Long-term measurements of concentration and dry deposition of atmospheric inorganic gaseous species at Cape Point, South Africa

J Swartz
20564759

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Supervisor: Dr PG van Zyl
Co-supervisor: Dr JP Beukes
Assistant Supervisor: Dr C Galy-Lacaux

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Abstract

Atmospheric aerosols and trace gases are emitted into the atmosphere by various anthropogenic and natural sources, which are removed through chemical transformation, as well as wet- and dry deposition. These atmospheric species not only affect the radiative budget and climate of the earth, but also influence the natural cycle and availability of chemical compounds that serve as essential nutrients in various ecosystems. Air pollutants can cause adverse effects on human- and animal health. The aim of this study was to assess long-term measurements of inorganic gaseous species conducted at the Cape Point Global Atmosphere Watch station (CPT GAW) from 1995 to 2013 in order to establish inter-annual and seasonal trends, as well as dry deposition of these species.

The CPT GAW station is located in a nature reserve approximately 60 km south of Cape Town in South Africa, which is locally and globally considered as an important atmospheric monitoring site due to its position at the south-western tip of Africa. The CPT GAW site is predominantly affected by clean background maritime air masses that are indicative of the Southern Hemisphere. In addition, it is also affected by local sources of atmospheric pollutants, which include the greater Cape Town conurbation and other industrial activities in this region. The primary measurements conducted at the CPT GAW involve the monitoring of greenhouse gases. Other continuous measurements include total gaseous mercury, $^{222}\text{Rn}$, solar radiation, precipitation chemistry and meteorological parameters. In addition, passive diffusive sampling of inorganic species is also performed at the CPT GAW. Passive sampling and precipitation collection are performed within the IGAC (International and Global Atmospheric Chemistry) endorsed DEBITS (Deposition of Biogeochemically Important Trace Species) program, of which the African part, IDAF (IGAC/DEBITS/AFRICA), was initiated in 1994.

Sulphur dioxide ($\text{SO}_2$), nitrogen dioxide ($\text{NO}_2$), ammonia ($\text{NH}_3$) and ozone ($\text{O}_3$) were measured at CPT GAW with passive diffusive samplers from 1995 to 2013 resulting in a 19-year data record for these species, while $\text{HNO}_3$ measurements commenced in 2003 resulting in an 11-year data record. For these measurements, duplicate sets of passive samplers were exposed for a period of one month, replaced, sealed and sent to the Atmospheric Chemical Research Group (ACRG) of the North-West
University’s Potchefstroom Campus (NWUPC) for analysis. These samplers were analysed using ion chromatography (IC) and ultraviolet-visible (uv/vis) spectroscopy. Mathematical software was used to calculate overlay back trajectories of air mass movement prior to arrival at the station using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration’s (NOAA) Air Resource Laboratory (ARL). Angular histograms of wind direction frequency were also compiled.

No long-term trends were observed for O\(_3\), NH\(_3\) and HNO\(_3\), which indicated small cyclic fluctuations. SO\(_2\) and NO\(_2\) did indicate distinct decreases up until 2002, after which an increase in annual average concentrations was observed. These increases were attributed to economic growth and the increasing population in South Africa. Distinct seasonal patterns were observed for SO\(_2\), NO\(_2\) and O\(_3\). NO\(_2\) peaked from April to August, while O\(_3\) revealed elevated levels from July to October. SO\(_2\) had higher concentration during two periods of the year, i.e. January to February and July to August. The SO\(_2\), NO\(_2\) and O\(_3\) peaks observed during the winter months (June-August) were partially attributed to an increase in the long-range transport of pollutant species that was indicated by an increase of air mass movement from the industrialised interior of South Africa arriving at the CPT GAW. Meteorological data also indicated greater effects of air masses passing over the Cape Town conurbation. Fire event frequencies indicated that increased burning during January and February could contribute to elevated SO\(_2\) concentrations measured during these two months. An increase in NO\(_2\) concentrations during the wet season was also attributed to increased microbial activity occurring with the onset of the wet season.

Gaseous deposition calculated with deposition velocities obtained in literature indicated that sulphur (S) deposition (SO\(_2\)) ranged between 0.6±0.5 and 1.4±1.2 kgS.ha\(^{-1}\).yr\(^{-1}\), while total nitrogen (N) dry deposition (NO\(_2\) + NH\(_3\) + HNO\(_3\)) was estimated to range between 3.1±1.0 and 4.0±1.3 kgN.ha\(^{-1}\).yr\(^{-1}\). O\(_3\) deposition was calculated to range between 11.7±2.2 and 57.1±10.6 kg.ha\(^{-1}\).yr\(^{-1}\). Estimated S dry deposition at CPT compared well with the other IDAF sites, with the exception of the industrially impacted Amersfoort, where S deposition was two times higher. NO\(_2\) and HNO\(_3\) dry N depositions were within the same range at all the IDAF sites. Relatively
large differences were observed for N deposition associated with NH$_3$. NH$_3$ fluxes at the CPT GAW were higher compared to other southern African sites, but lower compared to NH$_3$ deposition at sites in forests in central Africa. NH$_3$ had the highest contribution to total N deposition fluxes measured at the CPT GAW.

