the spatial and temporal evolution of atmospheric chemistry and a way to distinguish between natural and anthropogenic influences. In regions where biogeochemical cycles are disturbed by human activities, atmospheric deposition can either be a source of toxic substances or a source of nutrients for the ecosystems. So too, an understanding of chemical deposition is required to form a global and interdisciplinary approach aligned to a predictive capacity for determining ecosystem function and anthropogenic impacts on biogeochemical cycles (Brimblecombe *et al*. 2007; Whelpdale *et al.* 1996; Martins *et.al*. 2007; Pienaar, 2005).

It should be mentioned that potential adverse environmental impacts related to increased anthropogenic emissions into the atmosphere necessitate the execution of long-term atmospheric measurement programmes. In response, the Deposition of Biogeochemically Important Trace Species (DEBITS) task of the International Global Atmospheric Chemistry (IGAC) programme was initiated in 1990 in collaboration with the Global Atmosphere Watch (GAW) network of the World Meteorological Organisation (WMO) to investigate long-term concentrations, as well as wet and dry deposition of biogeochemical species (mainly C, N and S species) in temperate atmospheres (Lacaux *et al.*, 2003). The African component consists of thirteen strategically positioned deposition sites in southern and western Africa that are representative of prominent African ecosystems (https://indaaf.obs-mip.fr/). Four of these sites are situated in South Africa. This programme is currently operated in Africa under the International Network to study Deposition and Atmospheric chemistry in Africa (INDAAF) program.

Sulphur dioxide (SO_2) and nitrogen oxides (NO_X) are the principal acid-forming pollutants in the atmosphere. Anthropogenic sources of these species include fossil fuel combustion, vehicular emissions, pryometallurgy, household combustion and biomass burning, while NO_x is also naturally emitted from ecosystems. South Africa is regarded as a major source region of anthropogenic atmospheric SO_2 and NO_2. The highly industrialised Mpumalanga Highveld and Gauteng region accounts for about 90% of South-Africa's scheduled emissions, i.e. approximately 2 million t/year of SO_2 and 1 million t/year of NO_X. An NO_2 hotspot is clearly visible over the South African Mpumalanga Highveld (Lourens *et al*. 2011). This can be attributed to the fact that de-SO_x and de-NO_x technologies are not generally applied to off-gas treatments by South African industries. Notwithstanding the relevance of South Africa with regard to N and S emissions, as well as the need for long-term monitoring programmes, limited data has been published on deposition for this region.

Atmospheric removal of SO_2 and NO_2 emissions take place through a process of both wet and dry deposition. Dry deposition of atmospheric gaseous species at DEBITS sites (within SA) are assessed by measuring monthly concentrations of species using passive samplers. Dry deposition is then estimated using deposition velocities determined via inferential modelling for different land use categories, as reported by Zhang *et al*., 2003. Although a relatively good estimate for dry deposition fluxes can be determined, the modelled deposition velocities do not reflect actual diurnal and seasonal fluctuations associated with deposition of atmospheric gases. In addition, these modelled deposition velocities are determined for homogenous landscapes and do not consider disturbed regions where combinations of different land use categories occur. Furthermore, modelled deposition velocities do not reflect specific meteorological conditions associated with a specific region.

The Welgegund atmospheric monitoring station is a well-equipped regional background site, which is located approximately 100 km west on a private farm (www.welgegund.org). Welgegund is located in the Grassland Biome, which covers 28% of South Africa's land surface (Mucina & Rutherford, 2006). This biome has been significantly transformed, primarily as a result of cultivation, plantation forestry, urbanisation and mining (Daemane *et al*., 2010 and references therein). The immediate area surrounding Welgegund is grazed by livestock, with the remaining area covered by crop fields (mostly maize and to a lesser degree sunflower). Within a 60 km radius, a further three vegetation units of the Grassland Biome and another two of the Savannah Biome are also present. Welgegund is geographically located within the South African Highveld, which is characterised by two distinct seasonal periods, i.e. a dry season from May to September that predominantly coincides with winter (June to August) and a wet season during the warmer months from October to April. The dry period is characterised by low relative humidity, while the wet season is associated with higher relative humidity and frequent rains that predominantly occur in the form of thunderstorms.

In an effort to reduce the uncertainties associated with $SO_2$and NO_2 deposition derived from modelled deposition velocities in South Africa, as well as to contribute to the accumulation of data for South African INDAAF sites, online micrometeorological measurements of SO_2 and NO_2 fluxes were performed at Welgegund for a one-year period with a fast-response quantum cascade laser (QCL) instrument. This was the first time in South Africa that dry deposition velocities for the named atmospheric gaseous species were researched via active micrometeorological measurements. Monthly atmospheric SO_2 and NO_2 concentrations were also determined with passive samplers in order to compare SO_2 and NO_2 flux measurements at Welgegund to SO_2 and NO_2 concentrations measured in INDAAF. Micrometeorological active monitoring of SO_2 and NO_2 fluxes will significantly reduce the uncertainties associated with depositions derived from modelled deposition velocities.

1.2. Objectives

The general objective of this study was to perform micrometeorological measurements of SO_2 and NO_2 fluxes at a savannah-grassland-agricultural region for the first time in South Africa. Specific objectives include:

- Active micrometeorological measurement of SO_2 and NO_2 fluxes with a fast-response QCL instrument for one year at Welgegund;
- Processing high resolution QCL data for the entire sampling period with programmable mathematical software to determine SO_2 and NO_2 fluxes;
- Calculating SO_2 and NO_2 deposition velocities from active flux measurements;
- Determine temporal patterns for SO_2 and NO_2 deposition velocities and fluxes;
- Relate calculated deposition velocities to modelled deposition velocities in South Africa.

Chapter 2

Literature study

Chapter 2 provides an overview of relevant literature for this study. This chapter starts with an overall introduction to atmospheric pollution (Par. 2.1.) and, specifically, gaseous atmospheric pollutants (Par. 2.2.); while focusing on SO_2 and NO_2 atmospheric pollutants (Par. 2.3). Major atmospheric chemical reactions relating to SO_2 and NO_2 are discussed (Par. 2.4.), followed by a summary of health and environmental effects associated with these species (Par.2.5.). Deposition of gaseous atmospheric pollutants is also discussed (Par.2.6.) in line with dry deposition phenomena and fluxes. The scope of international deposition studies is also considered (Par.2.7.), followed by a discussion of deposition studies in South Africa (Par. 2.8.).

2.1. Atmospheric pollution

Atmospheric pollution can be defined as a release of contaminants in quantities large enough to alter the atmosphere's natural composition and which is harmful to the environment and all living organisms (Kampa & Castanas, 2007). The greatest concern for air pollution effects is for the troposphere – this being the lowest region of the atmosphere – and the stratosphere, the second major layer; given the proximity to earth's surface, these atmospheric layers are particularly vulnerable to pollution (Lourens, 2008). One of the greatest contributors to atmospheric pollution is the continuous increase and expansion of industrial activity, which has characterised the 20th and 21st centuries (Annegarn *et al*., 1996a; Pham *et al*., 1996; Zunckel *et al*., 2000; Smith *et al*., 2001; Mphepya *et al*., 2004). Naturally-occurring atmospheric cycles are inevitably disturbed by pollution, which may contribute to uncommon weather phenomena and other detrimental effects on the environment (Jacobson, 2002).

In South Africa, air quality studies focus mainly on priority areas identified by the national government, which include the industrialised Mpumalanga Highveld area, Vaal Triangle and Waterberg-Bojanala region (DEAT, 2007). These regions are characterised by ongoing industrial activity and densely-populated urban and rural areas. With South Africa identified as a major source of industrial pollution, the nation’s critical thresholds for environmental damage is significant at a global level (Josipovic, 2009). The scientific study and knowledge of atmospheric pollution progressed well in Western European and North American countries and great strides were made in their own atmospheric monitoring programmes. This is not generally the case in South Africa, where the emissions from industrial activities are comparable to developed, high-income nations; this includes building and industrial activities, motor vehicle emissions and the burning of fossil fuel for domestic use, such as heating and cooking (Elsom & Longhurst, 2004; Khare & Kansal, 2004). Even more, air quality is at a noticeable decline in South Africa due to the increase of ambient concentrations of gaseous species and aerosols (Blight *et al*., 2009). Listed in table 1 below are common sources of air pollution in South Africa.

Table 1 Common air pollution sources in South Africa (Blight *et al*., 2009).

Pollution sources	**Examples**
Fuel combustion (stationary activities)	Industrial and chemical processes
Fuel combustion (mobile activities)	Vehicles
Solid waste disposal	Incineration
Land surface disturbances (rise to dust)	Mine dumps, unpaved roads and agricultural activities.

2.2. Gaseous atmospheric pollutants

From initial release, gaseous pollutant species enter the atmosphere and undergo transformations until removed via wet and dry deposition. These processes take place as the initial steps of biogeochemical cycles, which are responsible for the formation and release of environmental chemicals (Mphepye et al., 2002, Whelpdale & Kaiser, 1996). Typical atmospheric contaminants associated with air quality include sulphur dioxide (SO_2), nitrogen oxide (NO) and –dioxide (NO_2), ozone (O_3), ammonia (NH_3), carbon monoxide (CO) and volatile organic compounds (VOCs). Figure 1 presents the main processes which occur through the gaseous pathways in the atmosphere and illustrates the physical and chemical transformation of major inorganic gaseous pollutant species, as well as the transport and deposition of these species. The understanding of such processes and transformations and how they culminate into pollutant species, is a key consideration in the study of atmospheric chemistry.

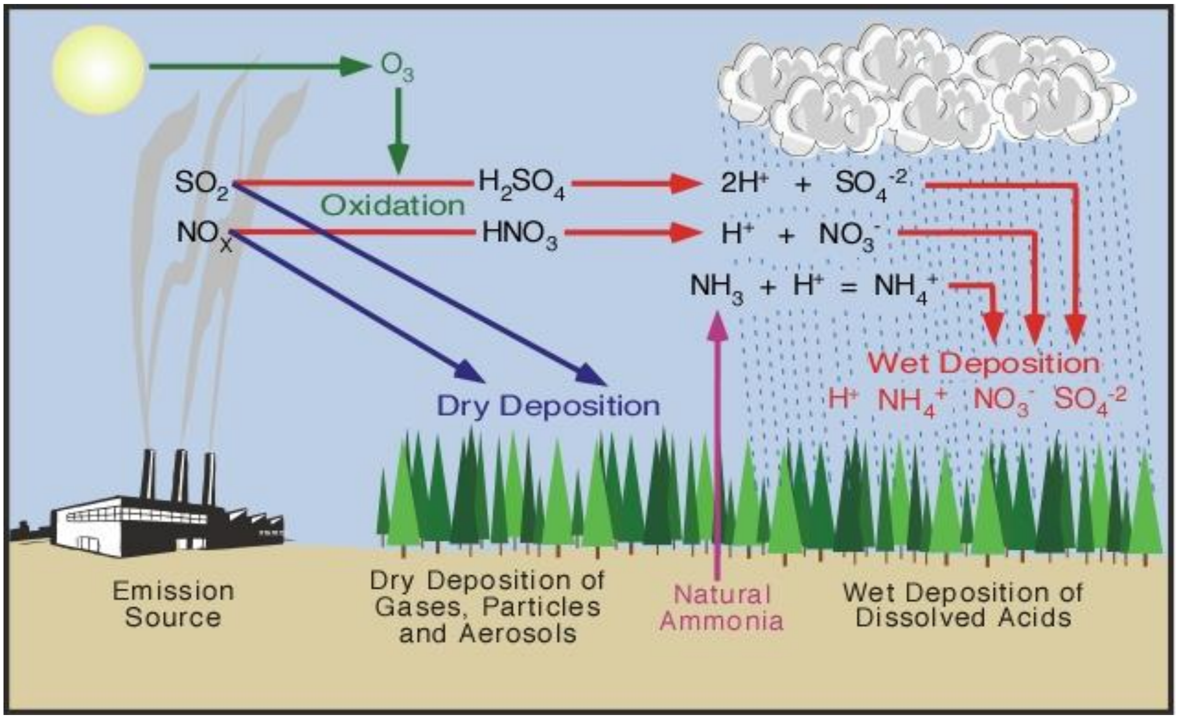


Figure 1 A simple diagram illustrating the pathway of major gaseous atmospheric pollutants (Pidwirny, 2006).

2.3. Sulphur- and nitrogen dioxide

There are several compounds of sulphur present in the atmosphere, e.g. SO_2, SO_3 and aerosol SO_4^{2-} (Mphepye at al., 2002, Whelpdale and Kaiser, 1996). SO_2 is described as a colourless gas detected by a pungent smell and released from stationary sources; the burning of fossil fuels for power generation is one example (Elsom, 1987). Additional sulphur-containing gaseous compounds present in the atmosphere include SO_3, hydrogen sulphide (H_2S), dimethyl sulphide ($(CH_3)_2S$) and carbon disulphide (CS_2), which can also lead to the formation of atmospheric SO_2.

The surge of industrial and economic development in developed countries is linked to increased SO_2 pollution and higher mean concentrations of atmospheric SO_2. Figure 2 illustrates the global sulphur emission trend from 1850 – 2000 (IPCC, 2001). Following the industrial revolution of the 18th century – and the consequent increase in power generation – a rapid increase in SO_2 levels is noticeable. However, a global awareness of air quality developed during the late twentieth century (promoted mostly by developed countries). In response, it became a priority for policy makers and leading industries to find cost-effective and efficient methods which could reduce pollution levels. As a result, first world countries witnessed a noticeable decline in mean SO_2 concentrations; this was attributed to the implementation of desulphurisation of stack emissions at both plants and factories (IPCC, 2007B). Conversely, South Africa has observed an upward trend and is currently the 9th highest sulphur-emitting country in the world (Stern, 2006).

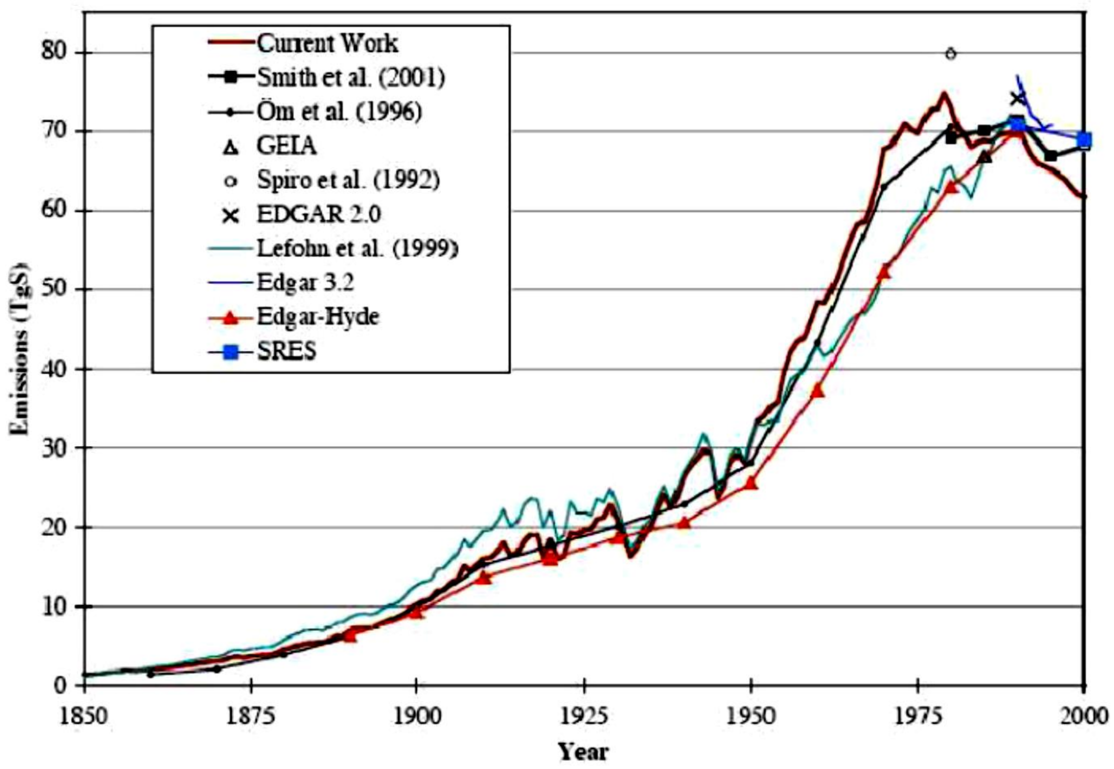


Figure 2 The world sulphur emissions trends (IPCC. 2001).

NO_2 is a product of high temperature combustion, mainly produced by vehicular emissions, coal-fired power plants, petrochemical industries and biomass burning. NO_2 is recognised as a prominent nitrogen-containing atmospheric pollutant and known to be mostly anthropogenic (Seinfeld & Pandis, 2006). Excessive NO_2 levels are typical of urban areas during early mornings and late afternoons, which is a result of increased motor vehicle activities. In addition to anthropogenic emissions, NO_2 is produced by lightning, as well as NO emissions from plants and soil. Naturally-occurring NO_2 is also produced by the oxidation of NH_4^+ and reduction of NO_3 and is required by a number of major chemical processes in the atmosphere (Seinfeld & Pandis, 2006).

Despite being the most prominent nitrogen-containing pollutant species in the atmosphere, NO_2 is vital to several reactions which occur within the troposphere. NO_2 is responsible for absorbing radiation over the complete range of the ultraviolet and solar spectrum (Seinfeld & Pandis, 2006). In South Africa, the Mpumalanga Highveld is a prominent NO_2 hotspot due to the proximity of several coal-fired power stations and a large petrochemical plant (Lourens *et al*., 2011). The cycle of nitrogen compounds is illustrated in figure 3 below (Palmgre *et al*., 1997).

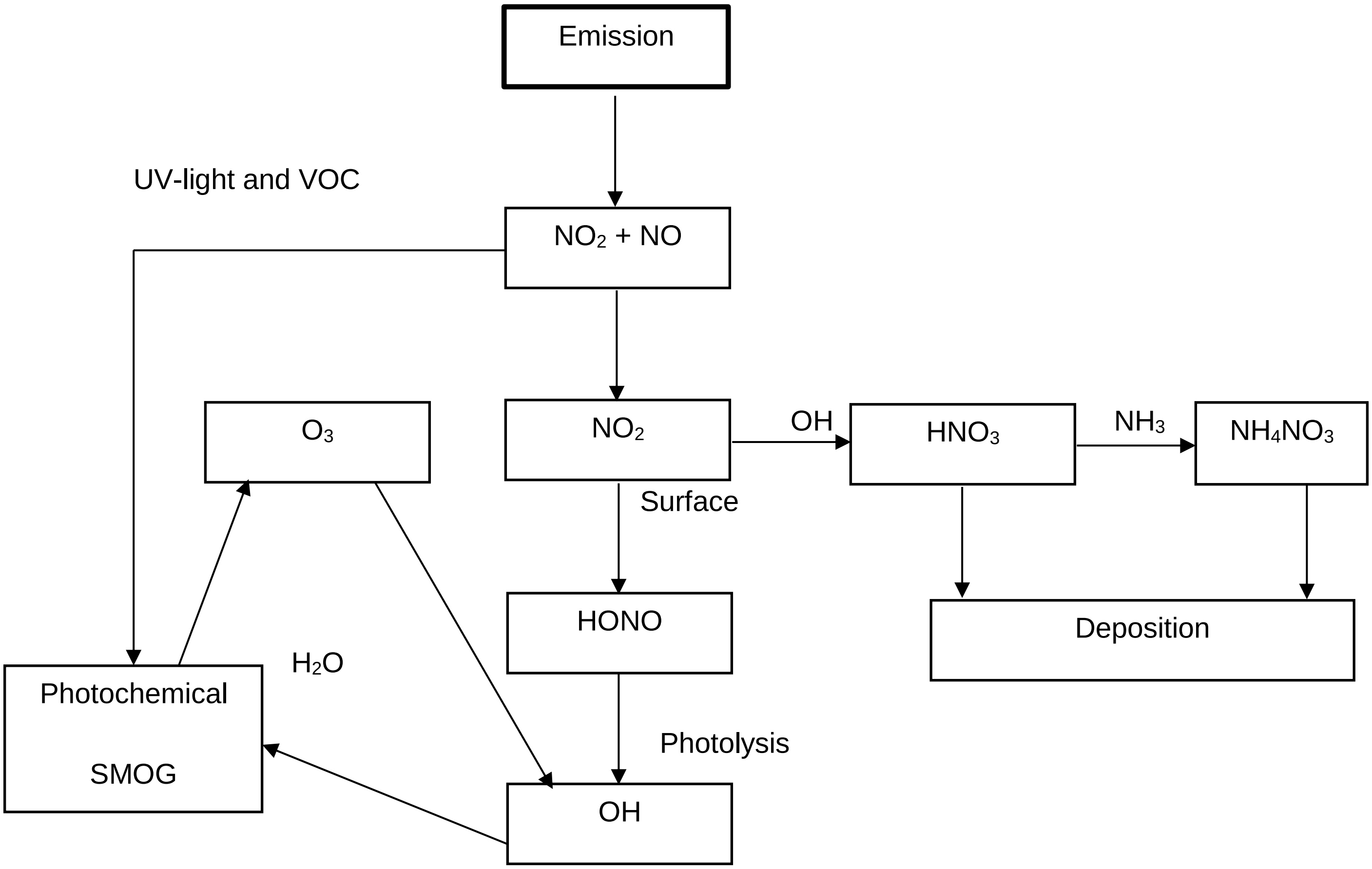


Figure 3 The cycle of nitrogen compounds.

2.4. Atmospheric chemical reactions of SO_2 and NO_2

2.4.1. SO_2

In the atmosphere SO_2 reacts with oxygen to produce SO_3 during the production of sulphuric acid (H_2SO_4):

$2SO_2 + O_2 \rightarrow 2SO_3$ 1

Under atmospheric conditions the reaction between SO_2 and O_2 is slow. For this reason, SO_3 is more readily produced through the hydroxyl radical ($HO^\bullet$) abstraction reaction:

$SO_2 + HO^\bullet + A \rightarrow HOSO_2 + A$ 2

$HOSO_2^\bullet + O2 \rightarrow HO_2^\bullet + SO_3$

A vibrational exchange species is represented by A. When SO_3 then reacts with water, sulphuric acid is formed:

$SO_3 + H_2O + A \rightarrow H_2SO_4 + A$

Other sulphate aerosols are also produced from SO_2 and the process and formation thereof will determine the properties of the sulphate aerosols. The production of these sulphates can be in the aqueous or gas phase (Houghton *et al*., 2001). After being formed, these particles group as molecular clusters and increase in size. The particles eventually form ultra-fine aerosols that continue to grow to large diameters.

In the atmosphere, SO_2 can also be secondarily formed. SO_2 can be formed from $(CH_3)_2S$, which undergoes a few reactions in the atmosphere.

$CH_3SCH_3 + HO^\bullet \rightarrow CH_3SCH_2O_2^\bullet$

$CH_3SCH_2O_2^{\cdot} \rightarrow CH_3S^{\cdot} + HCHO \rightarrow SO_2 + CH_3^{\cdot}$

H_2S undergoes HO abstraction from which the SH radical is formed, which leads to the formation of SO_2. (Seinfeld & Pandis, 1998):

$H_2S + HO^{\cdot} \rightarrow SH^{\cdot} + H_2O \rightarrow SO_2$

Residence times of SO_2 in the atmosphere ranges between twelve hours to six days (Kellogg *et al*., 1972).

2.4.2. NO_2

NO_2 is an important precursor for the formation of O_3. Although other species are also considered O_3 precursors, the only path from which surface O_3 can be formed is from the photochemical reaction of NO_2. O_3 influences the oxidative capacity of the atmosphere. If O_3 photolysis is the start of tropospheric chemistry then NO_2 can be seen as the precursor for all the chemistry in the troposphere (Pienaar & Helas, 1996). Once NO and O_3 are released into the atmosphere, these species undergo a series of chemical reactions (Fellenberg, 1997).

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + hv \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$ ($M = N_2$ or O_2)

The nitrate radical $NO_3^{\cdot}$ is produced by the reaction between NO_2 and O_3.

$NO_2 + O_3 \rightarrow NO_3^{\cdot} + O_2$

The nitrate radical reacts fast with NO and sunlight to form NO_2 and NO again:

$NO_3^{\cdot} + hv \rightarrow NO + O_2$ (<4600 nm)

$NO_3^{\cdot} + hv \rightarrow NO_2 + O(^3P)$ (<580 nm)

Other nitrogen oxides photolysis in the troposphere include:

$N_2O_5 + hv \rightarrow NO_3 + NO_2$ (<406 nm)

$HO^{\cdot} + NO^{\cdot} \rightarrow HONO$

$HO^{\cdot} + NO_2 \rightarrow HNO_3$

2.5. Environmental and health impacts of SO_2 and NO_2

2.5.1. SO_2

Atmospheric SO_2 poses the risk of causing severe damage to human health. Low SO_2 concentrations can lead to an increased risk of bronchitis following long-term exposure (especially smokers). The WMO recommends that short-term exposure to SO_2 should not surpass 125 $\mu g.m^{-3}$. Long term exposure should also not exceed 50 $\mu g.m^{-3}$ (Brimblecombe, 1996).

The individual environmental impact of SO_2 is minor and not particularly harmful. However, when SO_2 comes into contact with hydrocarbons, soot and high humidity to produce H_2SO_4 in the atmosphere as indicated above, its impacts are significant. With the carbon acting as nuclei for water condensation, this produces unpleasant smog which may reduce visibility (Van Velthoven & Kelder, 1996). The deposition of H_2SO_4 through fog, mist and rain leads to soil acidification, foliar harm, the damage of property and forest decline (Binkley *et al*., 1989, Linthurst, 1984). The effects on plant species may vary, but it is clear that some plants are more susceptible than other species, while trees and plants located in regions closest to sources of SO_2 pollution will be more affected. H_2SO_4 deposition can result in toxic metals being released into rivers, streams and lakes, which causes plant root damage and also leads to nutrient leaching (Binkley *et al*., 1989). In some cases, it was observed that the reduction of sulphur emissions contributes to the slow recovery of natural ecosystems, which take place for the duration of episodic events (Lawrence, 2002; Kowalik *et al*., 2007).

2.5.2. NO_2

As indicated above, NO_2 plays a major part in the formation of surface O_3, which results in photochemical smog (Brasseur *et al*., 1999). Photochemical smog is a cloud of pollution that causes reduced visibility, irritation to the nose, throat and lungs and may cause chest pain, coughing and nausea (van Loon and Duffy, 2005). Since NO_2 is considered the main source of O_3 production, it is also indirectly associated with O_3 greenhouse effects and the formation of $HO^{\bullet}$ radicals (Brasseur *et al*., 1999). An O_3 process is based on the continuous effect of direct and indirect reaction mechanisms. Combined with $HO^{\bullet}$ radicals, O_3 is responsible for converting primary pollutant species to secondary products, which are more readily available for removal from the atmosphere (Brasseur *et al*., 1999).

The known negative effects of NO_2 include corrosion in metals and damage to vegetation. Even at low concentrations (1 ppm), NO_2 can have serious negative health effects on humans and animals and may potentially damage the cells of the respiratory system. It is also indicated that even lower concentrations (0.5 ppm) can increase the likelihood of bacterial infections (Brimblecombe, 1996). At present, no accurate recommendations can be made for an air quality limit of NO_2 values. With observed changes in the pulmonary function of asthmatics sufferers when exposed to 0.3 ppm, a guideline of 0.21 ppm was set at low exposure (a time period of 1 hour) and 0.08 ppm at higher exposure (for a period of 24 hours) (Brimblecombe, 1996).

2.6. Deposition

From initial point of release, pollutant species undergo processes of transport and transformation in the atmosphere and are eventually deposited on the earth’s surface via wet or dry deposition. Wet deposition is a process by which these species are removed via precipitation, fog or cloud droplets and, conversely, dry deposition is the absorption of aerial pollutants found on the earth’s surface and also the settling of species onto soil. Wet deposition through precipitation is globally acknowledged to be more significant than dry deposition. However, the contribution of dry deposition on removal rates of atmospheric pollutants cannot be disregarded and in certain regions (e.g. arid ad semi-arid areas) it can be more significant than wet removal of atmospheric species. Fog or cloud droplets on vegetation can be considered important on a local scale, especially in areas were cloud coverage and water vapour is common (Mphepye at al., 2002, Whelpdale and Kaiser, 1996). Although these processes are dependent on weather conditions, it should be noted that atmospheric deposition is not continuous in most ecosystems (Baumgardner et. al, 2002). Furthermore, to fully understand the deposition of chemical species from atmosphere to earth, in-depth knowledge of regional and global emission sources is needed (Else, 1985; Else, 1987). This is important given that concern for deposition material entering the environment has increased over the last decade.

Sulphur and nitrogen deposition occur through wet and dry processes. Deposition of dissolved sulphur and nitrogen occurs through precipitation events, while these species can be deposited as a dry compound when discharged in close proximity to emission sources (Brasseur *et al*., 1999; Hewitt, 2001). When exposed to plants and other vegetation, direct gas absorption of sulphur and nitrogen loads can occur. In drier climates and regions closer to emissions sources, deposition to a terrestrial ecosystem occurs mainly through dry deposition (Lindberg, 1992; Padgett *et al*., 1999; Kennedy, 1986; Zunckel *et al*., 2000). Conversely, wetter weather conditions are characterised by fog and wet deposition (Lovett, 1992; Olbrich, 1993; Zunckel *et al*., 2000).

The process of removing particles or gases from the atmosphere through the delivery of mass to the surface by non-precipitation is also defined as ‘‘dry deposition’’ (Dolske & Gatz 1985). There are several factors that influence dry deposition of gases and particles from atmosphere to soil. Atmospheric particles and species are transported to earth where the chemical and physical nature of these species contributes to their absorption into terrestrial ecosystems and soil. Atmospheric turbulence, generated by wind and buoyancy, is also involved in the transportation of particles and gas species from atmosphere to earth. As atmospheric turbulences increase, the speed and efficiency at which gasses and particles are transported from atmosphere to earth likewise increase (Mphepye at al., 2002, Erisman & Draaijers, 1995). Dry deposition typically occurs in three steps: (1) species are transported from free atmosphere down to viscous sublayer; (2) species are transported across viscous sub-layers (via interception, inertial forces such as impaction and sedimentation); and (3) species interact with the surface (Mohan, 2016).

When deposition occurs close to emission sources, dry deposition is determined by the configuration of the source, the source type and the mixing of pollutants in the atmosphere. Deposition near high-stack emissions will be less, but will steadily increase downwind from the source where it will reach a maximum value and then decrease again. Conversely, dry deposition associated with ground-level sources occurs within the immediate proximity in the region of the source and will gradually reduce downwind. The concentration gradient is influenced less by the source at a certain distance from the source and determined primarily by dry deposition processes; this is the result of the pollutant species being absorbed by the boundary layer (Mphepye at al., 2002, Erisman and Draaijers, 1995). The boundary layer consists of two layers responsible for the transport of pollutants, i.e. the fully turbulent layer and the quasi-laminar layer.

2.7. Measurement of dry deposition fluxes

Different techniques have been used to measure dry deposition fluxes and measurements can be conducted either directly or indirectly. By measuring secondary quantities, flux concentrations can be determined using indirect methods. The secondary quantities include concentrations or vertical gradients of flux concentrations. In contrast, direct measurement methods are more expensive and require greater effort.

2.7.1. Micro-meteorological techniques

Micro-meteorological techniques are used to estimate deposition flux using local meteorology. This method is especially useful for determining fluxes of gaseous pollutants. The eddy co-variance technique is widely used, which takes into account the concentration of the pollutant species that is combined with the vertical component of the wind velocity to determine deposition flux. Another example of a micro-meteorological method used to determine dry deposition flux is the gradient method, which measures concentrations of the pollutant species at two or more heights. Measuring concentrations at two or more heights to determine deposition flux is challenging and requires more accuracy (Hicks, 1986).

Micro-meteorological measurements are carried out above surface and allows for the continuous measurement of flux. However, there are a few drawbacks to this technique; measurement can only be conducted within a small area (5 – 10 meters) due to the requirement of a constant flux layer that must be sustained above the vegetation. If flux measurements take place in close proximity to a pollutant source, measurements are complicated by an under-developed flux layer. Furthermore, measurements should be carried out when no sinks or sources above the surface atmosphere should be present to develop a constant flux layer. If present, sinks or sources in the atmosphere can result in swift chemical reactions. For accurate flux measurements, the differences in concentrations of pollutant species should not change rapidly over time; these measurements are suitable for measuring deposition and validating other models and methods (Hicks *et al*., 1987; Baldocchi *et al*., 1988). Even though there have been some instances where this technique has been used, it remains relatively unknown in South Africa.

2.7.2. Surface accumulation techniques

The surface accumulation technique uses natural surfaces to measure deposition flux. There are two examples of surface accumulation techniques, throughfall techniques and surrogate surfaces (fallout buckets). The deposition of large particles is determined by these techniques, where particles are intercepted by buckets which prevent them from reaching the surface. The limitation of the technique is that the collection surface does not simulate vegetation.

2.7.3. Inferential technique

According to Hicks *et al*. (1987), the inferential technique can be considered a direct technique. By measuring pollutant concentrations and meteorological parameters and by understanding the processes involved in dry deposition, dry deposition flux can be estimated by using the formula $F_d = -VdCs$, where Vd is the deposition velocity and Cs the pollutant concentration, assuming zero surface concentration of a pollutant. The dry deposition velocity depends on a few factors, which includes the properties of the constituent, meteorology and above-surface transport, alongside some surface properties. This technique was used successfully by a number of individual measuring sites (Schwede *et al*., 2011; Flechard *et al*., 2011; Delon *et al*., 2012), while patterns and regional deposition estimations were also measured at multiple sites (Baumgardner *et al*., 2002; Holland *et al*., 2005; Zhang *et al*., 2005). This technique has been used locally (South Africa) and internationally to determine dry deposition (e.g. Zunckel *et al*., 1996; Zunckel *et al*., 1999; Zunckel *et al*., 2000 Meyers & Yeun, 1987; Meyers *et al*., 1991; Matt & Meyers, 1993). This technique was used in Eastern parts of the United States to determine nitrogen deposition; it was found that 30 – 50 % of the total nitrogen deposition was contributed by dry deposition (Meyers *et al*., 1991). A study completed by Hesterberg *et al*., (1996) in Switzerland determined that dry deposition occurred in more instances than wet deposition by using this technique. In South Africa, the technique was used to research and determine deposition in major industrialised regions, which were categorised as pollutant areas (one example is the Mpumalanga region).

2.8. Micro-meteorological SO_2 and NO_2 deposition studies

2.8.1. SO_2

Utiyama *et al.* (2005) used the aerodynamic gradient method to measure SO_2 dry deposition to dead grass and loess soil in Beijing, with the surface reaction concept being utilised for inferring dry deposition. Deposition velocities measured were between 1-12 mm/s. Laboratory-based flow reactor measurements for 12 different sites were conducted by Sorimachi and Sakamoto (2007) in Northern China. This study examined up to 12 soil samples in deserts and arid loess plateaus. The canopy resistance ranged from 28-650 s m^{-1}, with the mean concentrations being close to 200 s m^{-1}. It should be noted that these values were depended on relative humidity.

In Northern Thailand, Matsuda *et al*. (2006) conducted micrometeorological SO_2 and O_3 flux measurements over a tropical forest in wet and dry seasons. During dry seasons, measured deposition velocities were rather low at 0.8-3.1 mm/s during day and night time for SO_2. Higher values were observed in the wet season with values ranging from 2.6-13.9 mm/s during the days and nights. This is due to greater non-stomatal uptake which was attributed to wetter conditions. The above-mentioned values were compared to SO_2 fluxes calculated with the inferential model by Zhang *et al*., 2003, which considered a non-stomatal resistance scheme. It was concluded that more SO_2 deposition studies are needed on this subject and that available research is limited. It was also recommended by Zhang *et al*., 2003 that more studies are needed to determine the effects of dew and rain on SO_2 deposition.

In Oshiba Highland (Nagano Japan), Matsuda *et al*. (2002) measured SO_2 dry deposition over a red pine forest, using a Bowen ratio technique. The median deposition velocity value for the daytime was 9 mm/s, which compared well with estimated inferential modelled values for wet conditions. The only exception was for dry or dry-wet surfaces where large differences were observed. These differences were attributed to relative humidity threshold value used in the inferential model which acted as an estimate of canopy wetness.

Sorimachi *et al*. (2003) completed a study which examined ecosystems in close proximity to the city of Beijing and measured SO_2 and O_3 dry deposition using the aerodynamic gradient method to short grassy vegetation. The study was conducted in late summer and early winter respectively. The mean value for late summer was 2 mm s^{-1}, with early winter being 4 mm s^{-1}. In Thailand, Jitto *et al*. (2007) used the Brown ratio technique over an irrigated rice canopy to measure SO_2 deposition velocity during a one-year experiment. During the day time, values were higher than those measured at night. The highest value was measured during the rainy season. Measured values ranged from 12.5, 6.7 to 15.1 mm s^{-1} in the summer, winter and rainy season respectively.

Due to micrometeorological measurements being expensive and labour-intensive, authors in Asia used long-term studies to monitor concentration and inferential models. In the Gansu province in China, Ta *et al*. (2005) measured long-term (11 years) SO_2 dry deposition values using Sulfation plates coated with K_2CO_3. The data was collected at 48 different sites in 11 cities around the province and showed a correlation between SO_2 dry deposition flux and local SO_2 emissions. During the winter months, measured values were higher when compared to the summer months. This is likely due to increased SO_2 emissions released in winter.

At sites where standard meteorological data are measured and combined with ambient concentration measurements (at a single height), inferential models can then be used to estimate dry deposition (Erisman, 1994; Smith *et al*., 2000; Zhang *et al*., 2002b). Takahashi *et al*. (2002) used concentration measurements conducted for one year at a site in the Japanese cedar forest (located in the Gumma prefecture) to estimate dry deposition in the area. The fluxes modelled were 8.8 mm s^{-1} (Takahashi *et al*., 2001) whereas the estimated value of dry deposition flux was 3.6 Kg S ha-1 yr-1. The value compared well with the net flux value of 4.0 Kg S ha-1 yr-1.

A number of long-term micrometeorological measurements were conducted during recent years in North America. However, with the decreased use of long-term measurements, there has been some progress in the use of inferential modelling for SO_2 uptake (Zhang *et al*., 2002b, 2003). SO_2 flux data was obtained using the micrometeorological method from 5 sites (a corn field, a soybean field, a pasture and 2 forests sites) in the eastern part of the USA (Finkelstein *et al*., 2000; Meyers *et al*., 1998). It was noted by Finkelstein *et al*., (2000) that in wet conditions, deposition velocities tend to increase and that natural wetness controlled canopy resistance via the resultant chemistry. In previous studies, the formation of dew has been recognised as an important sink of SO_2 (Fowler & Unsworth, 1974, 1979). In a study conducted in Eastern USA by Meyers *et al*. (1998), data showed that early morning dew was responsible for the high deposition rates at 2 of all 3 sites.

In the UK region, two rural sites have been used to record SO_2 fluxes since the mid-90s. The first site is situated at Sutton Bonnington in the English Midlands on agricultural land, with the second site located at Auchencorth Moss in Southern Scotland. Over the last 10 years, the study produced a number of unexpected results. One such result was the realisation that ambient concentrations decreased over the years, despite the steady increase of deposition velocities. The increase was attributed to the continued reduction in the (Rc) canopy resistance (Fowler *et al*., 2001, 2005, 2007).

Feliciano *et al*. (2001) collected flux-gradient data for a period of 3 years over short vegetation in the mid-90s at three different sites in Portugal. One site was located in the Northern region that was characterised by a humid coastal climate whilst the remaining two sites in South Portugal were characterised by semi-arid, hot and dry climate. The study was significant in providing Rc estimations for Southern Europe Mediterranean area. In south-west Finland, Derome *et al*. (2004) obtained experimental data during a 6 year period, while compiling the mutual influences of SO_2 and NH_3 on deposition rates. The study was not conducted through micrometeorological measurements, but through bulk precipitation collectors and fallout measurements. The site was located close to a Cu-Ni Smelter where large amounts of NH_3 gas was released. This revealed that the canopy resistance decreased whereas SO_2 and NH_3 concentrations increased.

2.8.2. NO_2

During the last decade, measurements of NO_2 and NO were used to evaluate surface-atmosphere interactions. Three specific topics were investigated: NO emissions from soils; the chemical reactions between nitrogen oxides and plant canopies; and NO_2 and HNO_3 deposition to soils and foliar. The measurements have been conducted on several different types of vegetation with the greatest concern being forests. Some of the measurements and interpretation of data was easier to gather over mature forest areas.

Especially at lower concentrations, NO and NO_2 flux measurements have shown irregular results. This can be the result of a shortcoming concerning the instrument's sensitivity and lack of specificity of instrumental displays. A few other issues may also have contributed, including the violation of conditions in which these fluxes can be measured, the interaction with canopies and the reactions of sunlight and soils (Duyzer *et al*., 1983). Due to complications of NO_2 measurements, limited data is available for the comparison of different models (Duyzer *et al*., 2004).

A study was conducted in Speulderbos, Netherlands by Duyzer *et al*. (2004) within the region of a 20 m high forest. The results did not compare well to modelled flux values and, despite a number of reasons which could be assumed for this result, a single explanation was not possible. One consideration was that NO_2 flux can either be downward and upward depending on the soil magnitude and that emissions recorded were further away (upwind) from the forest. Generally, NO_2 flux is directed towards the forest at high concentrations and at smaller concentrations when transported to the atmosphere.

An understanding of the different measuring models and processes in existence and their interaction is increasing. In saying this, there are still a lot of uncertainties associated with these methods, especially in the terms of field measurements where the accuracy of values has been unacceptably low (Fowler *et al*., 2009). Accordingly, there is a great demand for further studies which could help to improve these methods and models.

2.9. Deposition studies in South Africa

In an effort to better understand dry and wet deposition in South Africa, a few studies were conducted to record NO_X and SO_2. A number of studies were carried out in South Africa; a prominent example is a study conducted in the Mpumalanga Highveld priority area due to the increase in emissions from industries and which was designed to assess the effect of emissions on environmental and human health (Scorgie & Kornelius, 2009b). Nine power stations are scattered throughout the Mpumalanga Highveld, due to the proximity of several coal beds in the area. The dispersal of atmospheric pollutant species released by power stations in this region is prevented via air circulation (Tyson *et al*., 1988; Held *et al*., 1994; Zunckel *et al*., 2000). The Mpumalanga Highveld area has attracted scientific interest since the early 1980s; it has been predicted that deposition would increase within these areas given observed air circulations (Tyson *et al*., 1988; Piketh *et al*., 1999b). There were also a few studies carried out in Gauteng, Free State and Limpopo. It was reported by Wells *et al*., (1996) that 90% of the scheduled emission of SO_2 and NO_x originate from industries in the Mpumalanga Highveld. With South Africa being a semi-arid country, this emphasises the importance in understanding and measuring dry deposition. Examples of studies in South Africa include 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. All of the abovementioned studies were conducted using the inferential model with the first being Zunckel et al., (1996).

Sulphur wet and dry deposition was proved to be approximately 35 kg S $ha^{-1}year^{-1}$ close to high emission sources in the Mpumalanga Highveld and 8 kg S $ha^{-1}year^{-1}$ within the general Highveld area (Blight *et al*., 2009). Background sites in South Africa measured about 1 kg S $ha^{-1}year^{-1}$ (Blight *et al*., 2009). It is estimated through South African regional scale modelling that nitrogen deposition over the Highveld ranges between 6.7 kg N $ha^{-1}year^{-1}$ (Colett *et al*., 2010) and >15 kg N $ha^{-1}year^{-1}$ (Blight *et al*., 2009). It should be noted that the measuring and monitoring of deposition and the impact on the environment in South Africa remains infrequent and scarce.