**Keywords:** Atmospheric trace gas concentrations, DEBITS, Cape Point, gaseous dry deposition
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<tbody>
<tr>
<td>ACRG</td>
<td>Atmospheric Chemical Research Group</td>
</tr>
<tr>
<td>AR</td>
<td>Analytical Grade</td>
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<tr>
<td>ARL</td>
<td>Air Resource Laboratory</td>
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<tr>
<td>CCN</td>
<td>Cloud Condensation Nuclei</td>
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<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CNRS</td>
<td>Centre National de la Recherche Scientifique</td>
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<tr>
<td>CPT</td>
<td>Cape Point</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organisation</td>
</tr>
<tr>
<td>DEBITS</td>
<td>Deposition of Biogeochemically Important Trace Species</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethylsulphide</td>
</tr>
<tr>
<td>EOS</td>
<td>Earth Observation System</td>
</tr>
<tr>
<td>GAW</td>
<td>Global Atmosphere Watch</td>
</tr>
<tr>
<td>GDAS</td>
<td>Global Data Assimilation System</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single-Particle Lagrangian Integrated Trajectory</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatograph</td>
</tr>
<tr>
<td>IDAF</td>
<td>IGAC/DEBITS/Africa</td>
</tr>
<tr>
<td>IGAC</td>
<td>International and Global Atmospheric Chemistry</td>
</tr>
<tr>
<td>INSU</td>
<td>Institut National des Scientifique</td>
</tr>
<tr>
<td>IQR</td>
<td>Inter-quartile Range</td>
</tr>
<tr>
<td>IVL</td>
<td>Swedish Environment Research Institute</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>LIS</td>
<td>Laboratory Inter-comparison Study</td>
</tr>
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<td>LUC</td>
<td>Land Use Category</td>
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<td>MODIS</td>
<td>Moderate Resolution Imaging Spectrometer</td>
</tr>
<tr>
<td>MSA</td>
<td>Methanesulphonic Acid</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NCEP</td>
<td>National Centre for Environmental Prediction</td>
</tr>
<tr>
<td>NDIR</td>
<td>Non-dispersive Infrared</td>
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<td>NEDA</td>
<td>N-1-Naphthylethylenediamine</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td>NWU-PC</td>
<td>North-West University Potchefstroom</td>
</tr>
<tr>
<td>ORE</td>
<td>Environmental Research Observatory</td>
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<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RF</td>
<td>Radiative Forcing</td>
</tr>
<tr>
<td>SAWS</td>
<td>South African Weather Service</td>
</tr>
<tr>
<td>USNWS</td>
<td>United States National Weather Service</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organisation</td>
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Chapter 1

Introduction

In this chapter, a brief introduction to the study will be provided, while the general and specific objectives of the study will also be discussed.

1.1 Background

The atmosphere consists of various layers characterised by their chemical content, as well as different temperature and pressure profiles. It is, however, the lower atmosphere consisting of the troposphere and stratosphere that is of particular concern when studying atmospheric pollution, as this is where various life essential biological and chemical processes take place. It is estimated that up to 90% of the total atmospheric mass is found in the troposphere, which consists of less than 1% trace gases (Brasseur et al., 1999; Harrison, 1999; Connell, 2005).

The emission of atmospheric pollutants into the planetary boundary layer is considered to be the most common route for trace gases to be introduced into the atmosphere (Seinfeld & Pandis, 2006). Anthropogenic emission sources include fossil fuel combustion, pyrometallurgical processes and mining activities, while natural sources include lightning, volcanic action and microbial activity (Hao & Liu, 1994; Ayers et al., 1997; Fields, 2004; Mphepya et al., 2004; Connell, 2005; Seinfeld & Pandis, 2006; Monroe et al., 2007; Adon et al., 2010; Zbieranowski & Aherne, 2012; Abiodun et al., 2014).

The main mechanisms by which atmospheric aerosols and trace gases are removed from the atmosphere include dry- and wet deposition, as well as chemical transformation (Josipovic et al., 2011). Wet deposition is governed by washout and rainout processes that affect the evolution of clouds, while removing trace species and particulate matter from the atmosphere below the cloud base (Kajino & Aikawa, 2015). The dry deposition of gases is governed by the level of atmospheric turbulence, the characteristics of the deposition surface and the chemical properties (solubility and reactivity) of the depositing gas (Seinfeld & Pandis, 2006). Deposition
models are typically used to determine the dry deposition of gaseous species. The big leaf model, for instance, is a commonly employed model to calculate gaseous dry deposition velocities that are unique for each land use category (LUC) (Zhang et al., 2003).

South Africa is one of the largest industrial economies in Africa (Sivertsen et al., 1995; Rorich & Galpin, 1998). Research on atmospheric pollution in South Africa has been performed at various research stations in an attempt to efficiently monitor aerosol and trace gas emissions, as well as general air quality in South Africa. Most of these studies examined temporal concentration trends in close proximity to, or within large sources regions such as the Mpumalanga Highveld region. However, there are very few sites measuring long-term deposition in South Africa. There are four sites situated in the interior of South Africa that are operated within the framework of the African network of the IGAC (International and Global Atmospheric Chemistry)-endorsed Deposition of Biogeochemical Important Trace Species (DEBITS) programme, i.e. IDAF (IGAC/DEBITS/Africa) network, while one marine monitoring station is situated at Cape Point (CPT GAW) (Martins et al., 2007; Adon et al., 2010). The CPT GAW also forms part of the World Meteorological Organisation’s Global Atmosphere Watch network (WMO GAW) (Brunke et al., 2004). The objectives of IDAF are to determine the chemical composition of the atmosphere in the tropical belt of Africa, as well as to measure the atmospheric wet and dry deposition of chemical species in the atmosphere (Lacaux et al., 2003).

1.2 Problem statement

The CPT GAW station is located approximately 60 km south of one of the most popular tourist destinations in South Africa, i.e. Cape Town (Brunke et al., 2004; Brunke et al., 2010; Abiodun et al., 2014). The site is specifically a baseline station that predominantly measures clean maritime air as a result of the dominant north westerly wind (Baker et al., 2002). The maritime air masses measured at the CPT GAW are considered to be representative of the Southern Hemispheric background atmosphere (Brunke et al., 2004).
The site is equipped with a large number of instrumentation that conducts a large number of atmospheric measurements. The primary measurements conducted at the CPT GAW are the monitoring of greenhouse gases, i.e. CO, CO$_2$, CH$_4$ and N$_2$O. Other continuous measurements include total gaseous mercury, $^{222}$Rn, solar radiation, precipitation chemistry and meteorological parameters. Passive sampling that measures monthly average gaseous concentrations of atmospheric SO$_2$, NO$_2$, O$_3$, NH$_3$ and HNO$_3$ is also performed (Brunke et al., 2001; Baker et al., 2002; Brunke et al., 2004; Martins et al., 2007; Brunke et al., 2010; Brunke et al., 2012).

Temporal patterns of the atmospheric concentrations and deposition of SO$_2$, NO$_2$, O$_3$, NH$_3$ and HNO$_3$ at CPT GAW, as well as the establishment of the source of these species are not well documented in peer-reviewed literature (Martins et al., 2007). It is important to study long-term temporal trends in the concentrations and deposition of these species, since these species can be precursors to other atmospheric species, as well as being detrimental to various ecological and biological systems (Connell, 2005; Pöschl, 2005). By studying the spatial and temporal evolution of the chemical composition of the atmosphere, as well as the atmospheric dry deposition of chemical species, the extent of anthropogenic and natural influences on the atmosphere can be evaluated and monitored (Martins et al., 2007).

### 1.3 Objectives

The general aim of this study was to assess the long-term annual and seasonal trends of atmospheric inorganic gases and the dry deposition of these species, as well as to determine the possible sources of these species.

The specific objectives of this study were as follows:

- Long-term sampling of SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ with passive samplers at the CPT GAW station. Passive sampling commenced in 1995 at the CPT GAW station with passive samplers being prepared and analysed by the Atmospheric Chemistry Research Group at the North-West University, while being deployed and collected by the personnel of South African Weather Service operating the CPT GAW station.
➤ Analysis of passive samplers collected after 2005 with appropriate analytical techniques that comply with international analytical guidelines, and processing the analytical results to determine the atmospheric concentrations of inorganic gaseous species.

➤ Assess seasonal and inter-annual variability of atmospheric concentrations of inorganic gaseous compounds at the CPT GAW station.

➤ Determine possible sources of atmospheric inorganic species at the CPT GAW station by exploring air mass movement, meteorology and fire event frequencies.

➤ Determine the dry deposition of atmospheric inorganic gaseous compounds.
Chapter 2

Literature survey

In this chapter, a comprehensive literature study is presented. The composition and relevant properties of the atmosphere are discussed. The origin, evolution, transport and deposition of atmospheric pollutants, with specific focus on inorganic gaseous species, are also discussed, as well as their associated impacts on the environment and human health. The importance of long-term monitoring within the Deposition of Biogeochemical Important Trace Species (DEBITS) is also discussed. Lastly, a synopsis of meteorological and geographical aspects of the Western Cape, where atmospheric sampling was conducted, is presented.