2.10. Conclusion

South Africa is a developing country where efforts geared toward economic growth are prioritised (Venter *et al*., 2012, Wenig *et al*., 2003, Stern, 2006, Swap *et al*., 2003). From what is offered in the literature discussion above, it is evident that a number of gaps exist within current knowledge and that this requires further investigation, especially relating to deposition of atmospheric pollutants associated with economic growth and increased anthropogenic sources. Therefore this study attempted to offer a comprehensive and detailed perspective on SO_2 and NO_2 deposition through conducting direct flux measurements of these species in order to relate to flux values calculated from inferential models.

Research related to environmental sustainability is considered highly valuable at a global and local scale. Considering the magnitude of South African industrial operations, as well as the emission of atmospheric pollutants associated with regional open biomass burning and household combustion (for space heating and cooking), it is important to accurately determine the extent of NO_2 and SO_2 deposition. In this study, the deposition fluxes of SO_2 and NO_2 for a grassland-savanna area were determined for the first time via micrometeorological measurements conducted at Welgegund measurement station; in this way, deposition velocities for these species could be calculated. These measurements will help to reduce uncertainties associated with deposition fluxes determined (for these species) via estimated or modelled deposition velocities.

Chapter 3

Experimental

In this chapter, the sampling site description (Par 3.1.), measurement methods utilised (Par 3.2.) and data processing procedures (Par 3.3.) are presented.

3.1. Site description

Flux measurements were conducted at the Welgegund monitoring station (latitude 26° 34’10” S, longitude 26° 56’21” E; 1480 °m a.s.l.), which is situated on commercial farmland approximately 100 km west of Johannesburg (www.welgegund.org). In Figure 1 an image of the site is presented indicating its immediate surroundings, while Figure 2 shows the location of Welgegund on a map of southern Africa. Welgegund is considered to be a regional background site with no direct pollution sources in close proximity. However, the site is impacted by the major anthropogenic pollutant source regions towards the interior of South Africa, which is also indicated in Figure 2. In addition, it is evident from Figure 2 that Welgegund is also impacted by a relatively clean background region west of the site. The grey areas in Figure 2 indicate mixed source regions, which take into consideration the uncertainties associated with back trajectory analysis (Beukes *et al*., 2013). The major anthropogenic source regions influencing air masses measured at Welgegund include the western- and eastern Bushveld Igneous Complex (WBIC and EBIC), the Vaal Triangle, the Johannesburg–Pretoria metropolitan conurbation, the Mpumalanga Highveld, as well as the anti-cyclonic recirculation of aged air mass over the interior of South Africa. Additional sources also include regional biomass burning (veld fires), which usually occurs during the winter and spring (Vakkari *et al*., 2015).

Figure 1 Welgegund measurement station on a commercial farm during the wet season (www.welgegund.org)

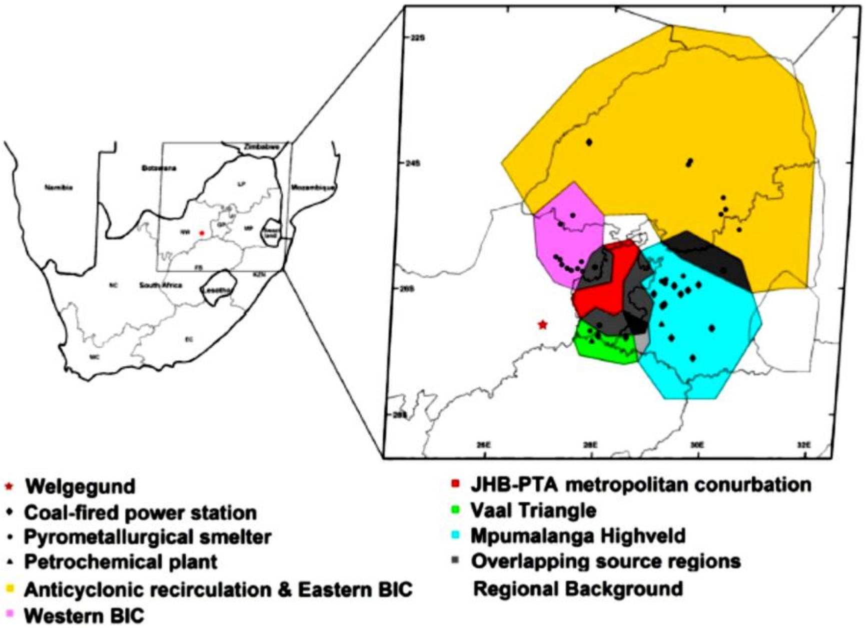


Figure 2 Map of southern Africa indicating the location of the Welgegund station, large point sources in the industrial hub of South Africa and source regions defined by Beukes *et al*., (2013).

Welgegund is located in the Grassland Biome and is largely impacted by cultivation, plantation forestry, urbanisation and mining (Daemane *et al*., 2010 and references therein). This biome covers 28 % of the land surface of South Africa (Mucina and Rutherford, 2006). The area surrounding the measurement trailer consists is characterised by open savannah rangeland that is grazed by sheep and cattle. The dominant vegetation in this region include short grass, thorn shrubs and agricultural crops (mainly maize). The dominant grass species are *Hyparrhenia hirta* and *Sporobolus pyramidalis*. Non-grassy forbs include *Acacia sieberiana*, *Rhus rehmanniana*, *Walafrida densiflora*, *Spermacoce natalensis*, *Kohautia cynanchica* and *Phyllanthus glaucophyllus,* with the soil consisting of a sandy tilt (www.welgegund.org). The area is considered as a dry region and trees in the above area do not grow very tall. The average height of the canopy is estimated to be 2.4 meters, while the height of the undergrowth varies according to the seasons and the grazing of the cattle and ranges from +-1.5 cm minimum and +- 3 cm maximum. The area has a relative even topography with no steep slopes.

The meteorology of the region where Welgegund is situated, i.e. the South African Highveld, is characterised by a distinct wet season occurring from October to April and a dry season occurring from May to September. The dry season coincided with the winter months (June to August), while the wet season is associated with the warmer months. The average rainfall for the sampling period was 397.45 mm with >90 % of the rain events taking place in the wet season. Temperatures at Welgegund ranged between average minimum temperatures of 2 °C and 15 °C in winter and summer, respectively, while average maximum temperatures were 22 °C and 32 °C in winter and summer, respectively during the sampling period.

3.2. Measurement methods

3.2.1. General site operation

The atmospheric measurement station was operated in cooperation between the North-West University (NWU) and the University of Helsinki (UH). All measurement instruments at Welgegund were placed inside a Eurowagon (length 4.5m, width 2.1m and height 2.3m) measurement trailer. A detailed description of the trailer can be found in Petäjä *et al*. (2013) and in a number of papers published on data generated at Welgegund (e.g. Tiitta *et al*., 2014, Venter *et al*., 2012). The measurement station was visited weekly to perform checks on all instruments. Weekly maintenance of the trailer consisted of inspection of all instruments, flow checks and cleaning of all inlets. Monthly maintenance was conducted during the first week of each month; this involved the replacement of filters on the gaseous instruments, the cleaning of all sensors and the calibration of PM_{10} measurement equipment. Comprehensive gas calibrations were performed on a quarterly basis. An electronic diary was kept to record all visits, as well as measurement periods associated with instrumentation malfunction or unusual operation (e.g. painting of the fence). All the instrumentation at Welgegund is connected to a master PC, which was linked to a GPRS modem that sends data to a server on a daily basis. Data stored on the server was downloaded daily and visually inspected to ensure data quality.

3.2.2. Active flux measurements

Welgegund was equipped with an eddy covariance system in August 2010. This system consists of a sonic anemometer (Metek USA-1) coupled to an infrared gas analyser (Licor 7000). These instruments were used to estimate vertical flux momentum of CO_2 and H_2O, as well as sensible- and latent heat. In February 2015 the station was equipped with an dual continuous wave quantum cascade laser (QCL) trace gas analyser (Aerodyne Research, Inc. CWQCL-76-D) instrument, which performs fast response measurement of atmospheric SO_2 and NO_2 concentrations required to determine SO_2 and NO_2 fluxes. The QCL instrument was connected to the anemometer to perform active micrometeorological (eddy covariance) flux measurements of atmospheric SO_2 and NO_2. The QCL inlets and anemometer are mounted on a tower 9.5 meters above the ground (tower shown in Figure 1) and measures at a frequency of 10 Hz (Räsänen *et al*., 2015). To estimate the vertical flux, the covariance of the vertical wind speed and the flux variable are combined with the measured time series. Although this principle appears relatively simple, the data processing requires several complex steps (Par. 3.3.1) to ensure accurate and relaible results (Aubinet *et al*., 2012). SO_2 and NO_2 flux measurements were conducted with the QCL instrument for the period 1.2.2015 to 31.1.2016.

Figure 3, shows an image (a) and flow diagram (b) of the QCL instrument utilised in this study. The QCL instrument contains a multipass cell with a volume of 0.51 L and an optical path of 76 m that is kept at a pressure between 35 and 40 Torr. Two laser positions are available and can be used simultaneously. The lasers (Alpes Lasers) were used in pulse mode, which is initiated by short pulses with a duration of approximately 10ns. This is divided by a beam splitter before it is sent through the multipass cell, along the bypass. A single detector detects both beams and is followed by the bypass pulse, which arrives 250 ns before the multipass pulse. The absorption lines are used to tune the laser frequency by using a sub-threshold current applied to the lasers between each pulse. At the start of pulse, the laser light intensity is lower and increases towards the end of the pulse sequence. The width of the scan for both beams is approximately 0.5 cm^{-1}. The signal obtained from the multipass cell is normalised by using the bypass signal. This is necessary to obtain a relatively constant intensity ratio, as the light intensity decreases when passing through the multipass cell (with the frequency of the two absorption lines). TDL-Wintel software is used to operate the QCL instrument, which utilises spectral parameters listed in the HITRAN database to estimated SO_2 and NO_2 concentrations.

(a)

Figure 3 The Quantum Cascade Laser analyser (Tuzson *et al*., 2008).

(b)

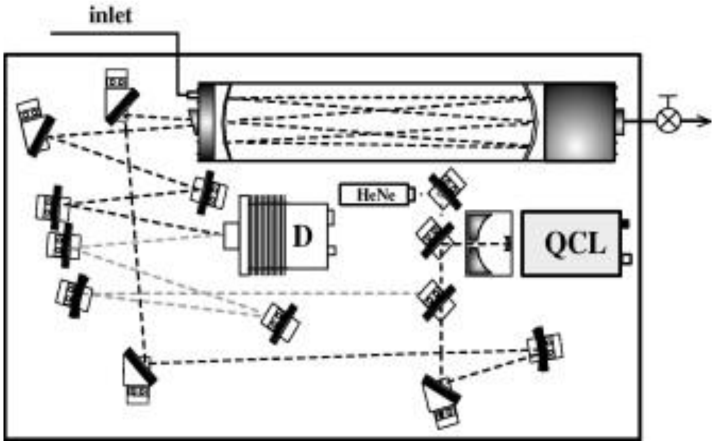


Figure 3 A flow diagram of the QCL instrument (Tuzson *et al*., 2008).

The Voight line width of the absorber and the width of the laser line are in the same order for the QCL (pulsed). During the fitting routine, this needs to be considered by combining the molecular absorbance with the laser line shape. The molecular concentration can be underestimated between 10 to 20% depending on the line depth, as a result of the non-Gaussian shape of the laser. Therefore, calibration with known standards is crucial for improved accuracy. A circulated water bath is used to stabilise the laser electronics (Nelson *et al*., 2004). The water system is also used to cool down the heat generated by the peltier, which also cools the lasers. The pulse electronics is also stabilised by the water cooling for a more uniform laser output power. To avoid degradation of the multipass cell mirrors, a 0.01 µm filter is used located at the inlet of the QCL. A needle valve is also used to control the cell- and flow pressure located at the inlet of the multipass cell, in addition to a vacuum pump which is located downstream of the multipass cell (Kroon *et al*., 2007).

In literature the QCL instrument has been used to measure various kind of flux measurements across the world. This includes N_2O, CO_2, CH_4, NO, NH_3, SO_2, H_2O and NO_2 measurements (Hensley et al., 2005, Santoni et al., 2014).

3.2.3. Ancillary measurements

Presented in Table 1 is a summary of all the measurements conducted at Welgegund. Details of parameters relevant in this study, are briefly described. Absolute concentrations of trace gases were measured with a Thermo-Electron 43S SO_2 analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan) and a Teledyne 200AU NOx analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA). Temperature and relative humidity were measured with a Rotronic MP 101A weather station, while wind speed and wind direction were measured with a Vector W200P and a Vector A101ML, respectively. A Thies 5.4103.20.041 recorded precipitation and a LiCor LI-190SB measured Photosynthetic Photon Flux Density (PPFD).

Table 1 A summary of all measurements conducted at Welgegund.

Measured property	Range/type
Meteorology	Wind speed and direction, ambient pressure, temperature, relative humidity, precipitation and vertical temperature
Solar radiation	Direct and reflected PPFD (PAR), direct and reflected global radiation, net radiation
Aerosol number size distribution	DMPS 10-840 nm
Air ion size distribution	AIS 0.4-40 nm
Aerosol Mass	PM_{10}
Trace gas concentrations	SO_2, NO_2, NO, O_3, CO
Light absorption by aerosol particles	Multi angle aerosol absorption photometer
Light scattering by aerosol particles	3-wave length nephelometer
Vertical aerosol profile	Vaisala CT25K ceilometer
Flux measurements	H_2O,CO_2 and sensible heat fluxes (eddy covariance) SO_2 and NO_2 fluxes (eddy covariance)
Soil measurements	Soil temperatures and moisture at different depths, soil heat flux

3.2.4. Passive gaseous sampling

In this study, passive samplers were used to determine monthly gaseous SO_2 and NO_2 concentrations. Passive samplers consisted of the following: an external polyethylene (PET) casing, a stainless-steel mesh, a (PTFE) Teflon filter and a saturated Wattman ash-less paper filter as indicated in Figure 4 (on following page). The paper filter is impregnated with an absorbing solution, which reacts selectively with the intended species. Equation 3.1 and 3.2 indicate the reactions occurring with the passive sampler to trap atmospheric SO_2 and NO_2.

$$2SO_2\ (g) + 4OH^- + O_2 \rightarrow 2H_2O + 2SO_4^{2-} \qquad (3.1)$$

$$2NO_2\ (g) + 3I^- \rightarrow 3NO_2^- + I_3^- \qquad (3.2)$$

These reactions between the atmospheric species, and the absorbing solution, creates a net flux and concentration gradient between the volume of air, the sorbent solution and the atmosphere (Aiuppa *et al*., 2004; Carmichael *et al*., 2003). As each molecular entity diffuses at a specific rate, the diffusion coefficient is relative to Fick's principles (Carmichael *et al*., 2003; Martins *et al*., 2007). Passive samplers were transported to the sampling site in an air-tight container and placed in a protective hood to prevent meteorological interference in the field (Martins *et al*., 2007). Passive samplers were exposed for a period of one month.

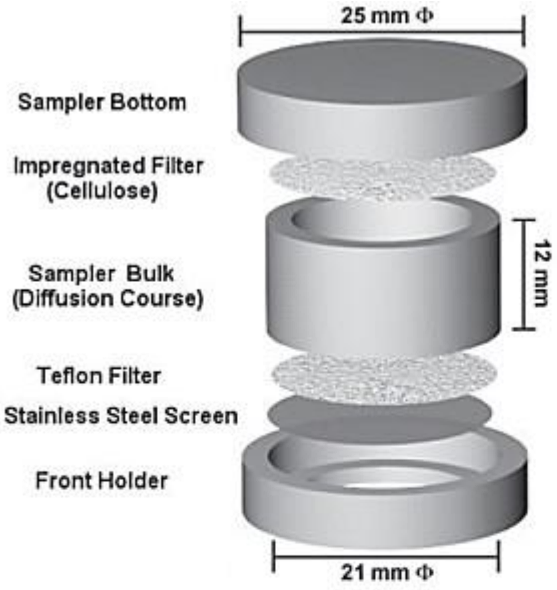


Figure 4 Passive sampler configuration and dimensions (Cruze *et al.*, 2005).

3.3. Data processing

3.3.1. Active flux measurements

The data obtained from the QCL measurements was visually inspected and corrected by using a fit-for-purpose program. The first step was to utilise diary entries to remove all data associated with uncertainties attributed to factors such as power cuts, calibrations and weekly checks. Thereafter, data was graphically presented and manually rechecked. Data collection was typically interrupted by power failures, incorrect laser alignments, instrument start-up errors, calibration after power failures and when general maintenance was performed.

Flux measurements in this study were subjected to specific criteria generally considered when performing micrometeorological flux measurements. From the flux-files, each 30 min-value was checked to determine that each 30 min-value is based on enough readings (data recorded). In Table 2, the acceptable number of observations and spikes within a 30-min period, as well as the following wind criteria, i.e. <u'u'>, <v'v'>, <w'w'>,and wind speed [m/s] is listed. The eddy covariance method is problematic during instances of weak turbulence and data collected during such periods should be discarded. The following data was also discarded; SO_2 and NO_2 variance (covariance values) 0>SO2’SO2’>25 and 0>NO2’NO2’>25. The eddy covariance method does not work if there is not enough turbulence (typically calm nights), therefore weak turbulence conditions are discarded (friction velocity (m/s): 0.2 – 1.5) After the data was “cleaned”, SO_2 and NO_2 deposition velocities were calculated by using the ‘cleaned’ flux and concentration values and used in this study.

Table 2 Rejection criteria applied to flux measurements

Table 2	
Number of observations	1730 – 17410
Number of spikes	0 – 60
<u'u'>:	0.00000001 – 50
<v'v'>:	0.00000001 – 50
<w'w'>:	0.00000001 – 10
wind speed [m/s]:	0.001 – 17 [m/s]
Friction velocity minimum	0.2 – 1.5 [m/s]
Friction velocity maximum	1.5 [m/s]

The deposition velocities, Vd, were calculated from the measured direct flux and ambient concentrations for SO_2 and NO_2 as follows:

$$(Vd) = -F/c \qquad (1)$$

where F is the directly measured flux and c is the ambient concentration.

The instantaneous flux, F(c) of a scalar contaminant in the atmosphere may be determined by measuring the concentration fluctuations, c', and correlating them with the vertical velocity fluctuations, w'. The vertical flux is then determined as:

$$F = cov(w,c) = \overline{w'c'}$$

Since the convention is that a positive and negative Vd denotes downward and upward fluxes, respectively, the negative flux values determined with the eddy covariance method for downward fluxes and positive fluxes associated with upward fluxes are multiplied with -1. There are uncertainties associated with deposition velocity (Vd) calculated for small atmospheric concentrations of species. Although the flux at low concentrations may be correctly measured, the calculated deposition velocity will be too high. The following minimum was set on the concentration values to address the above problem, i.e. SO_2 concentration ‹ 0.5 ppb and NO_2 concentration ‹ 0.55 ppb.

3.3.2. Passive sampling measurements

The atmospheric concentrations were determined from the concentrations determined for the species in the aqueous solution into which samples were extracted from the paper filters and converted to values in ppb by using the equation below:

$$c = xRT/DtM(Pa) \times L/A$$

$$xsampleblank/(g) = c.Vextracted/1000$$

where c (ppb) is the concentration in the atmosphere, x is the concentration in the aqueous solution (g), R (Pa.m3K-1mol-1) is the ideal gas constant, T (K) is the temperature, D (m2.s^{-1}) is the diffusion coefficient, t (s) is the time, Mr (g.mol^{-1}) is the molar mass, P (m) is the ambient pressure, L (m^3) is the path length and A is the area. Deposition fluxes were calculated from passive sampling measurements by using the ambient concentration and dry deposition velocity for SO_2 and NO_2 derived from an inferential model. The deposition fluxes rate, F were determined by the following equation:

$F = -V\mathrm{d}\ x\ C$

where Vd is the deposition velocity (downward flux) and C is the atmospheric concentration measured. The deposition velocities were derived from values in literature for the specific land use category.

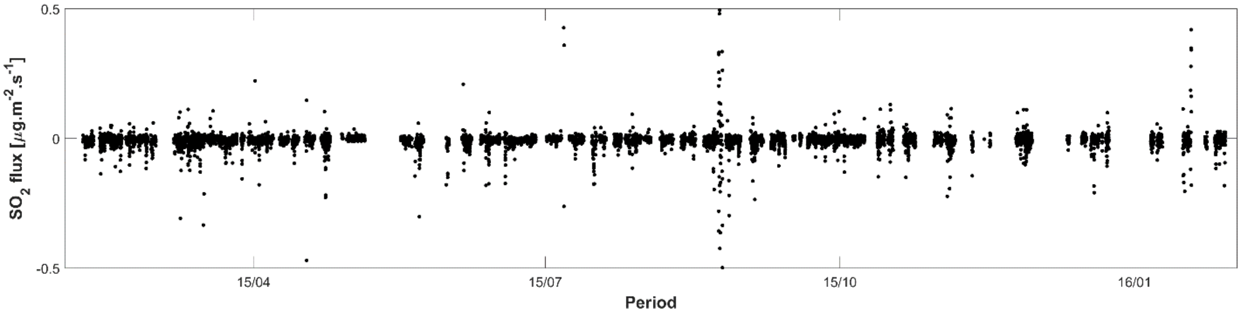
Chapter 4

Results and discussions

In this chapter, SO_2 and NO_2 fluxes measured with micrometeorological techniques and the calculated deposition velocities are presented and is furthermore contextualised (Par 4.1 – 4.3). Temporal patterns of SO_2 and NO_2 fluxes and deposition velocities are also presented and discussed (Par 4.2 and 4.3). Finally, deposition fluxes calculated with modelled deposition velocities (of previous studies conducted within South Africa) are compared to deposition fluxes calculated with deposition velocities determined in this study (Par 4.4).