2.1 Atmospheric composition

The atmosphere can generally be divided into two layers, i.e. the upper and lower atmosphere. The lower atmosphere refers to the part of the atmosphere containing the troposphere and extending to the top of the stratosphere, approximately 50 km above the surface of the earth. The upper atmosphere stretches from the mesosphere, includes the thermosphere and extends to the outermost region of the atmosphere, the exosphere, more than 500 km in altitude (Connell, 2005; Seinfeld & Pandis, 2006). The different layers of the atmosphere are characterised by temperature variations at different altitudes and differences in chemical composition (Harrison, 1999).

The troposphere consists of approximately 78% molecular nitrogen (N₂), 21% oxygen (O₂), 1% argon (Ar) and less than 1% trace gases and contains 85 to 90% of the total atmospheric mass. Extending to an altitude of approximately 12 km at the mid-latitudes, it is in the troposphere where, among various other processes, the biological processes of photosynthesis and respiration take place (Brasseur et al., 1999; Connell, 2005). Photosynthesis is an energy conversion process whereby the energy in solar radiation is converted into chemical energy by plants and stored in the form of carbohydrates. Carbohydrates are the building blocks of plants and...
therefore the basic input of energy for biological life. The reverse process is referred to as respiration (Connell, 2005). The troposphere essentially contains all of the water (H\textsubscript{2}O) vapour in the atmosphere, which is a region of constant air mass mixing and turbulence. This leads to weather patterns, frontal systems and other weather-related phenomena experienced (Harrison, 1999; Seinfeld & Pandis, 2006). The negative temperature gradient in the troposphere is such that the rate of temperature loss experienced by an air parcel rising to the tropopause (layer between the troposphere and stratosphere) is approximately 9.7 K.km\textsuperscript{-1}, where it would reach an approximate average temperature of 217 K (Seinfeld & Pandis, 2006). The tropopause is defined by the WMO as the layer where the lowest rate of temperature decrease occurs, which reduces to 2 K.km\textsuperscript{-1} or less, and does not exceed 2 K.km\textsuperscript{-1} for the next 2 km (Holton \textit{et al.}, 1995).

In contrast to the troposphere, the stratosphere exhibits a positive temperature gradient. At mid-latitudes, an isothermal region is encountered, generally between 11 and 20 km in altitude, while a gradual temperature increase is observed in the region stretching from 20 km to the stratopause where the approximate temperature is usually at 271 K. This temperature increase as a function of altitude serves to inhibit vertical mixing (Seinfeld & Pandis, 2006). The chemical composition of the stratosphere includes N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O and atomic oxygen (O), as well as importantly containing approximately 90% of the total atmospheric ozone (O\textsubscript{3}). Although O\textsubscript{3} is a particularly reactive and unstable chemical species, it survives due to the low stratospheric air pressure. The low pressure results in larger distances between molecules, leading to less-frequent intermolecular collisions. This leads to the formation of an O\textsubscript{3} layer at an approximate altitude between 20 and 30 km, which serves to absorb nearly all the ultraviolet (uv) solar radiation between the wavelengths 240 and 290 nm, thereby shielding plants, animals and humans from harmful radiation. Furthermore, it also serves to absorb biologically active UV-B radiation (290-320 nm). Increased levels of this type of radiation lead to a higher risk of susceptible individuals to contract skin cancer (Connell, 2005; Seinfeld & Pandis, 2006).

The upper atmosphere contains highly reactive chemical species such as O\textsubscript{2}+, NO\textsuperscript{+} and O\textsuperscript{+} that do not exist on the surface of the earth for any significant amount of
time. These highly reactive ions also absorb short wavelength radiation, in much the same manner as the $O_3$ layer in the stratosphere. The absorbed short wavelength solar radiation is of high energy and would damage the biological systems of the earth (Connell, 2005).

In a sense, the earth acts as a black body in that the same amount of energy is reemitted as is initially absorbed. While atmospheric gases do not directly influence the amount of incident solar radiation, the amount of reemitted energy is altered through processes such as scattering and absorption. Most of the reemitted radiation falls in the infra-red region, where $H_2O$ and carbon dioxide ($CO_2$) have major absorption bands (Connell, 2005).