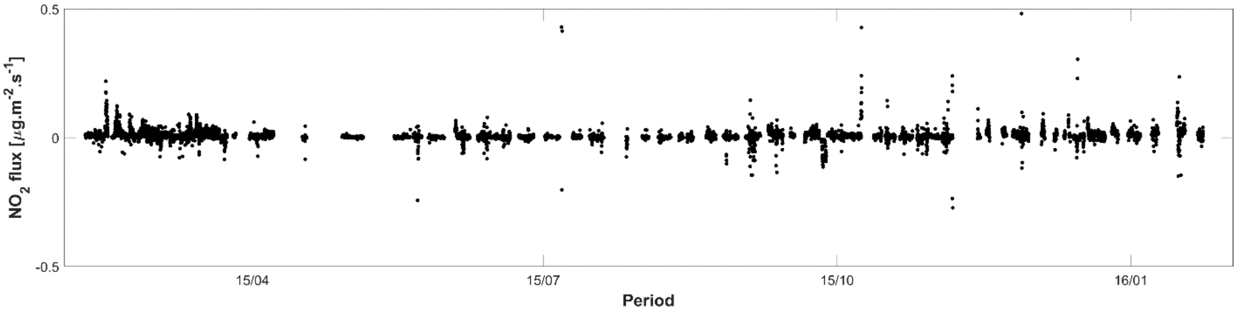
4.1. Data availability

As discussed in Section 3.3, the measured flux dataset was subjected to specific criteria in order to ensure good data quality. Therefore, data that did not comply with the selection criteria was excluded from the dataset. In Figure 1 and Figure 2, the “cleaned” time series of the SO_2 and NO_2 flux datasets, respectively, for the entire sampling period (1.2.2015 to 31.1.2016) are presented. Included in these figures are tables indicating the data collection percentages for each sampling month.



SO2	Feb'15	March'15	April'15	May'15	June'15	July'15	Aug'15	Sep'15	Oct'15	Nov'15	Dec'15	Jan'16
% data after cleaning and downtime exclusion	62.35	80.58	70.90	34.81	62.85	71.03	58.47	55.69	41.13	28.40	16.06	27.28

Figure 1 “Cleaned” time series of SO_2 flux measurements



NO2	Feb'15	March'15	April'15	May'15	June'15	July'15	Aug'15	Sep'15	Oct'15	Nov'15	Dec'15	Jan'16
% data after cleaning and downtime exclusion	79.02	87.43	36.11	44.42	69.65	42.54	48.92	56.88	60.48	42.36	38.04	27.89

Figure 2 “Cleaned” time series of NO_2 flux measurements

The data coverages for SO_2 and NO_2 flux measurements were 50.8% and 52.8% for the entire sampling period, which could be considered representative datasets for SO_2 and NO_2 fluxes for the one-year sampling period. The data coverage percentages compare relatively well to similar micrometeorological flux measurement studies. Neirynck *et al*., 2011, for example, reported 36% data coverage for SO_2 flux measurements conducted with similar techniques used in this study after applying rejection criteria. For most of the months, more than 40% data coverage was achieved in this study. The majority of gaps in the flux datasets can be attributed to the occurrences of power outages experienced at the measurement site. Following a power outage, both lasers responsible for measuring SO_2 and NO_2 concentrations (in addition to flux measurements) of the quantum cascade laser (QCL) instrument require realignment in order to obtain accurate measurements. After several power outages, the auto start function of the instrument malfunctions and the automatic alignment of both lasers cannot be achieved, which then requires manual realignment of both lasers. Therefore, the months with higher data collection percentages can be ascribed to regular upgrades of the auto start function and quick intervention after power outages.

The high data collection percentages obtained during February 2015 to April 2015 for SO_2 and February 2015 to March 2015 for NO_2 can be linked to the optimum alignment of both lasers after the initial installation of the instrument at Welgegund, as well as a limited number of power outages occurring during this period. The lower data collection percentage obtained for NO_2 compared to SO_2 during April 2015 was due to a more significant problem associated with the alignment of the NO_2 laser, which required specialised assistance to resolve all problems with the instrument. The higher data collection percentages in June 2015 to July 2015 for SO_2 and June 2015 for NO_2 can be attributed to an upgrade of the auto start function after both lasers were realigned. The lowest data collection percentages obtained from November 2015 to January 2016 for SO_2 and NO_2 flux measurements can be ascribed to problems experienced with the functioning of the lasers and the occurrence of regular power outages. In addition, December and January also coincided with the summer holiday in South Africa – a period during which the measurement station is operated with skeleton staff and is less frequently visited for routine maintenance checks, which caused delays in manual interventions after the occurrence of power outages.

Quality assurance of measured SO_2 and NO_2 flux measurements was also performed by comparing absolute SO_2 and NO_2 concentrations measured with the QCL instrument, to the SO_2 and NO_2 concentrations routinely measured at Welgegund; i.e. the Thermo-Electron 43S SO_2 analyser and the Teledyne 200AU NO_x analyser, respectively, presented in Figure 3 and 4. It is evident form these figures that there are relatively good correlations between the SO_2 and NO_2 concentrations measured with the different instruments, which increases confidence in the accuracy of fluxes measured in this study. However, the Thermo-Electron 43S SO_2 and the Teledyne 200AU NO_x analysers are calibrated frequently for accurate absolute measurements, whereas the QCL instrument is less often calibrated. This is as the result of the fact that absolute concentration measurements are not required for flux measurements.

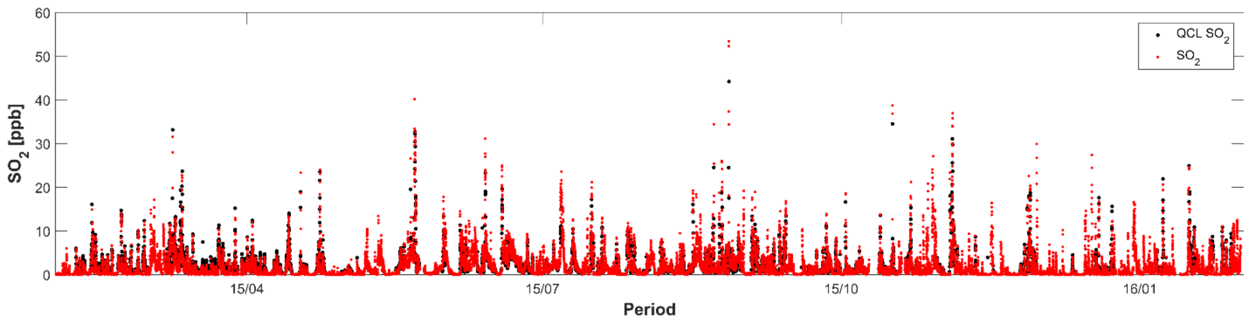


Figure 3 Comparison of the SO_2 concentrations measured with the QCL instrument and the SO_2 concentrations measured with the Thermo-Electron 43S SO_2 analyser

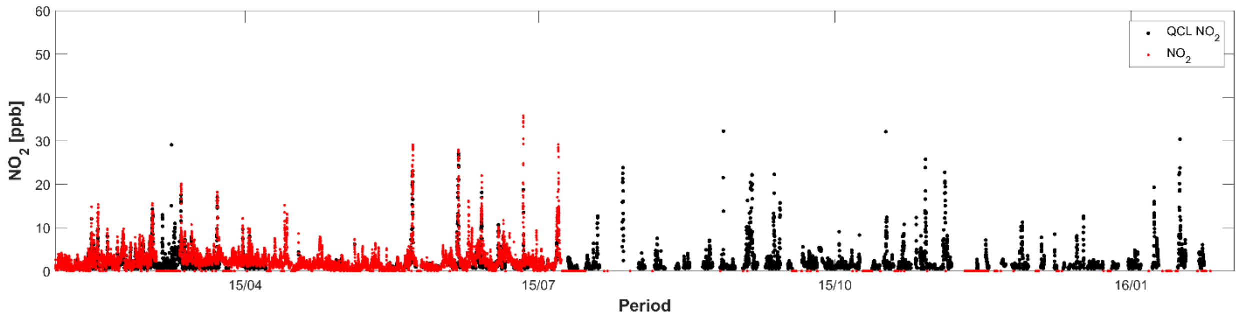


Figure 4 Comparison of the NO_2 concentrations measured with the QCL instrument and the NO_2 concentrations measured with the Teledyne 200AU NO_x analyser

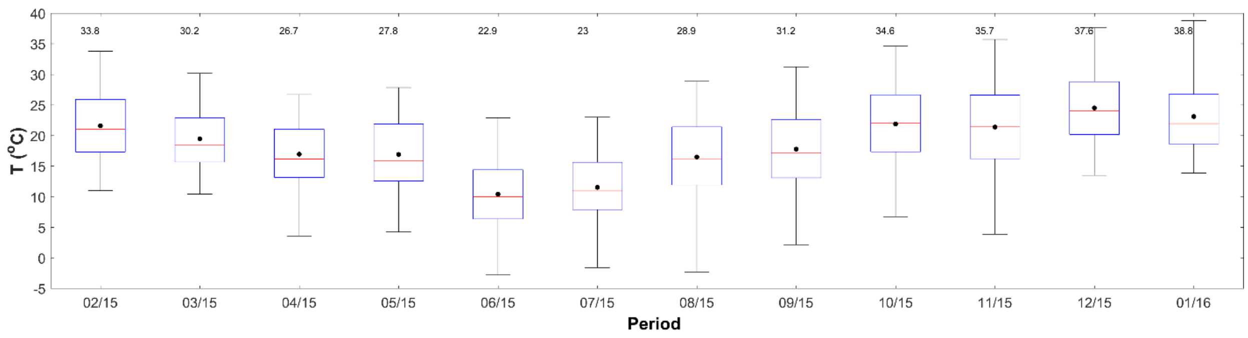
4.2. Meteorology

In order to link measured SO_2 and NO_2 fluxes to local meteorological conditions, the following monthly meteorological parameters, including temperature, global radiation, soil temperature, precipitation, relative humidity (RH) and soil moisture measured at Welgegund (during the sampling period) are presented in Figure 5; these metrological patterns do not only influence the atmospheric concentrations of SO_2 and NO_2, but also biogenic activity crucial to the study of surface-atmosphere interactions.

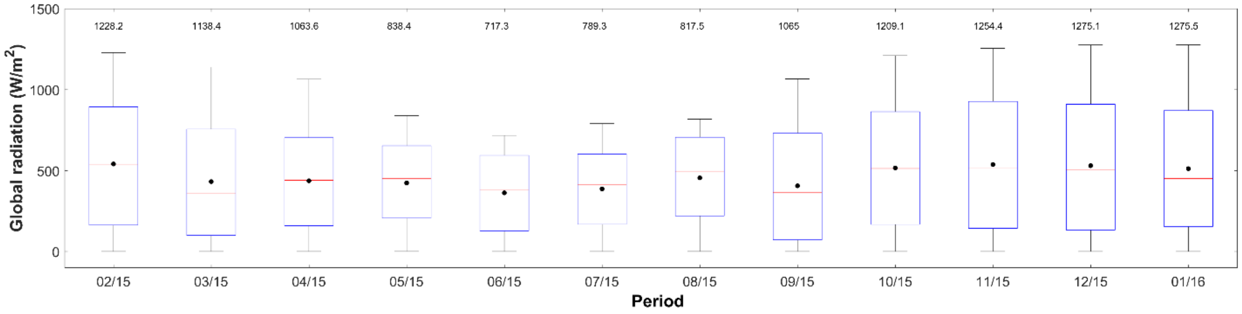
The changes in monthly ambient- and soil temperatures (Figure 5a and c), as well as global radiation (Figure 5b) correspond with South African seasons, i.e. summer from December to February, autumn from March to May, winter from June to August and spring from September to November. However, it is evident that even in winter months, relatively high temperatures also occur and may reach temperatures of 23 °C, which is typical for the North-Western region of South Africa (Bothma, 2004). In addition, although global radiation levels were higher in summer than in winter, no large differences were observed between monthly mean and median global radiation levels throughout the entire year.

From Figure 5 (d), it is evident that this region is also characterised by a distinct wet- and dry season, with precipitation occurring mainly from October to April, i.e. the warmer months, which is typical for the interior of South Africa as discussed in Chapter 3 (Jaars *et al*., 2016). A few rain events occurred in late August and September during the sampling period of this study, which is unusual for this region within South Africa. In addition, rainfall in this location of South Africa is usually characterised by relatively large inter-annual variability (Conradie *et al*., 2016). Although monthly median and mean RH were relatively higher for certain months (February 2015, March 2015, April 2015 and January 2016) during the wet season, no distinct seasonal pattern for RH was observed during the sampling period (Figure 5e). Relatively higher RH was also measured during the dry season months June 2015, July 2015 and September 2015, which could most likely be attributed to uncharacteristic rain events occurring during these months. Soil moisture measurements mirrored the seasonal precipitation pattern with higher soil moisture measured during the wet season (Figure 5f).

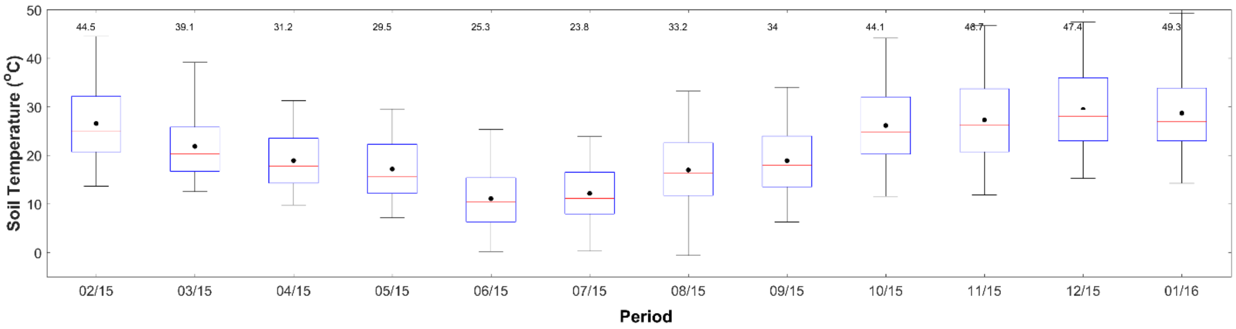
(a)


T (°C)
40
35
30
25
20
15
10
5
0
-5
33.8
30.2
26.7
27.8
22.9
23
28.9
31.2
34.6
35.7
37.6
38.8
02/15
03/15
04/15
05/15
06/15
07/15
08/15
09/15
10/15
11/15
12/15
01/16
Period

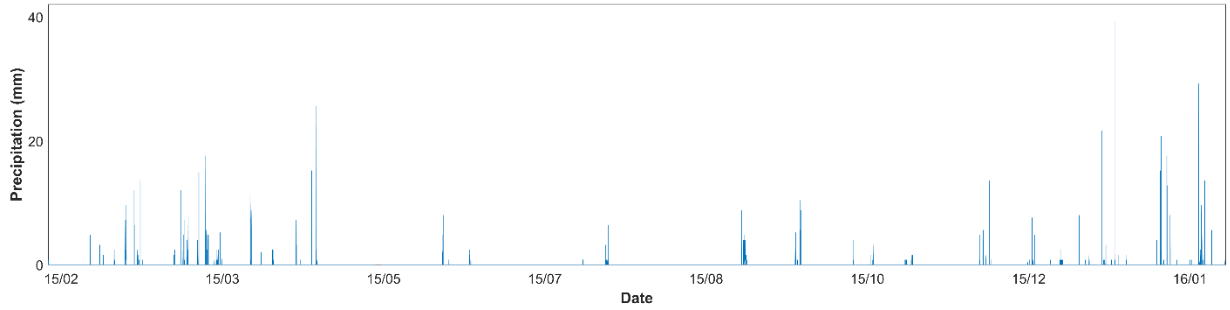
(b)


Global radiation (W/m²)
1500
1000
500
0
1228.2
1138.4
1063.6
838.4
717.3
789.3
817.5
1065
1209.1
1254.4
1275.1
1275.5
02/15
03/15
04/15
05/15
06/15
07/15
08/15
09/15
10/15
11/15
12/15
01/16
Period

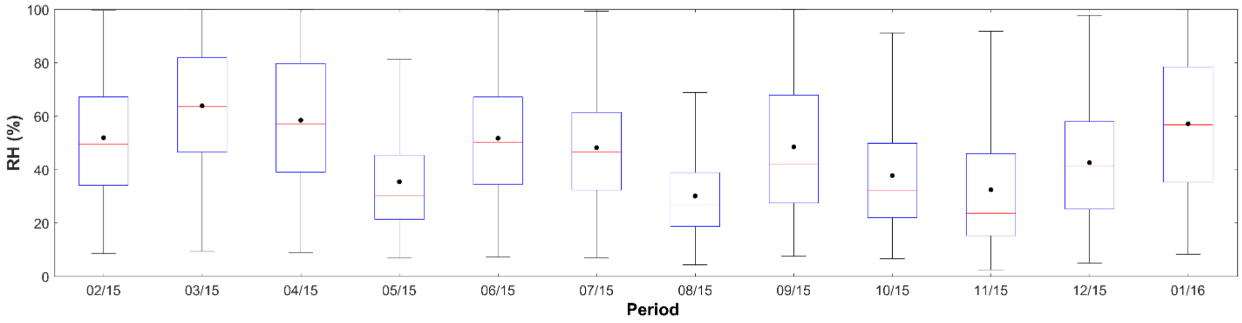
(c)


Soil Temperature (°C)
50
40
30
20
10
0
44.5
39.1
31.2
29.5
25.3
23.8
33.2
34
44.1
46.7
47.4
49.3
02/15
03/15
04/15
05/15
06/15
07/15
08/15
09/15
10/15
11/15
12/15
01/16
Period

(d)



(e)



(f)

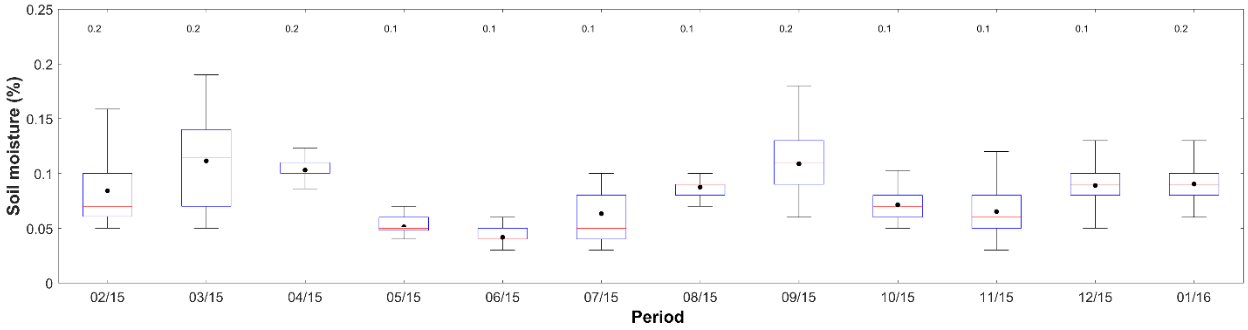


Figure 5 Monthly variations of (a) temperature, (b) global radiation, (c) soil temperature, (d) precipitation, (e) relative humidity and (f) soil moisture at 5/20 cm depth. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ or 99.3 % coverage if the data have a normal distribution. The values displayed near the top of graphs indicate the maximum values.

4.3. SO_2 fluxes and deposition velocities

In Table 1, the median (mean) interquartile range (IQR), ±2.7σ, the maximum and minimum values of the fluxes measured and the deposition velocities calculated for SO_2 at Welgegund from 1.2.2015 to 31.1.2016 are given. The median (mean) SO_2 fluxes, i.e.-0.01 $\mu g.m^{-2}.s^{-1}$ (-0.01 $\mu g.m^{-2}.s^{-1}$) reveal a net downward flux for atmospheric SO_2, which indicate that Welgegund can be considered a sink of atmospheric SO_2. The 75th percentile, +2.7 σ and the maximum SO_2 fluxes however, indicate instances of upward SO_2 flux. Deposition velocities were calculated from the measured SO_2 fluxes and – concentrations as described in Chapter 3. The median (mean) deposition velocity calculated for the sampling period was 0.16 cm. s^{-1} (0.16 cm. s^{-1}).