### 2.2 Atmospheric pollution

A definition of air pollution is given by Weber (1982): It is defined as the presence of substances in the ambient atmosphere resulting from anthropogenic or natural activity that lead to adverse effects to humans and the environment. The most common route by which gaseous pollutants are introduced into the atmosphere is through their emission into the planetary boundary layer, from where these emissions may be dispersed or readily diluted (Seinfeld & Pandis, 2006). This boundary layer typically extends to the first 1 km of the troposphere. The boundary layer along with the free troposphere and the stratosphere is most affected by air pollution, influencing air quality and affecting climate change (Harrison, 1999; Seinfeld & Pandis, 2006).

Acidic atmospheric compounds, such as nitric and sulphuric acid ($HNO_3$ and $H_2SO_4$ respectively), hold various risks to environmental and human health and are very closely related to air pollution (Atkins et al., 2006). While acid and base species exist in solid, gaseous and liquid phases, hydrogen ions and acidity only exist in aqueous solution. However, because of the gas-liquid equilibrium of acids and bases in a multi-phase system such as the atmosphere, this definition is not well suited as it is limited only to free hydrogen ions ($H^+$) (Möller, 1999). An alternative definition can read as follows: Atmospheric acidity is the acidity in the respective
phases (aqueous, aerosol and gaseous phases) that represent the sum of individual compounds that were measured (Waldman et al., 1992).

Atmospheric pollutants are emitted by natural processes and anthropogenic activities. Typical natural sources include volcanoes, microbial activities, crustal erosion, pollen and oceans. Anthropogenic emissions of atmospheric pollutants are usually related to the combustion of fossil fuels (e.g. coal-fired power stations, petrochemical industries and vehicular emissions), pyrometallurgical processes, mining activities and household combustion for space heating and cooking (Hao & Liu, 1994; Scholes et al., 1996; Ayers et al., 1997; Fields, 2004; Mphepya et al., 2004; Connell, 2005; Seinfeld & Pandis, 2006; Monroe et al., 2007; Adon et al., 2010; Zbieranowski & Aherne, 2012; Abiodun et al., 2014).

The impacts of atmospheric pollutants are usually associated with climate change and/or air quality. Increased levels of these species can either have a net warming or cooling effect on the climate of the earth. Greenhouse gases, for instance, absorb outgoing infrared radiation that causes and increase in temperature. Climate change is globally regarded as one of the most important occurrences, since it will have large-scale political, social and economic impacts. Furthermore, air pollutants can cause serious human health problems, depending on the concentration and duration of exposure to these species. Pollutants can have an influence on respiratory systems or it can enter the blood stream causing other health problems. Ecotoxicological research also indicates that the impact of air pollution on the ecosystems ranges from changes in the population of terrestrial and aquatic ecosystems to the extinction of vulnerable species (Scholes et al., 1996).

### 2.2.1 Types of atmospheric pollution

Atmospheric pollutants are generally categorised as two types of species, i.e. particulate matter (PM) (aerosols) and gaseous pollutants, although they are closely connected with each other via physical, chemical and meteorological atmospheric processes (Martins et al., 2007; Josipovic et al., 2010; Petäjä et al., 2013).
Aerosols

Aerosols generally have a cooling effect (a negative radiative forcing (RF)) on the atmosphere and contribute to climate change by two means (Martins, 2009), i.e. the direct and indirect effect. The direct effect entails absorption and scattering of thermal and solar radiation by aerosol particles in the atmosphere. The scattering and reflection of incoming solar radiation influence the balance between incoming and outgoing energy in the earth’s atmosphere, also referred to as the earth’s radiative budget. The indirect effect refers to the change in the microphysical and optical properties of cloud condensation nuclei (CCN) (Takemura, 2005). Cloud droplet and ice particle formation in the earth’s atmosphere requires the presence of some nucleation point and aerosols serve as such CCN. The formation of cloud droplets in the absence of CCN would require the initial formation of droplet embryos on very small sizes and therefore a very small radius of curvature (Andreae & Rosenfeld, 2008).

The contribution of the indirect effect of aerosols to climate change is two-fold. Firstly, as the number of atmospheric aerosol particles increases, the effective radius of the droplets decreases, resulting in higher cloud albedo. Albedo refers to the fraction of incoming solar radiation that is reflected back into space. The fraction not reflected is absorbed by the atmosphere and by the earth’s surface (Twomey, 1974). Secondly, because of the decrease in effective radius of the droplet size, precipitation decreases. Significant differences have been found in the effective radius of droplets in precipitating and non-precipitating clouds. For non-precipitating clouds, the largest radius was limited to between 15 and 20 µm, whereas it was limited to 30 µm for clouds in which precipitation does form. The rapid growth of cloud droplets into rain droplets is likely the cause of these differences, and indications are that cloud droplet threshold sizes exist and are consistent on a global scale (Kobayashi, 2007).