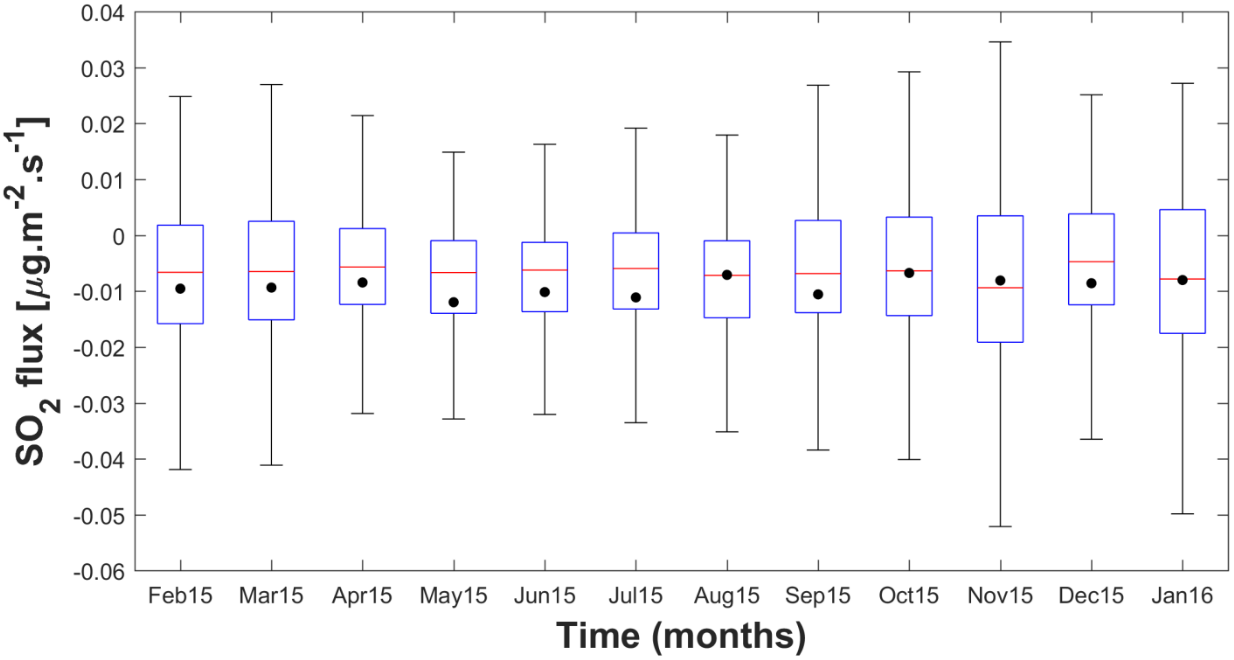
Table 1 Statistical distribution of SO_2 fluxes and deposition velocities measured at Welgegund

	Flux ($\mu g.m^{-2}.s^{-1}$)	V_d ($cm.s^{-1}$)
Median (mean)	-0.01 (-0.01)	0.16 (0.16)
IQR (25th – 75th)	-0.01 – 0.001	0.04 – 0.29
±2.7σ	-0.04 and 0.01	-0.39 and 0.68
Maximum	1.56	43.42
Minimum	-2.0	-19.24

4.3.1. Seasonal pattern

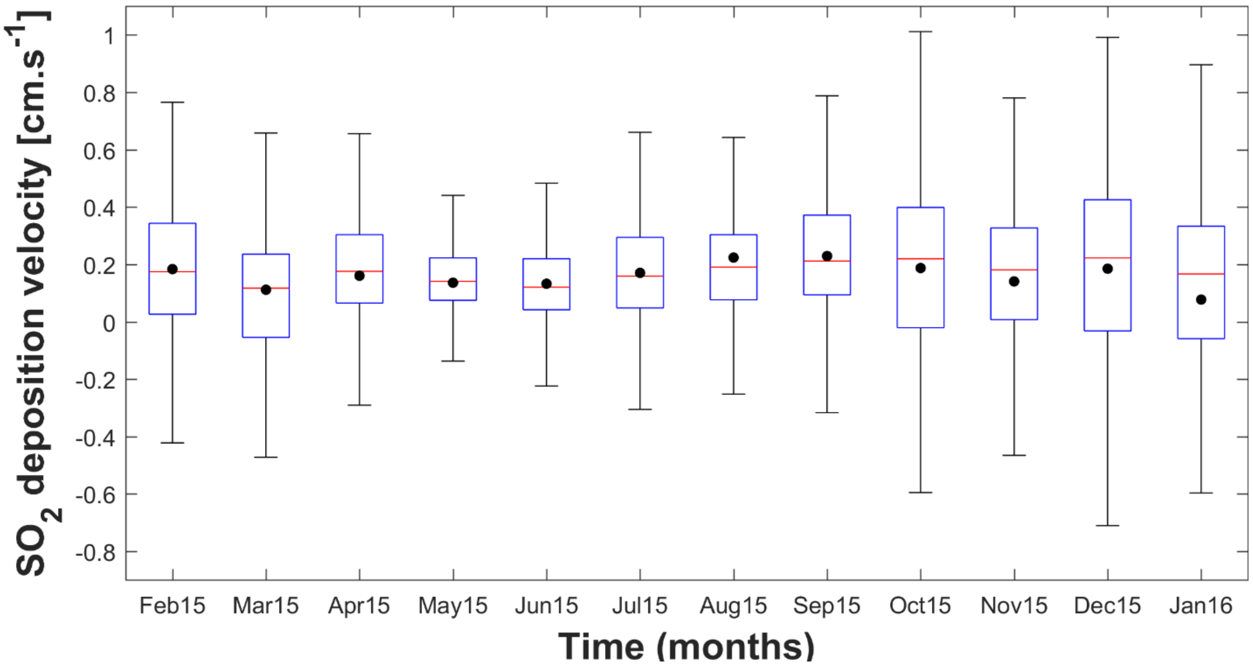
In Figure 6 (a) the monthly SO_2 fluxes are presented, while the monthly SO_2 deposition velocities and – concentrations are given in Figure 6 (b) and (c), respectively. It is evident that the median (mean) SO_2 fluxes measured indicated no distinct seasonal pattern for SO_2 fluxes measured at Welgegund. As mentioned above, the monthly variations in Figure 6 (a) also indicate that Welgegund can be considered a sink for SO_2 as indicated by the predominant downward atmospheric SO_2 flux measured during each of the months. However, the ranges of the box-and-whisker plots for the Welgegund SO_2 flux measurements were relatively smaller from May to August, which coincide with the end of the South African autumn and the winter season (dry season) as indicated in Section 4.2, i.e. colder and dryer months (Figure 5).

(a)



SO$_2$ flux [μg.m^{-2}.s^{-1}]
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
Feb15
Mar15
Apr15
May15
Jun15
Jul15
Aug15
Sep15
Oct15
Nov15
Dec15
Jan16
Time (months)

(b)



SO$_2$ deposition velocity [cm.s^{-1}]
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
Feb15
Mar15
Apr15
May15
Jun15
Jul15
Aug15
Sep15
Oct15
Nov15
Dec15
Jan16
Time (months)

(c)

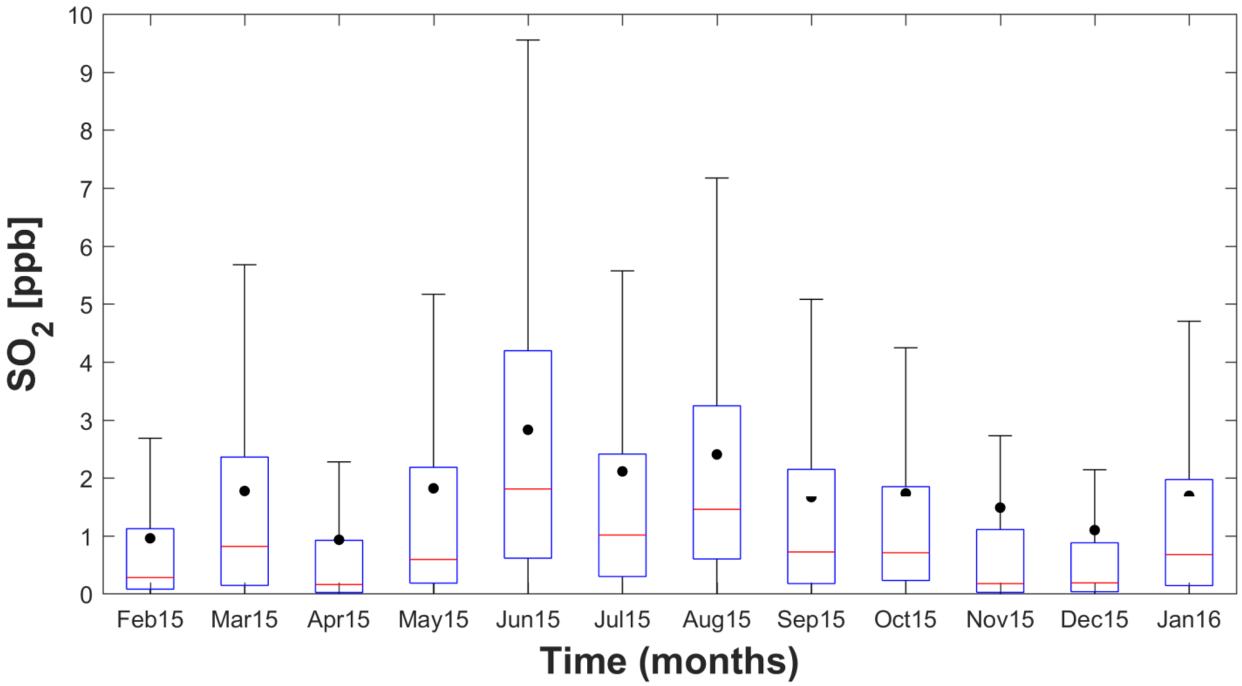


Figure 6 Monthly SO_2 fluxes (a), -deposition velocities (V_d) (b) and –concentrations (c) measured at Welgegund. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3 % coverage if the data have a normal distribution

In an effort to explain the seasonality observed in the statistical distribution, i.e. relatively narrower/smaller ranges of the box-and-whisker plots from May to August, the monthly SO_2 flux measurements were separated into deposition and upwards fluxes, which are presented in Figure 7. The median (mean) of deposition fluxes was -0.011 $\mu g.m^{-2}.s^{-1}$(-0.019 $\mu g.m^{-2}$ s^{-1}), while the median (mean) of the upward fluxes was 0.006 $\mu g.m^{-2}.s^{-1}$(0.017 $\mu g.m^{-2}.s^{-1}$). It is evident that the upwards SO_2 fluxes revealed no distinct seasonal pattern, while the deposition fluxes were higher during the wet season in the warmer months. Upward SO_2 fluxes are usually attributed to the release of deposited SO_2 in solution to the atmosphere when the chemical system attempts to achieve equilibrium (Neirynck *et al.*, 2011). This may occur when sulphite ions in water layers are converted to gas phase SO_2 and evaporated at low ambient SO_2 levels (Erisman *et al.*, 1999). It is generally considered that SO_2 dry deposition is predominately controlled by non-stomatal processes, e.g. leaf area, turbulence, wetness and acidity (Fowler *et al*., 2009, Finkelstein *et al*., 2000). Therefore SO_2 dry deposition is expected to increase during the warmer wet season (Figure 5) due to increases in biomass and photosynthetic activity, precipitation, relative humidity and turbulence (Fowler *et al.*, 2009). Several studies have indicated the significance of canopy wetness on SO_2 deposition fluxes, i.e. higher SO_2 deposition fluxes associated with the wet periods (Finkelstein, 2001; Zhang *et al*., 2001; Matsuda *et al*., 2006; Neirynck *et al*., 2011). Neirynck *et al*. (2011) attributed high flux variability associated with SO_2 fluxes measured at a mixed suburban forest in Belgium to the wetness of the canopy with higher SO_2 fluxes occurring for rain wetted canopies. In a study conducted by Feliciano *et al*. (2001) over short vegetation in Portugal (of which one of the sites was located in relatively dry agricultural area) it was indicated that deposition fluxes were slightly higher for wet canopies. Feliciano *et al*. (2001) also concluded that the annual SO_2 deposition was dominated by non-stomatal mechanisms, while stomatal uptake was relatively important when vegetation was biologically active.

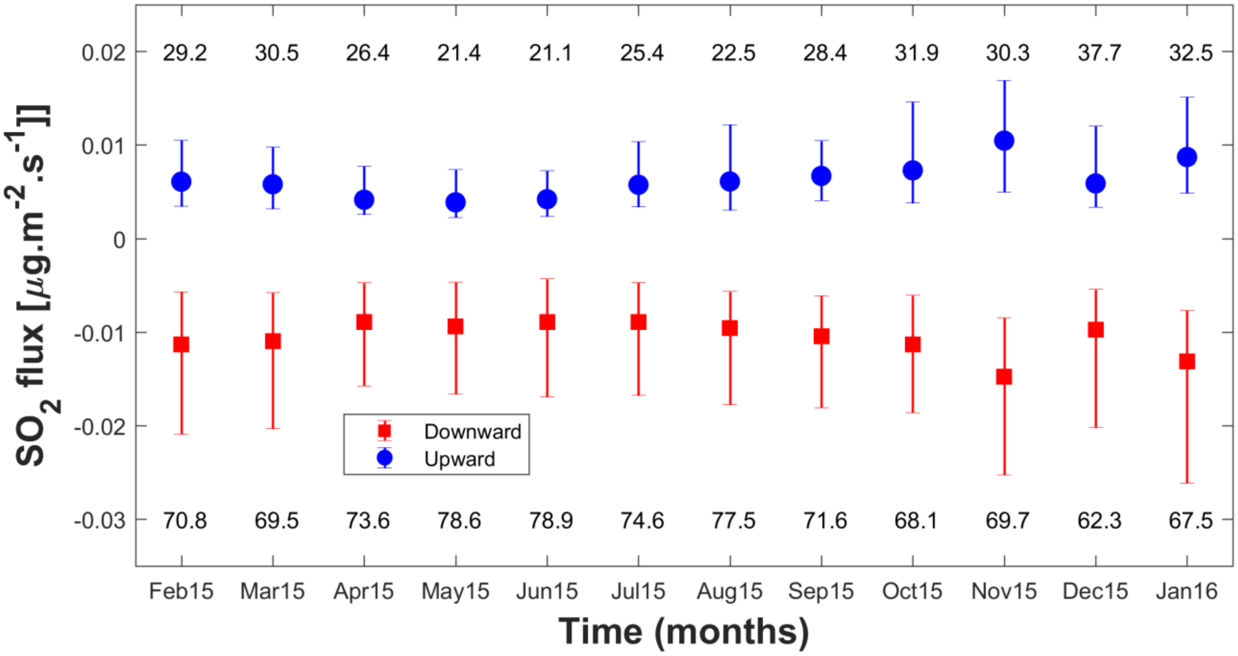


Figure 7 Monthly SO_2 upward and deposition fluxes measured at Welgegund. The red boxes for downward fluxes and the blue circle for the upward fluxes indicate the median values. Error bars indicate upper and lower quartiles.

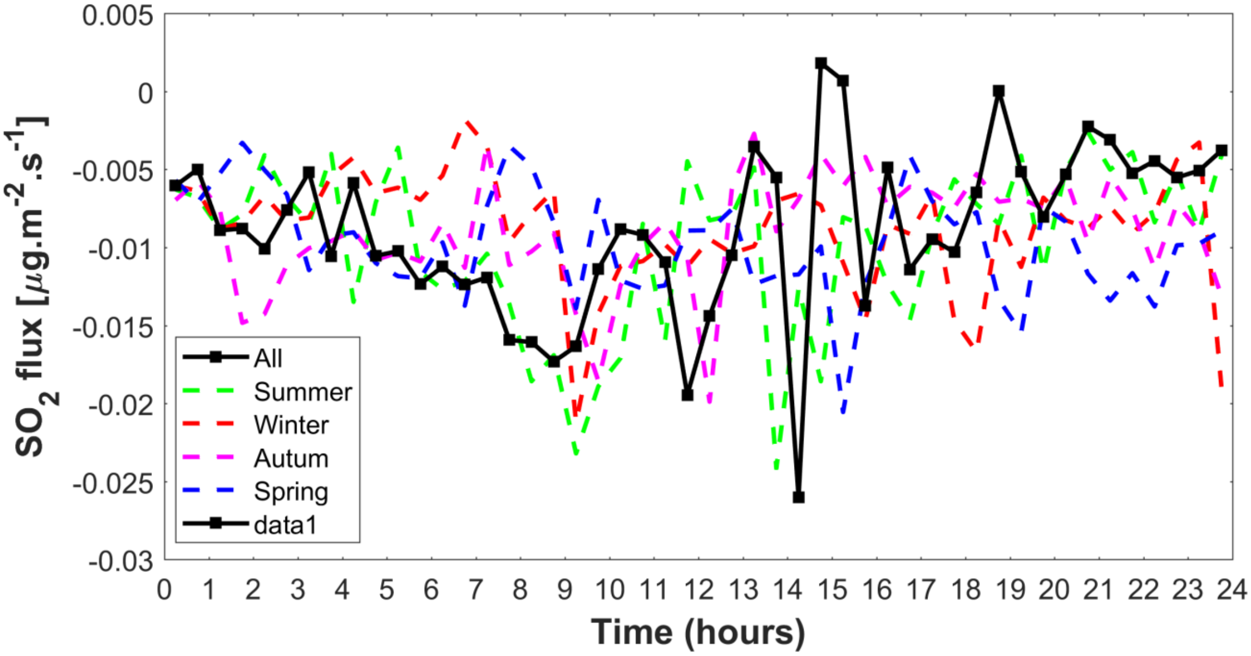
Deposition velocities were calculated from SO_2 fluxes and –concentrations as described in Chapter 3. From Figure 6 (c) it is evident that relatively higher SO_2 concentrations occurred at Welgegund during the dry winter months (June to August), which is typical for the South African Highveld (e.g. Venter *et al*., 2012; Lourens *et al*., 2011). Increased SO_2 concentrations in winter are attributed to more pronounced inversion layers trapping pollutants near the surface of the earth, thus inhibiting vertical mixing and dispersion of emitted SO_2 (Venter *et al*., 2012, Tosen & Turner, 1990, Held *et al.*, 1996, Lydia, 2010). SO_2 emissions in South Africa are usually associated with coal-fired power stations, petrochemical industries and pyrometallurgical industries producing metals from S-rich ores (Venter *et al*., 2012). As indicated in Chapter 3, although Welgegund is considered a regional background site, it is impacted by the major pollution source regions in the north-eastern interior of South Africa, which include the western Bushveld Complex where a large number of pyrometallurgical smelters are located. However, since Welgegund is not in close proximity to major point sources, a relatively weaker seasonal variability is observed due to well mixed air mass influencing Welgegund.

Similar to SO_2 fluxes measured at Welgegund, no distinct seasonal trend was observed for the net SO_2 deposition velocities (Figure 6b). The ranges of the box-and-whisker plots for SO_2 deposition velocities were also relatively narrower from May to August with the whiskers of the plot indicating more occurrences of higher deposition velocities calculated during the wet season. In addition, the ranges of the box-and-whisker plots for the calculated deposition velocities from May to August seems slightly narrower in comparison to the ranges of the box-and-whisker plots of the corresponding flux measurements during the same period, which can be attributed to the relatively higher SO_2 concentrations measured during winter. The median deposition velocity during the wet season, i.e. 0.18 cm. s^{-1} was slightly higher compared to the 0.16 cm. s^{-1} median deposition velocity measured during the dry season. As indicated above, these occurrences of relatively higher deposition velocities during the wet warmer months can be attributed to increased leaf area surface and photosynthetic activity associated with increased solar radiation, relative humidity and precipitation (Figure 5), as well as increased canopy wetness. Increased turbulence during spring and summer is also considered to contribute to higher deposition velocities (Zunckel *et al.,* 1999a) Furthermore, relatively higher deposition velocities in the wet season also resulted in increased deposition fluxes (Figure 7) associated with relatively lower SO_2 concentrations measured during this period (Figure 6c).

4.3.2. Diurnal pattern

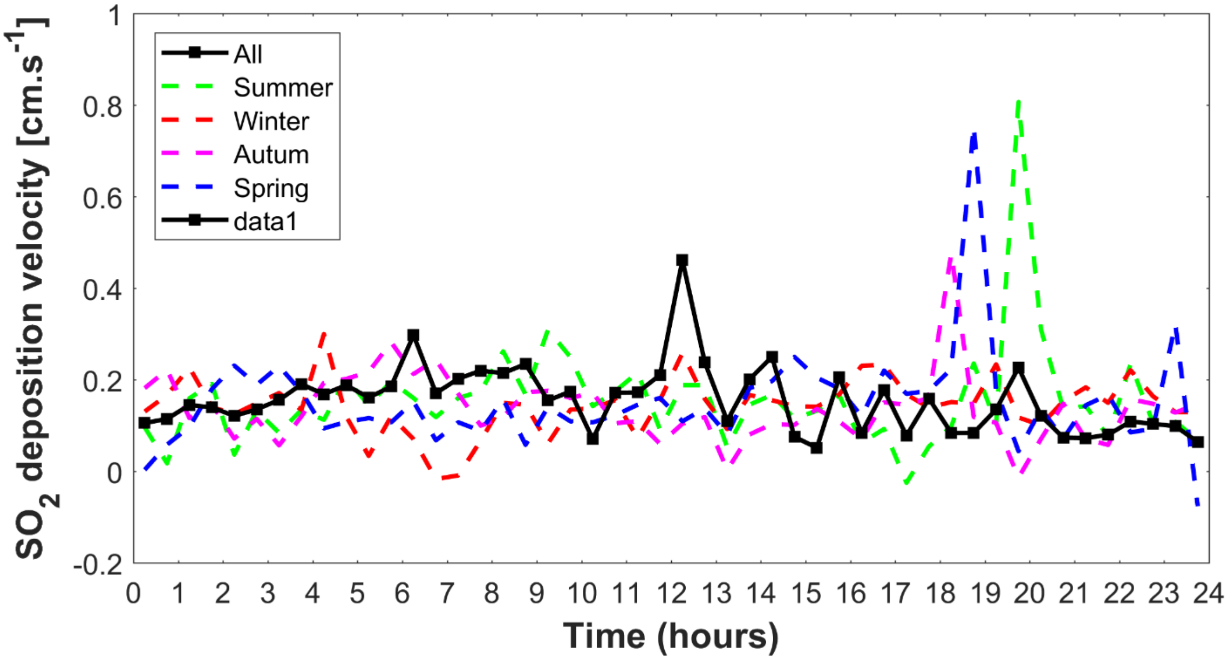
The mean hourly SO_2 fluxes, -deposition velocities and – concentrations are presented in Figure 8 (a), (b) and (c), respectively for each of the seasons and for the entire sampling period. Although the mean hourly SO_2 fluxes fluctuate between each hour of the day, there seem to be a slight diurnal pattern with higher SO_2 fluxes occurring between 06:00 and 18:00 in summer and 07:00 and 18:00 in winter with SO_2 fluxes peaking at midday. Higher daytime deposition fluxes are expected, since deposition velocities should increase during daytime due to increased convective mixing and solar radiation, as well as dilated leaf stomata (Zunckel *et al*., 1999a). However, as indicated in Figure 8 (b), no diurnal pattern was evident for mean deposition velocities calculated from measured SO_2 fluxes and -concentrations at Welgegund. The mean hourly SO_2 concentrations (Figure 8c) indicate a single morning SO_2 peak, which coincide with the break-up of inversions layers – typical for the South African Highveld (Venter *et al*., 2012, Tosen and Turner, 1990, Held *et al.*, 1996). Therefore, SO_2 concentrations measured at Welgegund can be attributed to the downward mixing of high-stack emissions (Venter *et al*., 2012) being transported to the regional background site. The higher peaks of SO_2 concentration in winter can be attributed to inversion layers being more persistent during winter with the break-up of the inversion layer occurring later in the morning and more pronounced regional recirculation of polluted air masses (Figure 8b). Therefore, the slightly higher SO_2 fluxes during daytime can be attributed to increased SO_2 concentrations during daytime and not diurnal patterns in deposition velocity.