Gaseous

Despite their low abundances in the atmosphere, trace gases play a crucial role in the radiative budget of the earth as well as atmospheric chemistry (Seinfeld & Pandis, 2006). A large number of inorganic and organic trace gases is
predominantly emitted into the troposphere from the surface of the earth, and is subjected to various physical and chemical transformations. In recent history, it has become apparent that the atmospheric chemical composition is being altered over a range of scales by increased anthropogenic activity (Monks & Leigh, 2009).

Volatile organic compounds (VOCs) are emitted into the atmosphere through natural and anthropogenic processes (Brasseur et al., 1999). Petrochemical industries, production processes and fossil fuel combustion are among the most important anthropogenic sources of VOCs, while biomass combustion is considered one of the most relevant natural sources in South Africa (Jaars et al., 2014). VOCs consist of a considerable portion of aromatic hydrocarbons, such as benzene and toluene, among others, which leads to increased tropospheric O$_3$ concentrations (Atkinson, 2000).

Halogenated organic compounds (halocarbons) act as greenhouse gases because of their strong reaction with infra-red radiation in the 8 to 13 μm range. Halocarbon concentrations are optically thin in the present-day atmosphere, which allows for reemitted infra-red radiation from the surface and lower tropospheric to reach the upper parts of the troposphere. The radiation is absorbed and again reemitted, but at lower temperatures, resulting in a net warming effect on the atmosphere (McLandress et al., 2014). Halocarbons such chlorofluorocarbons (CFC) are nearly exclusively of anthropogenic origin, adding to atmospheric chlorine concentrations. The emission of various CFCs has been attributed to their wide use as refrigerants, foam blowing agents, propellants, solvents and cleaning agents (Zhang et al., 2010; Santella et al., 2012). Due to their contribution to stratospheric O$_3$ depletion, their production and use are now regulated under the Montreal Protocol adopted in 1987 and its subsequent amendments. This has led to a decline in atmospheric CFC mixing ratios of approximately 98% by the year 2000. Similar to CFCs, sulphur hexafluoride (SF$_6$) atmospheric concentrations are predominantly caused by anthropogenic activity. This species is used in the electric insulation of high voltage switchgear. Although voluntary emission control and reductions have been reported, its production and emission have not been adequately regulated and as a result, SF$_6$ mixing ratios are increasing in the remote atmosphere by a rate of up to 0.3 ppt per year (Santella et al., 2012).
Inorganic trace gases have short residence times in the atmosphere. However, these species play crucial roles in the chemistry of the atmosphere due to their high reactivity. The major inorganic gaseous species include ozone (O$_3$), nitrogen oxide (NO), nitrogen dioxide (NO$_2$), ammonia (NH$_3$), nitric acid (HNO$_3$) and sulphur dioxide (SO$_2$). Trace gases containing nitrogen and sulphur are produced by various natural and anthropogenic sources. Developed countries have been restricting the industrial emission of these gases, and as a result their concentrations are generally on the decrease. However, this is not the case in developing countries, as emission control procedures are not as widely utilised. Nitrogenous gaseous species are also involved in the formation or depletion of O$_3$ and therefore have an influence on the impacts associated with O$_3$. Species such as NO$_2$, NH$_3$, HNO$_3$ and SO$_2$ are short-lived in the atmosphere and as a result significant vertical mixing is not usually observed for these species. Although these species do not have a direct apparent influence on RF on the atmosphere, they do lead to the formation of aerosol particles (Martins, 2009).

Since the main objective of this study was related to atmospheric inorganic gaseous species, these species are further discussed in terms of sources, chemical transformations, sinks and impacts.

### 2.3 Inorganic atmospheric gaseous species

#### 2.3.1 Sources

The major anthropogenic sources of atmospheric SO$_2$ include the combustion of fossil fuels, pyrometallurgical processes and biomass burning (wild fires and household combustion) (Hao & Liu, 1994; Fields, 2004; Josipovic et al., 2011). SO$_2$ mixing ratios for continental background air range from 20ppt to more than 1ppb, while ranging from 20 to 50ppt for the unpolluted marine boundary layer. However, in urban areas, atmospheric SO$_2$ concentrations can be several hundred parts per billion (Seinfeld & Pandis, 2006). SO$_2$ concentrations tend to be higher over populated areas due to domestic and industrial burning of coal and coal-derived fuels, as well as sulphur-containing ore-refinement and smelting. Therefore, SO$_2$
concentrations are directly related to industrial and economic development (McGranahan & Murray, 2003; Connell, 2005). In coal, sulphur constitutes between approximately 1 and 3%, while this ratio is somewhat higher in petroleum products (Connell, 2005). Approximately 90% of the SO$_2$ (1.9 million t/a) and NO$_2$ (0.9 million t/a) species released into the southern African atmosphere originate from coal combustion on the Mpumalanga Highveld (Josipovic et al., 2007). Natural sources of sulphurous gases include the decomposition of plant and animal matter, as well as volcanoes. SO$_2$ and other sulphurous species, such as hydrogen sulphide (H$_2$S), are released in huge quantities, along with nitrogen and other particulate matter during volcanic eruptions (Monroe et al., 2007). Oceanic biological processes introduce gaseous dimethylsulphide (DMS) (CH$_3$SCH$_3$) into the maritime atmosphere where it undergoes various photochemical reactions to eventually form methanesulphonic acid (MSA) (CH$_3$SO$_3$H) and sulphates as major end products, with SO$_2$ and many stable, and unstable intermediates also forming (Ayers et al., 1997).