(a)



SO_2 flux [μg.m^{-2}.s^{-1}]
0.005
0
-0.005
-0.01
-0.015
-0.02
-0.025
-0.03
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Time (hours)
All
Summer
Winter
Autum
Spring
data1

(b)



SO_2 deposition velocity [cm.s^{-1}]
1
0.8
0.6
0.4
0.2
0
-0.2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Time (hours)
All
Summer
Winter
Autum
Spring
data1

(c)

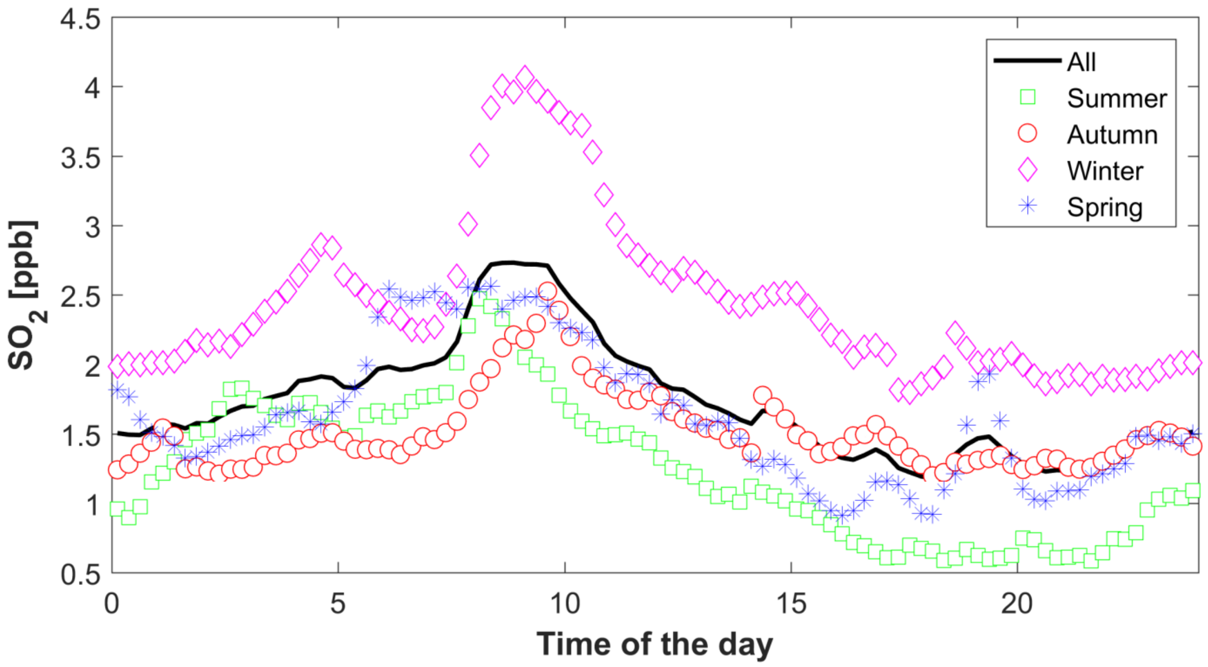


Figure 8 Hourly median/mean SO_2 fluxes (a), -deposition velocities (V_d) (b) and –concentrations (c) measured at Welgegund

4.3.3. Contextualisation

Although micrometeorological measurements of SO_2 and NO_2 fluxes have been conducted in South Africa, these studies have not been published in peer-reviewed literature. The limited studies on SO_2 and NO_2 fluxes and deposition velocities for South Africa published in literature are based on fluxes calculated from deposition velocities estimated with inferential models and measured concentrations of these species (Zunckel *et al.*, 1999a; Zunckel *et al*., 1999b; Zunckel *et al*., 1996; Mphepya, 2002; Phala, 2015). In Table 2, a summary of inferred SO_2 deposition velocities and -fluxes calculated in South Africa for different vegetation types are given. In general, it is evident from Table 2 that SO_2 fluxes and deposition velocities determined in this study are in the same order of magnitude compared to SO_2 fluxes and deposition velocities calculated with inferential models. However, significant differences in temporal patterns for deposition velocities are observed, which can be attributed to the meteorological input parameters utilised in these models.

Seasonal patterns of SO_2 fluxes and deposition velocities were determined by Zunckel *et al*. (1999a) from June 1996 to May 1997 at Elandsfontein and Palmer, which are located in the north-eastern interior of South Africa on the Mpumalanga Highveld. Deposition velocities calculated with an inferential model indicated distinct seasonal variations with the highest deposition velocities occurring during summer and the lowest in winter. Average summer SO_2 deposition velocities were estimated to be up to two times higher in summer compared to winter. However, SO_2 deposition fluxes showed no distinct seasonal pattern for both these stations located within the South African Highveld, which was attributed to higher SO_2 concentrations during winter (off-set by corresponding lower deposition velocities), while lower SO_2 levels in summer coincided with increased deposition velocities. Mphepya (2002) also calculated SO_2 and NO_2 deposition velocities at Palmer and Elandsfontein from 1996 to 1998, which also indicated higher SO_2 deposition velocities in summer compared to winter. SO_2 deposition velocities measured during the daytime were approximately two times higher in summer than in winter. Phala (2015) also indicated higher SO_2 deposition velocities during summer (approximately 1.5 times higher) from SO_2 deposition velocities estimated with an inferential model from 2008 to 2012 at Lephalale in the north-western interior of South Africa. An inferential model was utilised to calculated SO_2 deposition velocities at a high-altitude site at Ben MacDhui Mountain in the south-eastern escarpment of South Africa during an intensive two-week monitoring campaign in March and June 1996, which also indicated higher SO_2 deposition velocities in summer (Zunckel *et al*., 1999b). Deposition fluxes calculated by Mphepya (2002), Zunckel at al., (1999b) and Phala (2015) indicated higher deposition fluxes in winter, which was attributed to increased SO_2 concentrations during winter. The distinct seasonal patterns of the inferred deposition velocities in the above mentioned studies, i.e. higher deposition velocities in warmer months can be attributed to increased solar radiation, turbulence and leaf surface, which are utilised as input parameters in the inferential model.

Deposition velocities were also calculated during two short SO_2 concentration monitoring campaigns at Blyde in the eastern escarpment and Skukuza in the Lowveld in 1996 (Zunckel *et al*., 1999a). Similar deposition velocities were calculated for the summer and winter campaign at these two sites, which was attributed to photosynthetically active vegetation in these frost-free regions during winter. However, deposition fluxes were higher in winter at both these sites; this was linked to increased SO_2 concentrations, especially at Blyde which closer to the industrialised Highveld compared to Skukuza.

Diurnal patterns for deposition velocities calculated with an inferential model at Elandsfontein and Palmer by Zunckel *et al*. (1999a) indicated distinct diurnal patterns for these sites. Deposition velocities increased gradually from 06:00 reaching a maximum during midday, after which deposition velocities decreased steadily until 18:00. Night-time deposition velocities remained relatively constant. The corresponding deposition fluxes calculated from the inferred deposition velocities and measured concentrations, showed a similar pattern to that observed with deposition velocities. However, Palmer had a weaker diurnal deposition flux variation due to lower SO_2 concentrations.

In addition, SO_2 concentrations at Elandsfontein and Palmer had a similar single peak in the mornings as determined for Welgegund. Daytime and night-time deposition velocities calculated with an inferential model for Palmer and Elandsfontein for each of the seasons by Mphepya (2002) also indicated higher daytime deposition velocities for all the seasons with daytime SO_2 deposition velocities to night-time SO_2 deposition velocities ratios increasing from winter to summer. Time series plots for inferred deposition velocities at Ben MacDhui mountain determined during two short-term campaigns indicated diurnal patterns with deposition velocities peaking at about mid-day (Zunckel *et al*., 1999b) whereas minimum deposition velocities occurred during evenings; similar diurnal variations were observed for deposition velocities calculated for short-term measurements at Blyde and Skukuza (Zunckel *et al*., 1999a).

Table 2 Comparison of mean SO_2 deposition velocities calculated and mean deposition fluxes measured in this study to mean SO_2 deposition velocities and -fluxes estimated with inferential modelling in other parts of South Africa

			Mean deposition velocities (cm.s^{-1})								Mean deposition fluxes (μg.m^{-2}.s^{-1})						
Location	Date	Vegetation	Summer		Autumn		Winter		Spring		Summer		Autumn	Winter		Spring	Reference
Welgegund	Feb 2015 – Jan 2016	savannah-grassland-agriculture	0.180		0.136		0.176		0.186		-0.009		-0.010	-0.009		-0.008	This study
Palmer	Jun 1996 – May 1997	grassland-agriculture	0.272		0.266		0.192		0.196		0.012**		0.018**	0.027**		0.017**	Zunckel *et al*. (1999a)
	1996 – 1998	grassland-agriculture	Day	Night	Day	Night	Day	Night	Day	Night							Mphepya (2002)
			0.370	0.150	0.260	0.120	0.140	0.100	0.240	0.120							
Elandsfontein	Jun 1996 – May 1997	grassland-agriculture	0.260		0.222		0.164		0.212		0.086**		0.074**	0.061**		0.083**	Zunckel *et al*. (1999a
	1996 – 1998	grassland-agriculture	Day	Night	Day	Night	Day	Night	Day	Night							Mphepya (2002)
			0.350	0.150	0.260	0.120	0.150	0.100	0.220	0.110							
Lephalale	2008 – 2012*	dry deciduous forest	0.191		0.150		0.126		0.174								Phala (2015)
Ben MacDhui	Mar and Jun 1996	alti mountain grassland	LAI 0.5	LAI 1.5			LAI 0.5	LAI 1.5			LAI 0.5	LAI 1.5		LAI 0.5	LAI 1.5		Zunckel *et al*. (1999b)
			0.32	0.47			0.19	0.19			0.008	0.012		0.004	0.004		
Blyde	22 Aug – 20 Sep; 29 Oct – 30 Nov	forest / grassland	0.45				0.39				0.012**			0.030**			Zunckel *et al*. (1999a)
Skukuza	22 Aug – 20 Sep; 29 Oct – 30 Nov	forest / grassland	0.42				0.46				0.015**			0.021**			Zunckel *et al*. (1999a)

*Deposition velocities measured and presented for each year were averaged for entire period

**Deposition fluxes were converted from μg.m^{-2}.h^{-1} to μg.m^{-2}.s^{-1}

4.4. NO_2 fluxes and -deposition velocities

Table 3 presents the median (mean), interquartile range (IQR), ±2.7σ, the maximum and minimum fluxes measured and deposition velocities calculated for NO_2 at Welgegund for the one-year measurement period. Contrary to SO_2 fluxes, the median (mean) NO_2 fluxes, i.e. 0.005 $\mu g.m^{-2}.s^{-1}$ (0.01 $\mu g.m^{-2}.s^{-1}$) reveals a net upward flux for atmospheric NO_2. Therefore, Welgegund can be considered a net source of atmospheric NO_2 with only the +2.7 σ and minimum NO_2 flux values indicating instances of downward NO_2 flux. The median (mean) deposition velocity for NO_2 calculated from the measured NO_2 fluxes and –concentrations as described in Chapter 3 was - 0.16 cm. s^{-1} (-0.33 cm. s^{-1}), with the negative sign denoting upward fluxes.

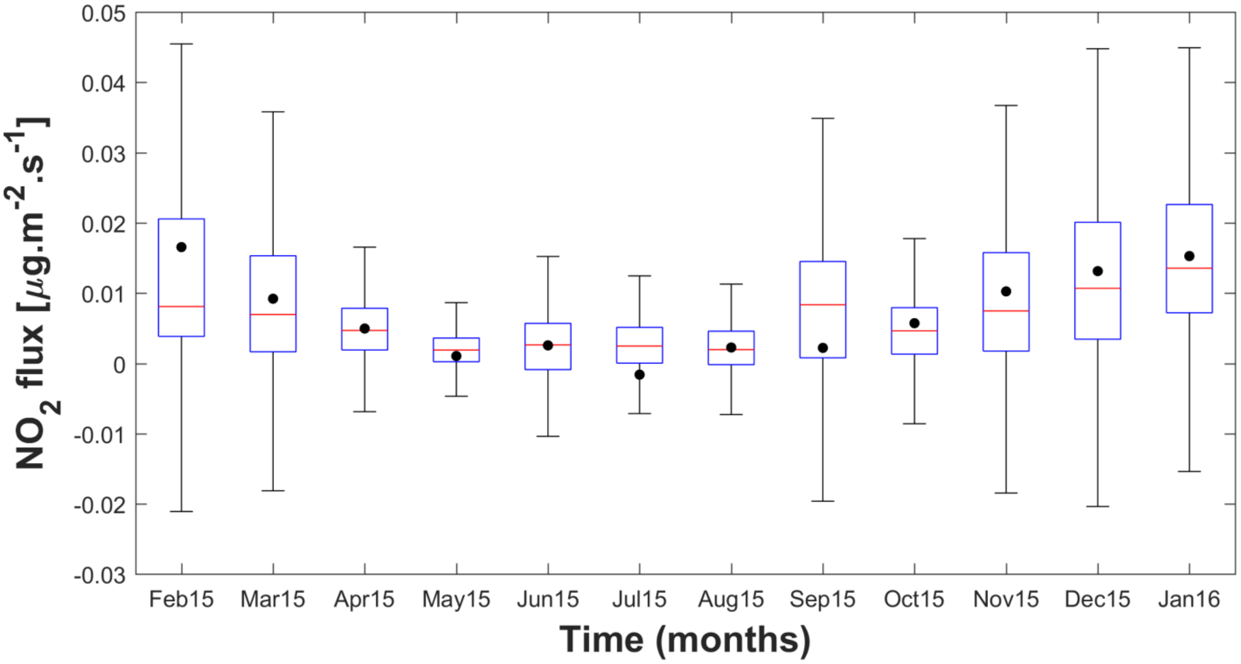
Table 3 Statistical distribution of NO_2 fluxes and deposition velocities measured at Welgegund

	Flux ($\mu g.m^{-2}.s^{-1}$)	V_d (cm/s)
Median (mean)	0.005 (0.01)	-0.16 (-0.33)
IQR (25th – 75th)	0.001 – 0.01	-0.42 – -0.004
±2.7σ	-0.01 and 0.04	-1.61 and 0.24
Maximum	1.58	49.23
Minimum	-1.97	-17.86

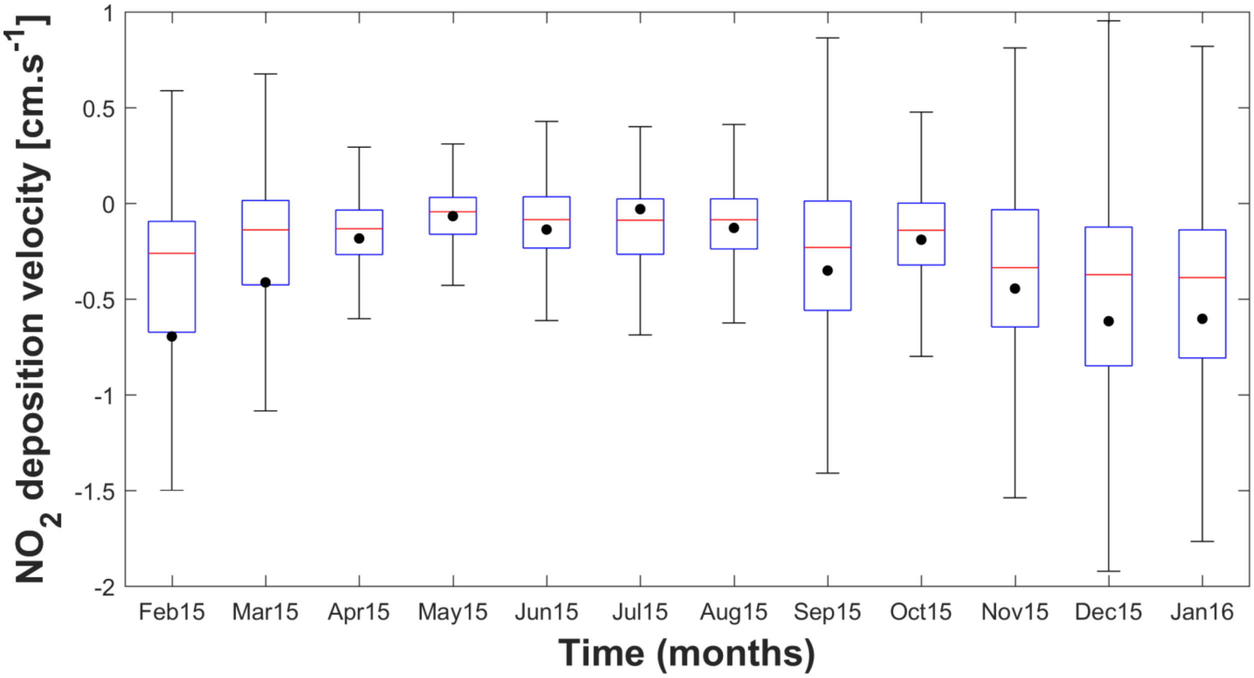
4.4.1. Seasonal pattern

In Figure 9 (a), (b) and (c), the monthly NO_2 fluxes, -deposition velocities and -concentrations are presented, respectively. In contrast to SO_2 fluxes and -deposition velocities, distinct seasonal patterns are observed for NO_2 fluxes and deposition velocities. In addition, the monthly variation in NO_2 fluxes also signify that Welgegund is a net source of atmospheric NO_2 indicated by the positive mean (median) NO_2 flux values measured for all the months, with the exception of the negative mean NO_2 flux measured during July 2015. Lower net upward fluxes and net negative deposition velocities were measured from May 2015 to August 2015, which are indicated in the median (mean) values and the ranges of the box-and-whisker plots. These months coincided with the colder and dryer months as indicated in Figure 5. Fluxes increased with the onset of spring (microbial activity) in September 2015 with highest median (mean) NO_2 upward fluxes occurring during the wet season. The seasonal patterns of net upward fluxes correspond with the seasonal trends observed for temperature, soil temperature and precipitation (Figure 5). The median (mean) flux for the dry season was 0.003 $\mu g.cm^{-2}.s^{-1}$ (0.001 $\mu g.cm^{-2}.s^{-1}$), while the median (mean) fluxes measured during the wet season was 0.008 $\mu g.cm^{-2}.s^{-1}$ (0.011 $\mu g.cm^{-2}.s^{-1}$). The net NO_2 flux direction generally depended on NO_2 concentrations and the amount of NO released from soil.