The combustion of fossil fuels produces nitrogen oxides (NO$_X$), which include NO and NO$_2$. It is estimated that approximately 50% of the total NO$_X$ present in the atmosphere is the result of fossil fuel combustion (Hao & Liu, 1994; Fields, 2004; Josipovic et al., 2011). Anthropogenic NO$_2$ is also produced during the oxidation of reactive nitrogen during the Haber-Bosch process used in fertiliser production (Zbieranowski & Aherne, 2012). NH$_3$ is the most abundant alkaline atmospheric gaseous component and serves to neutralise a significant portion of atmospheric acids formed by the oxidation of SO$_2$ and NO$_X$. NH$_3$ is emitted by various natural and anthropogenic sources. Natural sources include animal and human excreta, fertilisers and cut grass (Sutton et al., 1998; Krupa, 2003). NH$_3$ is a reduced form of nitrogen and therefore owes its origin to many of the same NO$_X$ anthropogenic emission sources, such as fossil fuel combustion (Asman et al., 1998; Zbieranowski & Aherne, 2012). It has been estimated that global NH$_3$ emission may total 50 Mt N yr$^{-1}$ (Asman et al., 1998). Atmospheric HNO$_3$ is only introduced into the atmosphere as a by-product of the chemical reaction between NO$_X$ and HO$^-$-radicals, or by the heterogeneous conversion of nitrous oxide (N$_2$O$_5$), a colourless gas emitted primarily by bacterial action in soils (Brasseur et al., 1999; Fields, 2004; Connell, 2005).
As mentioned in section 2.1, stratospheric O\textsubscript{3} has a very important function in the atmosphere. However, tropospheric O\textsubscript{3} is considered an atmospheric pollutant, since it is considered to be a short-lived greenhouse gas, as well as having detrimental impacts on human health and vegetation. Approximately only 10% of atmospheric O\textsubscript{3} is found in the troposphere (Connell, 2005). O\textsubscript{3} is as secondary pollutant that is produced as a by-product during the reaction of NO\textsubscript{X} with volatile organic compounds (VOC) in the presence of sunlight and heat (Abiodun et al., 2014). This occurs due to VOCs reacting with tropospheric hydroxyl radicals (’OH), which leads to the production of peroxyl (RO\textsubscript{2}•) and hydroperoxy (HO\textsubscript{2}•) radicals. NO is readily oxidised by these radicals, resulting in a prominent sink for O\textsubscript{3} being removed (Atkinson, 2000).

### 2.3.2 Transport, evolution and chemical transformation

Various meteorological events and mechanisms govern the transport of particulate and gaseous species through the atmosphere, resulting in processes such as dilution and coagulation taking place. If favourable atmospheric conditions persist, trace gases can be transported over significant distances, during which time they are subjected to various physical and chemical processes. When SO\textsubscript{2} is emitted into the atmosphere, it may be oxidised to form sulphate (SO\textsubscript{4}\textsuperscript{2−}) through processes occurring in the gas and liquid phases, on solid surfaces, or a combination of these phases (McGranahan & Murray, 2003; Connell, 2005; Martins, 2009; Adon et al., 2010). The chemical transformation of SO\textsubscript{2} depends on this oxidation to form SO\textsubscript{4}\textsuperscript{2−}, which in the presence of moisture, forms sulphuric acid as shown in equation 2.1 (Connell, 2005).

\[
2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4
\]  

(2.1)

Sulphuric acid is readily neutralised by NH\textsubscript{3}, as mentioned previously, and forms (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} or NH\textsubscript{4}HSO\textsubscript{4} as reaction products, depending on the availability of atmospheric NH\textsubscript{3} as shown by reaction equations 2.2 and 2.3 (Seinfeld & Pandis, 2006).

\[
\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4
\]  

(2.2)
Nitrogen is crucial for the earth’s capability to sustain biological life and is predominantly supplied by the atmosphere. The atmospheric nitrogen cycle is illustrated in Figure 2.1.