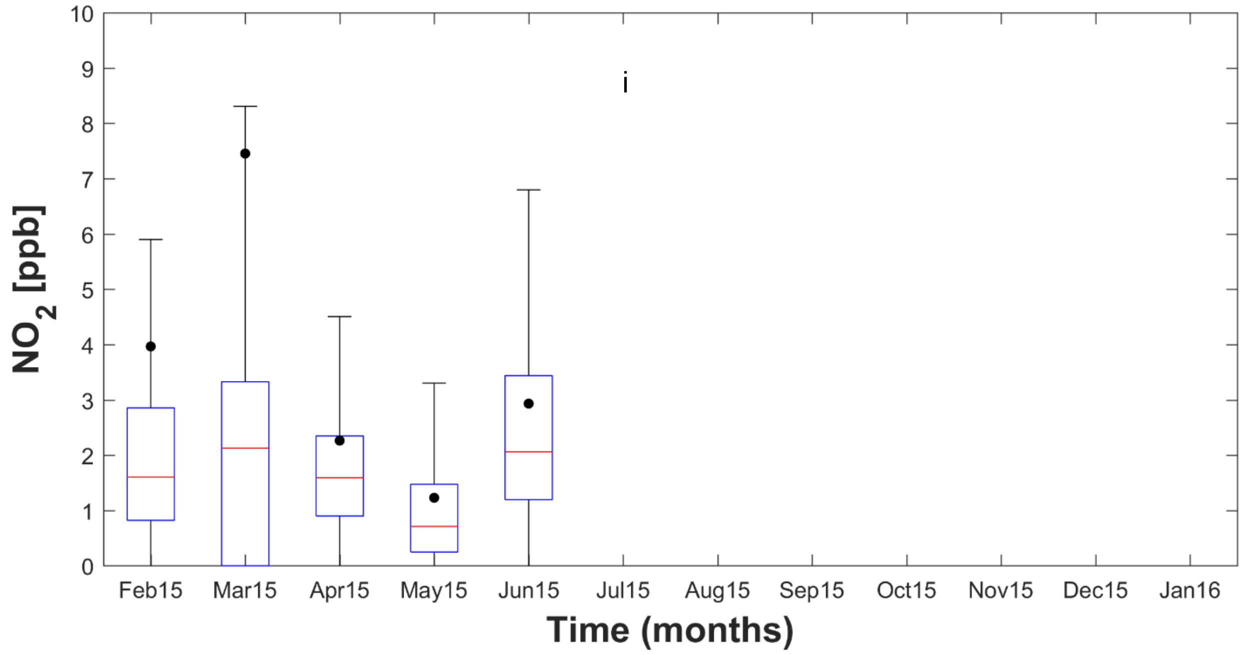
(a)



(b)


NO$_2$ deposition velocity [cm.s^{-1}]
1
0.5
0
-0.5
-1
-1.5
-2
Feb15
Mar15
Apr15
May15
Jun15
Jul15
Aug15
Sep15
Oct15
Nov15
Dec15
Jan16
Time (months)

(c)


NO$_2$ [ppb]
10
9
8
7
6
5
4
3
2
1
0
i
Feb15
Mar15
Apr15
May15
Jun15
Jul15
Aug15
Sep15
Oct15
Nov15
Dec15
Jan16
Time (months)

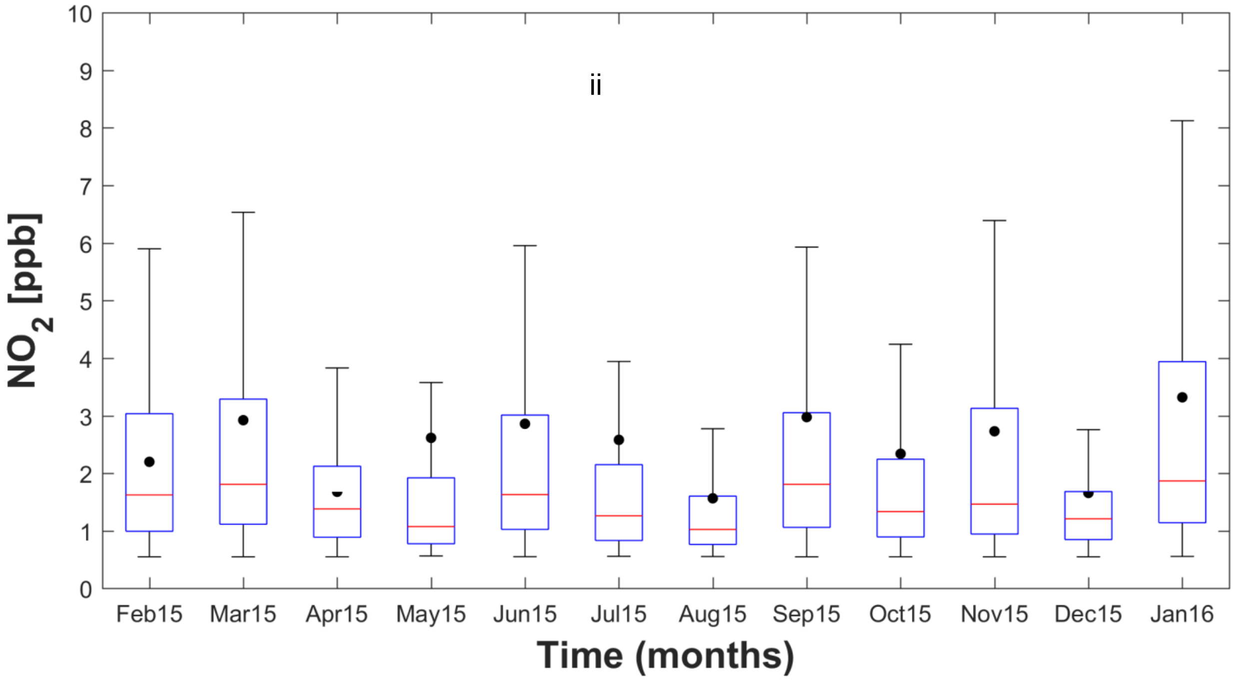


Figure 9 Monthly NO_2 fluxes (a), -deposition velocities (V_d) (b) and –concentrations (c) measured at Welgegund. Top pane in (c) presents NO_2 concentrations measured with the Teledyne instrument, while the bottom pane in (c) presents NO_2 concentrations measured with the Aerodyne flux instrument. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3 % coverage if the data have a normal distribution

As mentioned above, measured NO_2 concentrations were used to calculate NO_2 deposition velocities. The monthly NO_2 concentrations given in Figure 9(c) indicate no significant seasonal variation. Atmospheric NO_2 concentrations on the South African Highveld are usually characterised by increased NO_2 levels during winter and early spring, which is attributed to increased household combustion (for space heating and cooking) (Venter *et al.*, 2012) and decreased vertical dispersion associated with more pronounced inversion layers during winter (Tosen and Turner, 1990, Held *et al.*, 1996). In addition, regional open biomass burning occurring during late winter and early spring also contribute to increased NO_2 concentrations. Therefore the absence of a distinct seasonal pattern in atmospheric NO_2 can be attributed to different NO_2 sources contributing to atmospheric NO_2 during different times of the year. The typical sources in winter and early spring, i.e. household combustion and open biomass burning would contribute to NO_2 levels measured during this period, whereas the wet season corresponds to an upsurge of NO emissions associated with increased microbial activity and radiation (Figure 5).

The absence of seasonal patterns observed for NO_2 concentrations, also indicate that NO_2 flux patterns are mainly related to factors influencing NO_2 deposition velocities. This is also indicated by the seasonal pattern of deposition velocities, which follows an inverse seasonal trend compared to the net NO_2 fluxes, i.e. higher negative deposition velocities associated with higher net upward fluxes. It is also evident from Figure 9(c) that monthly median (average) NO_2 levels were generally low at Welgegund. NO_2 fluxes measurements conducted by Duyzer *et al.*, 2004 over a forest region indicated that lower NO_2 concentrations coincided with upward fluxes, while higher NO_2 levels were associated with net deposition. Lower NO_2 concentrations are also more susceptible to the influence of chemical reactions and NO emissions.

The monthly NO_2 flux measurements were also separated into deposition and upward fluxes and presented in Figure 10, in order to highlight observed seasonal NO_2 flux and deposition velocity patterns. The median (mean) of downward fluxes was - 0.005 $\mu g.m^{-2}.s^{-1}$(-0.017 $\mu g.m^{-2}$ s^{-1}), whereas the median (mean) of the upward fluxes was 0.008 $\mu g.m^{-2}.s^{-1}$ (0.012 $\mu g.m^{-2}.s^{-1}$). As expected, upward NO_2 fluxes mimics the seasonal pattern observed in Figure 9(a), i.e. higher fluxes observed during the warmer wet months (Figure 5) coincided with increased microbial activity, while upward fluxes were lowest during the cold and dry months. As indicated for the seasonal pattern of the net fluxes, the temporal trends of upward fluxes correspond to the seasonal patterns of temperature, soil temperature and precipitation. A more complex relation is observed between upward fluxes and soil moisture. Lower soil moisture in May 2015 to July 2015 correspond with the lowest upward fluxes, while higher upward fluxes in October 2015 and

November 2015 are also associated with lower soil moisture. In addition, higher upward fluxes in September 2015 correspond to relatively higher soil moisture. Upward NO_2 fluxes can be ascribed to NO emissions from soil related to nitrification (Fowler *et al*., 2009), while studies have also indicated that photolysis of HNO_3 on plant surfaces can also contribute to emissions of reactive N species (Raivonen, 2006). Soil temperature and soil moisture have been indicated as important parameters associated with NO emissions, especially for a specific site, while on a regional scale factors such N deposition, soil type and vegetation are also important (Pilegaard, *et al*., 2006, Farmer and Cohen, 2008, Fowler *et al*., 2009). Various studies have indicated that increased NO emissions rates correspond to increased soil temperatures (Slemr & Seiler, 1984, Skiba, 1998), while soil NO emissions exhibit a more complex relationship with soil moisture (Fowler, 2009). For example, Pilegaard *et al.*, 2006 attributed lower soil moisture to increase NO emissions due to the aerated soil favouring nitrification, while Venterea *et al*., 2005 indicated that soil moisture is important to mediate chemical processes resulting in NO formation.

Most chemical transport models use temperature, soil moisture and ecosystems type as input parameters (Yienger & Levy, 1995). In addition, N fertilisation (especially anhydrous ammonia) of agricultural soils is also generally regarded to contribute significantly to NO soil emissions (Skiba *et al*., 1997; Venterea and Rolston, 2000; Slemr and Seiler *et al*., 1984; Oikawa *et al*., 2015). The occurrences of significantly higher NO_2 upward fluxes indicated by the whiskers in Figure 9(a) in February 2015, November 2015, December 2015 and January 2016 may be attributed to increased use of fertilisation in this region during these months. As indicated in Chapter 3, Welgegund is located on a commercial farm where maize is cultivated. These months correspond to the main growth season of maize crops during which these soils can be excessively fertilised. The maize soils in this region are considered to be sandy; as such, the fertiliser is easily lied (Advanced Crop Care, 2011).

A higher NO_2 upward flux observed in September 2015 can be attributed to the soil preparation for planting during which the soil is turned and prepared for new plantings, which can also result in increased NO emissions (Prieur , 2016).

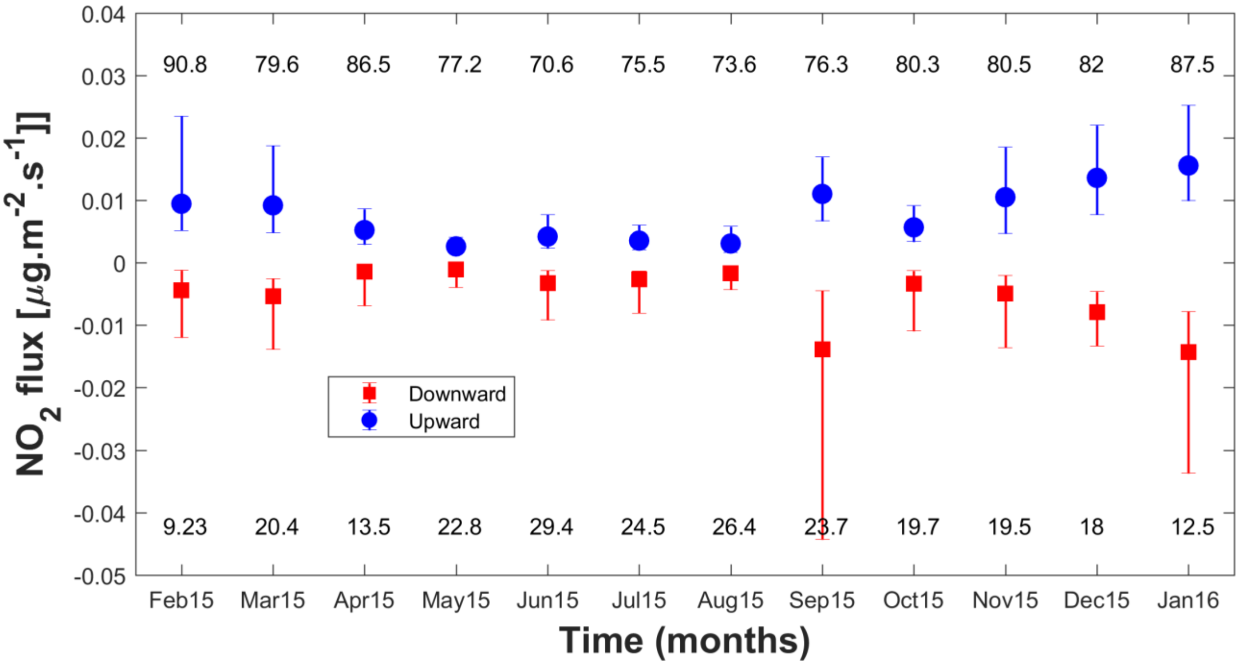


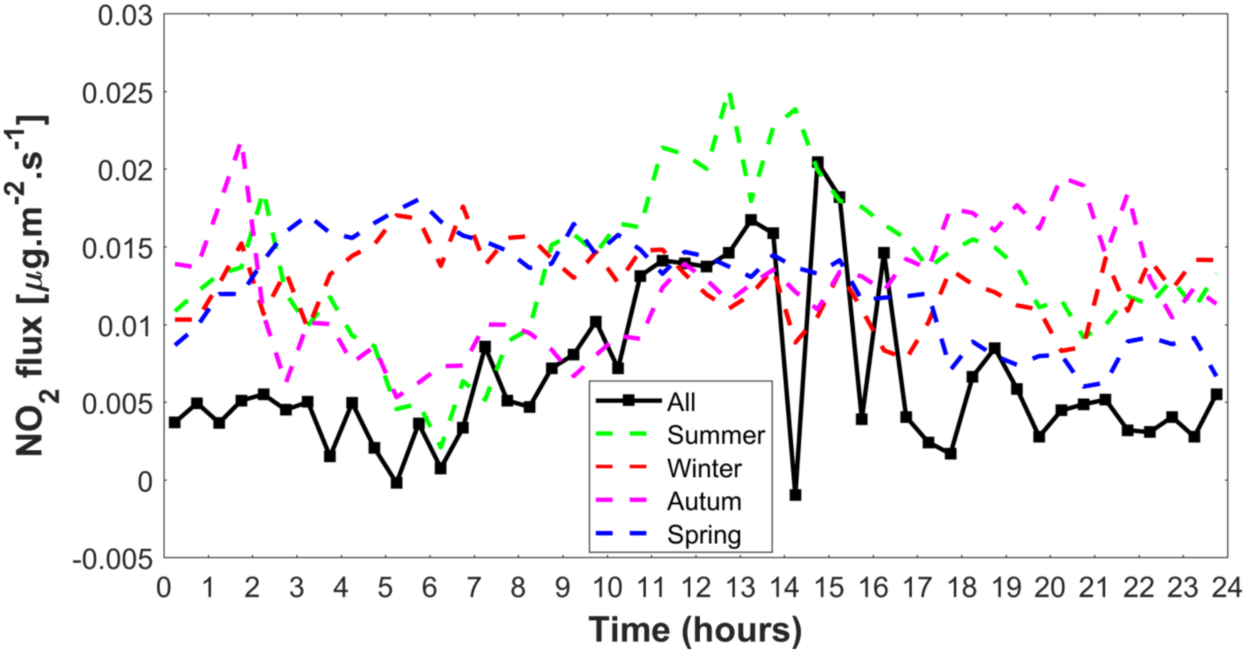
Figure 10 Monthly NO_2 upward and deposition fluxes measured at Welgegund. The red boxes for downward fluxes and the blue circle for the upward fluxes indicate the median values. Error bars indicate upper and lower quartiles.

Similar to upward fluxes, downward fluxes also indicate a seasonal pattern with higher downward fluxes similarly occurring during the warm and wet season (Figure 5). In addition, significantly higher downward NO_2 fluxes occurred in September 2015. The stomatal uptake of NO_2 is widely recognised as the main sink of NO_2 as indicated in various studies (Rondon, *et al*., 1993, Gut *et al*., 2002, Stella *et al*., 2013). Therefore factors associated with increased biomass e.g. leaf area index (LAI), temperature, precipitation and soil moisture can be considered relevant to increased NO_2 deposition. However, NO_2 deposition can either be enhanced or decreased by wetness (Eugster & Hesterberg, 1996). It is also well documented that increased NO_2 deposition is associated with increase in turbulence (Thoene *et al*., 1991, Ramge *et al*., 1991). The cold winter months in the South African Highveld is characterised by stable meteorological conditions due to the persistence of a high-pressure cell over this region. During summer this high-pressure system shifts southwards allowing tropical easterly flow to be prevalent, which is associated with low air pressure and generally unstable conditions. This increase in turbulence could also contribute to the significant increase in NO_2 deposition during September, which is generally characterised by high turbulence. Higher transport of NO_2 to the canopy could also contribute to increased NO_2 deposition (Duyzer *et al.*, 2004). Although no distinct seasonal pattern is observed for NO_2 concentrations, increased NO_2 emissions from open biomass burning occurring in September could also contribute to increased NO_2 deposition. In addition, the higher NO_2 deposition observed in January 2016 can be attributed to increased NO_2 concentrations associated with higher NO emissions as indicated by the relatively high upward NO_2 flux.

4.4.2. Diurnal patterns

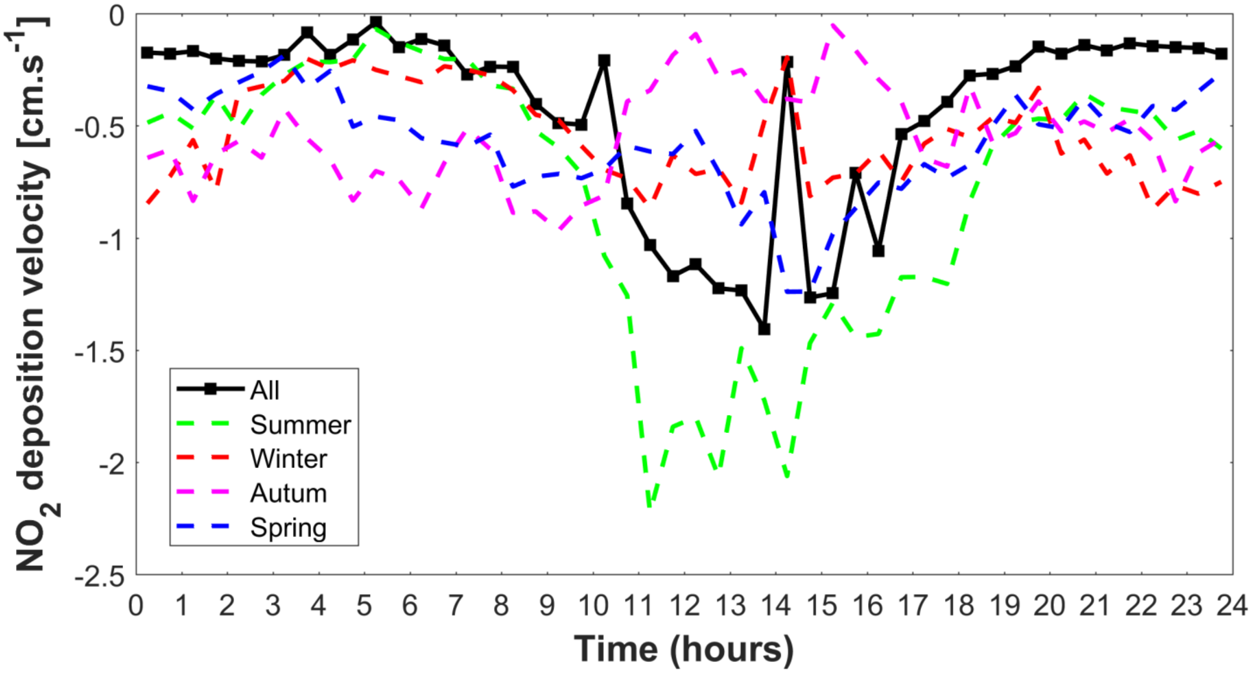
In Figure 11 (a), (b) and (c) the mean hourly NO_2 fluxes, -deposition velocities and –concentrations are presented. Similarly to the SO_2 diurnal flux patterns, hourly fluctuations are also observed for NO_2 diurnal flux variability. No distinct diurnal patterns are observed for NO_2 fluxes during autumn, winter and spring, as well as for their respective deposition velocities. However, during summer NO_2 fluxes increase during daytime from 06:00 to 18:00, while their corresponding deposition velocities are more negative from 10:00 to 18:00. These summer diurnal patterns are also reflected in the diurnal trend calculated for the entire sampling period. The higher NO_2 fluxes corresponding to more negative deposition velocities can be attributed to increase NO soil emissions associated with increased daytime temperature and soil temperature. In addition, increased photolysis of HNO_3 could also contribute to increased NO_x emissions. As mentioned previously, summer months also coincide with increased precipitation (Figure 5), so causing more atmospheric HNO_3 to be transported to plant surfaces. As indicated in Section 4.4.1, increased NO emissions in this region during summer coincided with increased temperature, soil temperature and precipitation; fertilisation of the agricultural soil was also prevalent during summer. NO_2 concentrations revealed distinct bimodal diurnal patterns for all seasons with an early morning peak between 04:00 and 10:00, as well as a late afternoon/early evening peak from 18:00. These peaks are more pronounced during winter due to increased household combustion for space heating and more pronounced inversion layers. These peaks can be attributed to the regional influence of household combustions (Venter *et al.*, 2012). Note that diurnal NO_2 concentration patterns are not reflected in the net NO_2 upward fluxes.

(a)



0.03
0.025
0.02
0.015
0.01
0.005
0
-0.005
NO$_2$ flux [μg.m^{-2}.s^{-1}]
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Time (hours)
All
Summer
Winter
Autum
Spring

(b)



0
-0.5
-1
-1.5
-2
-2.5
NO$_2$ deposition velocity [cm.s^{-1}]
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Time (hours)
All
Summer
Winter
Autum
Spring

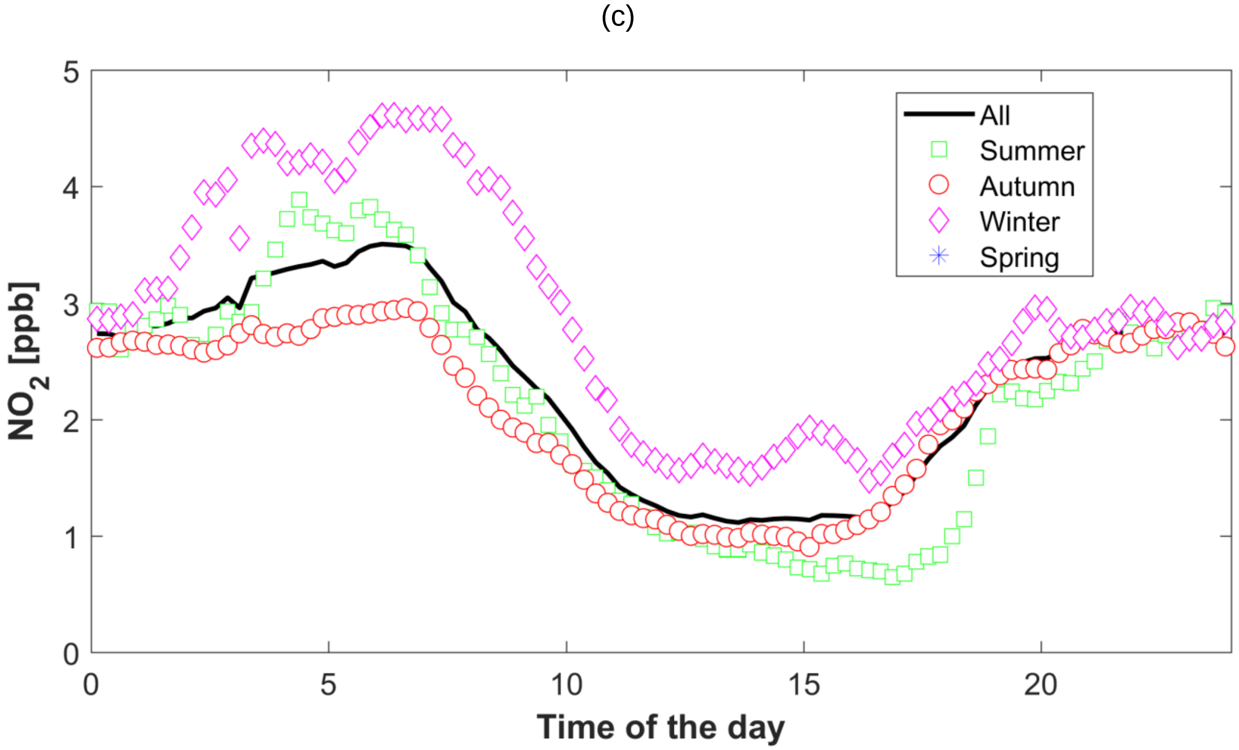


Figure 11 Hourly NO_2 fluxes (a), -deposition velocities (V_d) (b) and –concentrations (c) measured at Welgegund.

4.4.3. Contextualisation

Only two studies have been conducted in South Africa in which deposition velocities of NO_2 were calculated with an inferential model, which are presented in Table 4. It is evident from these inferred positive deposition velocities that the net NO_2 flux is downward and that upward NO_2 fluxes are not accounted for in the inferential model. The NO_2 deposition velocities calculated by Mphepya (2002) at Palmer and Elandsfontein from 1996 to 1998 indicated that NO_2 deposition velocities were higher in summer than in winter. Daytime deposition velocities were also higher for all the seasons, with the daytime NO_2 deposition velocities to night-time NO_2 deposition velocities ratios increasing from winter to summer. Daytime deposition velocities in summer were approximately three times higher than night-time values. Phala (2015) also indicated higher NO_2

deposition velocities during summer (approximately 1.5 times higher) at Lephalale compared NO_2 deposition velocities inferred for winter, while similar deposition velocities were modelled for autumn and spring. Therefore deposition fluxes calculated in these studies by Mphepya (2002) and Phala (2015) can be considered an overestimation of N deposition for these regions according to the net upward fluxes determined for NO_2 with micrometeorological measurements in this study. Furthermore, Mphepya (2002) and Phala (2015) also attributed seasonal variances in fluxes to lower deposition velocities which coincide with higher NO_2 concentrations during winter; this is compared to higher deposition velocities coinciding with lower NO_2 concentrations during winter. In general higher NO_2 concentrations contributed to higher NO_2 deposition fluxes in winter.

It is also evident from Table 4 that the averages of net upward fluxes (and their corresponding deposition velocities) were ~15 times higher during summer compared to winter at Welgegund, while spring and autumn net upward fluxes and their associated deposition velocities were similar. Therefore, micrometeorogical measurements indicate the exact opposite trend compared to inferred deposition velocities; i.e. a more negative deposition velocity during summer compared to winter, contributing to increased NO_x emissions in summer and not increased deposition as indicated by inferential modelling.

Table 4 Comparison of mean NO_2 deposition velocities calculated and mean deposition fluxes measured in this study to mean NO_2 deposition velocities and -fluxes estimated with inferential modelling in other parts of South Africa

			Mean deposition velocities ($cm.s^{-1}$)								Mean deposition fluxes ($\mu g.m^{-2}.s^{-1}$)				
Location	Date	Vegetation	Summer		Autumn		Winter		Spring		Summer	Autumn	Winter	Spring	Reference
Welgegund	Feb 2015 – Jan 2016	savannah-grassland-agriculture	-0.638		-0.221		-0.098		-0.329		0.015	0.005	0.001	0.006	This study
Palmer	1996 – 1998	grassland-agriculture	Day	Night	Day	Night	Day	Night	Day	Night					Mphepya (2002)
			0.240	0.080	0.130	0.040	0.050	0.040	0.110	0.040					
Elandsfontein	1996 – 1998	grassland-agriculture	Day	Night	Day	Night	Day	Night	Day	Night					Mphepya (2002)
			0.260	0.080	0.140	0.100	0.050	0.040	0.120	0.050					
Lephalale	2008 – 2012*	dry deciduous forest	0.122		0.082		0.070		0.096						Phala (2015)

*Deposition velocities measured and presented for each year were averaged for entire period
**Deposition fluxes were converted from $\mu g.m^{-2}.h^{-1}$ to $\mu g.m^{-2}.s$

4.5. Comparison of deposition fluxes calculated from passive SO_2 and NO_2 measurements

To-date, several deposition studies conducted in South Africa have derived SO_2 and NO_2 deposition fluxes from passive sampling measurements (Mphepya, 2002, Josipovic *et al*., 2009, Martins, 2009). In addition, these passive samplers are used at most of the sites belonging to the INDAAF deposition network in Africa to measure SO_2 and NO_2 concentrations (Adon *et al*., 2013). Passive samplers were used to determine monthly SO_2 and NO_2 concentrations for one year during the micrometeorogical SO_2 and NO_2 flux measurement period presented in this study, to calculate deposition fluxes from these concentrations.

Passive sampling data was then compared to deposition velocities calculated from micrometeorological measurements and to deposition velocities determined with inferential models in South Africa. In addition, SO_2 and NO_2 deposition velocities estimated by Zhang *et al*. (2003) for LUCs, which are typically considered to be representative of a grassland savannah region in southern Africa, were also used. These deposition fluxes are presented in Table 5 (a) & (b).

It is evident from table 5 (a) that SO_2 deposition flux determined from this study are in the same order of magnitude and shows the same seasonal variations, when compared to deposition flux calculated from different studies in South Africa. As mentioned previously, this is also true of deposition velocities observed for several (inferential model) studies conducted in South Africa; and additionally, the calculated deposition velocities in this study (micrometeorological). However, differences in temporal patterns were observed and can be attributed to the meteorological input parameters utilised in these models. Deposition flux determined deposition velocities measured from Zhang *et al*. (2003) are significantly higher with the same seasonal variations. The higher deposition flux is attributed to higher deposition velocities (predicted dry maximum deposition velocity) determined by Zhang *et al*. (2003). SO_2 deposition flux increased during the warmer wet months due to the increase of biomass and photosynthetic activity, precipitation, relative humidity and turbulence (Fowler *et al.*, 2009). This is expected of SO_2 deposition flux which is predominately controlled by non-stomatal processes (Fowler *et al*., 2009, Finkelstein *et al*., 2000).

From positive deposition flux data indicated by table 5 (b), it is evident that Welgegund is a net source of atmospheric NO_2. The deposition fluxes initially increase in spring due to microbial activity, with the highest value occurring during the warm, wet season. Increased negative deposition velocities (measured during the summer months) are associated with higher emission fluxes. The higher values in summer can be attributed to increased fertilisation in the region. Meteorological conditions also influence deposition flux, with winter marked by more stable meteorological conditions compared to summer and spring. This is linked to an increase of turbulence and higher deposition velocities occurring during these months (Thoene *et al*., 1991, Ramge *et al*., 1991). A similar trend in deposition flux is seen from other studies illustrated by table 5 (b), with higher values occurring in the warmer, wet months. As explained above, deposition flux determined from the deposition velocities measured by Zhang *et al*. (2003) are significantly higher and feature the same seasonal variations. The higher deposition flux is attributed to higher deposition velocities (predicted dry maximum deposition velocity) determined by Zhang *et al*. (2003).

Table 5 SO_2 deposition flux calculated from deposition velocities used in different studies (a). NO_2 deposition flux calculated from deposition velocities used in different studies (b)

(a)

SO2 Deposition kg/ha/yr										
Sample period		Deposition velocities presented in previous studies and QCL calculated deposition velocities								
Date in	Date out	SO2 Ambient concentration (ug/m-3)	Zhang *et al*., 2003 thorn shrubs, dry (1.1 cm/s)	Zhang *et al*., 2003 thorn shrubs, wet (2.3 cm/s)	Zhang *et al*., 2003 short grass and forbs, dry (1.3 cm/s)	Zhang *et al*., 2003 short grass and forbs, wet (1.9 cm/s)	Mphepya, 2002 Elandsfontein (Summer 0.255, Winter 0.125, Autumn 0.19 and Spring 0.175 cm/s)	Martins, 2009 Amersfoort (Summer 0.27, Winter 0.18 cm/s)	Zunckel, 1998, Elandsfontein (Summer 0.260, Winter 0.164, Autumn 0.222 and Spring 0.212 cm/s)	QCL calculated value Potchefstroom (Summer 0.180, Winter 0.176, Autumn 0.136 and Spring 0.186 cm/s)
12/30/2014	1/28/2015	3.6549	-1.27	-2.65	-1.50	-2.19	-0.29	-0.31	-0.30	-0.21
1/28/2015	2/23/2015	5.1352	-1.78	-3.72	-2.11	-3.08	-0.41	-0.44	-0.36	-0.29
2/23/2015	4/1/2015	2.1746	-0.75	-1.58	-0.89	-1.30	-0.13	-0.19	-0.15	-0.09
4/1/2015	4/29/2015	7.86	-2.73	-5.70	-3.22	-4.71	-0.47	-0.67	-0.55	-0.34
4/29/2015	5/27/2015	3.1047	-1.08	-2.25	-1.27	-1.86	-0.12	-0.18	-0.16	-0.17
5/27/2015	6/26/2015	5.0566	-1.75	-3.67	-2.07	-3.03	-0.20	-0.29	-0.26	-0.28
6/26/2015	7/29/2015	5.7509	-1.99	-4.17	-2.36	-3.45	-0.23	-0.33	-0.30	-0.32
7/29/2015	8/12/2015	12.5105	-4.34	-9.07	-5.13	-7.50	-0.69	-0.71	-0.84	-0.73
8/12/2015	8/26/2015	10.349	-3.59	-7.51	-4.24	-6.20	-0.57	-0.59	-0.69	-0.61
8/26/2015	9/30/2015	5.0173	-1.74	-3.64	-2.06	-3.01	-0.28	-0.28	-0.34	-0.29
9/30/2015	11/18/2015	2.4104	-0.84	-1.75	-0.99	-1.44	-0.19	-0.14	-0.16	-0.10

(b)

NO2 Deposition kg/ha/yr									
Sample period		Deposition velocities presented in previous studies and QCL calculated deposition velocities							
Date in	Date out	NO2 Ambient concentration (ug/m-3)	Zhang *et al.*, 2003 thorn shrubs, dry (0.8 cm/s)	Zhang *et al.*, 2003 thorn shrubs, wet (0.8 cm/s)	Zhang *et al.*, 2003 short grass and forbs, dry (0.8 cm/s)	Zhang *et al.*, 2003 short grass and forbs, wet (0.8cm/s)	Mphepya, 2002 Elandsfontein (Summer 0.165, Winter 0.045, Autumn 0.1025 and Spring 0.08 cm/s)	Martins, 2009 Amersfoort (Summer 0.16, Winter 0.11 cm/s)	QCL calculated value Potchefstroom (Summer - 0.638, Winter - 0.098, Autumn - 0.221 and Spring - 0.329 cm/s)
12/30/2014	1/28/2015	7.3491	-1.85	-1.85	-1.85	-1.85	-0.38	-0.37	1.48
1/28/2015	2/23/2015	12.71355	-3.21	-3.21	-3.21	-3.21	-0.66	-0.64	2.56
2/23/2015	4/1/2015	2.5938	-0.65	-0.65	-0.65	-0.65	-0.08	-0.13	0.18
4/1/2015	4/29/2015	11.06295	-2.79	-2.79	-2.79	-2.79	-0.36	-0.56	0.77
4/29/2015	5/27/2015	5.5413	-1.40	-1.40	-1.40	-1.40	-0.08	-0.19	0.39
5/27/2015	6/26/2015	3.87105	-0.98	-0.98	-0.98	-0.98	-0.05	-0.13	0.12
6/26/2015	7/29/2015	5.01075	-1.26	-1.26	-1.26	-1.26	-0.07	-0.17	0.15
7/29/2015	8/12/2015	15.62175	-3.94	-3.94	-3.94	-3.94	-0.39	-0.54	0.48
8/12/2015	8/26/2015	5.9736	-1.51	-1.51	-1.51	-1.51	-0.15	-0.21	0.62
8/26/2015	9/30/2015	7.17225	-1.81	-1.81	-1.81	-1.81	-0.18	-0.25	0.74
9/30/2015	11/18/2015	2.6724	-0.67	-0.67	-0.67	-0.67	-0.14	-0.09	0.28

Chapter 5

Conclusion and future perspective

In this chapter, major findings and successes of the project are summarised and evaluated (Par 5.1). Thereafter, the shortcomings encountered for each objective of this investigation are considered (Par 5.2) and recommendations are made for future research (Par 5.3).

5.1 Project evaluation

In conclusion, it should be mentioned that the present study provided micrometeorological measurements of SO_2- and NO_2 fluxes at a grassland-savanna-agricultural region for the first time within South Africa. Therefore, this study makes an important contribution to deposition studies for a region where deposition velocities were predominantly determined with inferential models for similar land use categories. This project also reduces the relatively significant uncertainties associated with SO_2- and NO_2 deposition velocities in South Africa, a region in which atmospheric SO_2 and NO_2 is considered important due to the large number anthropogenic sources of these species; this significance is augmented by the fact that de-SO_x and de-NO_x technologies are not applied within these regions. The project was evaluated in view of the successes and shortcomings in accordance with the objectives of the study listed in Chapter 1.

- ***Active micrometeorological measurement of SO_2- and NO_2 fluxes with a fast-response QCL instrument for one year at Welgegund***

  Data was successfully collected for a one-year period, i.e. from 1.2.2015 to 31.1.2016 at the Welgegund atmospheric monitoring site. The data coverages were 50.8% (ranging between monthly collection percentages of 34 – 81%) and 52.8% (ranging between monthly collection percentages of 27 – 88%) for SO_2 and NO_2 flux measurements, respectively for the entire sampling period, which was considered to be representative datasets. Data coverage percentages also compared relatively well to similar micrometeorological flux measurement studies conducted at other regions. Most of the gaps in the flux datasets was attributed to the regular occurrences of power outages at the measurement site. The site was visited regularly, while weekly checks at the monitoring site enabled optimal instrument operation and accurate data collection. In addition to the SO_2 and NO_2 flux measurements, general meteorological parameters e.g. temperature, soil temperature and precipitation were also measured.

- ***Processing high resolution QCL data for the entire sampling period with programmable mathematical software to determine SO_2- and NO_2 fluxes***

  The high resolution data was "cleaned" (i.e., filtered for errors) and converted into 30 minute averaged data, by utilising programmable mathematical software. Scripts were co-written by researchers at the North-West University and the University of Helsinki. During the data processing, automatic and manual calibration corrections were performed, while data coverage associated with uncertainties in regard to data quality (e.g. during power outages and maintenance) was removed from the dataset. The SO_2 and NO_2 fluxes were also calculated with programmable mathematical software from the fast-response SO_2 and NO_2 concentrations measured and the micrometeorological measurements.

  The median (mean) SO_2 fluxes, i.e.-0.01 $\mu g.m^{-2}.s^{-1}$ (-0.01 $\mu g.m^{-2}.s^{-1}$) indicated a net downward flux for atmospheric SO_2, which indicate that Welgegund can be considered a sink of atmospheric SO_2, while the median (mean) NO_2 fluxes, i.e. 0.005 $\mu g.m^{-2}.s^{-1}$ (0.01 $\mu g.m^{-2}.s^{-1}$) reveals a net upward flux for atmospheric NO_2 with Welgegund considered to be a net NO_2 emitter.

- ***Calculating SO_2 and NO_2 deposition velocities from active flux measurements***

  SO_2 and NO_2 deposition velocities could be calculated from the measured SO_2 and NO_2 flux and -concentration measurements with the equation Vd = -flux/concentration. Since negative flux values are associated with downward fluxes and positive flux values with upward fluxes, positive deposition velocities denoted deposition and negative deposition velocities upward fluxes. The median (mean) deposition velocity calculated for SO_2 the sampling period was 0.16 cm. s^{-1} (0.16 cm. s^{-1}) and - 0.16 cm. s^{-1} (-0.33 cm. s^{-1}) for NO_2.

- ***Determine temporal patterns for SO_2- and NO_2 fluxes and deposition velocities***

The data collected with the QCL for SO_2 and NO_2 could be used to establish temporal patterns. No distinct seasonal pattern was observed for SO_2 fluxes and –deposition velocities with monthly variations also signifying that Welgegund is a SO_2 sink. The colder and dryer months, however, did reveal relatively narrower ranges of the box-and-whisker plots for the SO_2 fluxes and –deposition velocities compared to the wet and warmer months, which could be attributed to increased SO_2 deposition associated with the wetness of the canopy, as well as increased in biomass, photosynthetic activity and turbulence. Diurnal SO_2 flux patterns indicated a marginal increase between 06:00 and 18:00 in summer and 07:00 and 18:00 in winter with the mean daytime dry deposition flux being higher than mean night-time dry deposition flux. Slightly higher SO_2 fluxes during daytime could be attributed to increased SO_2 concentrations during daytime since no diurnal pattern was observed for SO_2 deposition velocities.

Distinct seasonal patterns were observed for NO_2 fluxes and deposition velocities, while monthly variations also revealed that Welgegund was a net source of NO_2. The highest NO_2 fluxes and most negative deposition velocities were associated with the warm and wet months, which could be attributed to increased temperature, soil temperature, precipitation and biogenic activity. Separation of the net fluxes into upward and downward fluxes indicated that both fluxes exhibited seasonal variability, which could be attributed to seasonal patterns of NO emissions from soil and NO_2 deposition. It was also discovered that fertilisation of the agricultural soil in the region was a potentially significant source of NO soil emissions. In addition, no seasonal pattern was observed for NO_2 concentrations at Welgegund, which also indicated that NO_2 flux patterns are mostly related to factors influencing NO_2 deposition velocities. During summer, net daytime NO_2 fluxes increased significantly with the corresponding deposition velocities having more negative values, while no distinct diurnal pattern was observed for net NO_2 fluxes and deposition velocities during the other season. Higher daytime NO_2 fluxes could mainly be attributed to increased daytime temperature and soil temperature.

- ***Relate calculated deposition velocities to modelled deposition velocities in South Africa***

  The SO_2 and NO_2 fluxes and –deposition velocities determined via micrometeorological measurements in this study were compared to fluxes and –deposition velocities calculated from inferential models in the limited studies available for South Africa (Zunckel *et al*., 1999a, Zunckel *et al*., 1999b, Mpepya, 2002, Phala, 2015). SO_2 fluxes and -deposition velocities determined in this study were in the same order of magnitude compared to SO_2 fluxes and deposition velocities calculated with these inferential models. However, inferential models indicated distinct seasonal patterns not observed from micrometeorological measurements. In addition, inferential models also indicated higher daytime to night-time ratios compared to ratios observed in this study. The comparison of NO_2 fluxes and –deposition velocities between two studies in South Africa in which an inferential model (Mpepya, 2002, Phala, 2015) was used to calculate NO_2 fluxes and –deposition velocities, indicated that inferential models do not account for upward fluxes as indicated by the net downward fluxes calculated with these models. Therefore, NO_2 deposition fluxes calculated from modelled deposition velocities overestimate N deposition for these regions, since N upward fluxes are not considered.

5.2 Shortcomings:

The major limitations in this study can be attributed to instrument operation, which is the result of limited expertise and knowledge of the instrument. As indicated, this was the first time micrometeorological measurements were conducted with this instrument in South Africa and accordingly operational problems were to be expected. In addition, instrument calibration and laser alignment was also initially a problem, which was partially improved during the sampling period. The occurrence of power outages in conjunction with the laser alignment which required manual intervention after these power outages also contributed to limitations and this could not be controlled. During the sampling period, large scale load shedding was scheduled and initiated by the South African Government (Du Preez, 2015). These operational problems and power outages contributed to the data coverage for certain months being relatively low.

Another shortcoming in this project was that there were no micrometeorological measurements available for SO_2 and NO_2 fluxes in South Africa. In addition, limited SO_2 and NO_2 fluxes and –deposition velocities calculated with inferential models were also available, especially for NO_2 fluxes, which can be considered understudied in this region. In addition, no SO_2 and NO_2 flux and deposition velocity data calculated with inferential models was available for the Welgegund station, or the region in proximity of Welgegund.

5.3 Future perspective

The following recommendations are suggested for future studies:

- It is recommended that similar meteorological measurements are continued in South Africa. Measurement must not only continue at the Welgegund station, but also in other regions with different vegetation types and land uses. It will be especially important to determine SO_2 and NO_2 fluxes in the highly industrialised Mpumalanga Highveld region where nine coal-fired power stations, a large petrochemical plant, pyrometallurgical industries and other industries and mines are located. Satellite measurements have also indicate this region as an NO_2 hotspot (Lourens *et al*., 2011). Although, numerous atmospheric studies have been conducted in this region, SO_2 and NO_2 fluxes and deposition velocities have not been accurately quantified (Josipovic *et al*., 2011, Colette *et al*., 2010).

- Inferential modelling of SO_2 and NO_2 fluxes must also be conducted at Welgegund, in order to directly compare with micrometeorogical measurements. Many of the required meteorological measurements required as input data are measured at Welgegund, while satellite data could also be obtained for parameters not measured at Welgegund. Fowler *et al.* (2009) also indicated that there is limited data available for verification of models, while large differences exist between modelled and measured NO_2 fluxes

- It is also recommended that, in view of the influence of power outages on data coverage, that a more stable power supply is ensured at Welgegund by installing an electricity generator, for example.
- Capacity building and knowledge transfer through the training of technicians/scientists in South Africa to operate these types of sophisticated instrumentation is also important to increase not only improved data coverage, but also better spatial resolution.

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