Figure 2.1: Nitrogen cycle containing the most common atmospheric nitrogenous compounds and atmospheric reactions, as adapted from Seinfeld and Pandis (2006)
The chemically stable N\textsubscript{2} molecule is essentially inert and needs to be converted to a form that enables it to be chemically utilised in biological systems. As mentioned previously, the most important atmospheric nitrogen-containing trace species are NO, NO\textsubscript{2}, N\textsubscript{2}O, HNO\textsubscript{3} and NH\textsubscript{3}.

The process by which N\textsubscript{2} is chemically transformed into other nitrogenous compounds is termed nitrogen fixation (Chameids \textit{et al.}, 1994; Seinfeld & Pandis, 2006). Numerous different natural and anthropogenic fixation processes occur. However, one of the most prominent anthropogenic nitrogen fixation processes is combustion, which leads to the production of NO\textsubscript{X} (Seinfeld & Pandis, 2006). The reactive NO\textsubscript{X} can be transported for hundreds of kilometres and is a major precursor for the formation of photochemical smog and acid rain (Chameids \textit{et al.}, 1994). Although NO\textsubscript{2} and NO are both emitted by combustion, NO\textsubscript{2} is also formed as a secondary species through the oxidation of NO in the atmosphere as shown in \textbf{equation 2.4} (Connell, 2005; Seinfeld & Pandis, 2006).

\begin{equation}
2\text{NO} + \text{O}_2 \rightarrow \text{NO} + \text{NO}_2 \tag{2.4}
\end{equation}

The oxidation of atmospheric NO\textsubscript{X} results in the formation of HNO\textsubscript{3} as shown by \textbf{equations 2.5} to \textbf{2.9}, which is readily deposited owing to its exceptional water solubility (Fields, 2004). The relatively stable nitrogen trioxide radical (NO\textsubscript{3}•) is formed by the oxidation of NO\textsubscript{2} with O\textsubscript{3}, and is easily broken down by incident sunlight. Depending on the radiation frequency either NO\textsubscript{2} or O• is formed as products or both NO• and O\textsubscript{2} are formed.

\begin{equation}
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3^\cdot + \text{O}_2 \tag{2.5}
\end{equation}

\begin{equation}
\text{NO}_3^\cdot \overset{hv}{\rightarrow} \text{NO}^\cdot + \text{O}_2 \text{ or } \text{NO}_2 + \text{O}^\cdot \tag{2.6}
\end{equation}

During the night, in the absence of sunlight, NO\textsubscript{3}• readily reacts with NO and excess NO\textsubscript{2} to form dinitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}), which can lead to the production of nitric acid by reacting with moisture (\textbf{equations 2.7} to \textbf{2.9}) (Connell, 2005).

\begin{equation}
\text{NO}_3^\cdot + \text{NO} \rightarrow 2\text{NO}_2 \tag{2.7}
\end{equation}

\begin{equation}
\text{NO}_3^\cdot + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \tag{2.8}
\end{equation}
\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3
\] (2.9)

\(\text{HNO}_3\) is neutralised by atmospheric \(\text{NH}_3\) (or \(\text{NH}_4^+\)) to form ammonium nitrate (\(\text{NH}_4\text{NO}_3\)) (Seinfeld & Pandis, 2006).

Nitrification is the process by which \(\text{NH}_4^+\) is oxidised to \(\text{NO}_2^-\) and \(\text{NO}_3^-\) as a result of microbial action. By-products produced during this process include \(\text{N}_2\) and \(\text{NO}\), which are released into the atmosphere where they undergo various interactions with other atmospheric species. Denitrification refers to the reduction of \(\text{NO}_3^-\) to species such as \(\text{N}_2\), \(\text{NO}_2\), \(\text{N}_2\text{O}\) or \(\text{NO}\) (Seinfeld & Pandis, 2006).

Tropospheric \(\text{O}_3\) is a short-lived greenhouse gas that is commonly found in smog together with other photochemical oxidants and aerosols (McGranahan & Murray, 2003; Adon et al., 2010; Abiodun et al., 2014). As mentioned, \(\text{O}_3\) is a secondary pollutant that is formed in the atmosphere. The photochemical production of \(\text{O}_3\) is shown in equations 2.10 and 2.11, where \(X\) is usually either \(\text{N}_2\) or \(\text{O}_2\) (Connell, 2005; Seinfeld & Pandis, 2006).

\[
\text{NO}_2 \xrightarrow{\text{hv}} \text{NO}^- + \text{O}^-
\] (2.10)

\[
\text{O}^- + \text{O}_2 + X \rightarrow \text{O}_3 + X
\] (2.11)

The photolysis of \(\text{O}_3\) in the presence of \(\text{H}_2\text{O}\) vapour is considered the primary source of hydroxyl radicals (\(\text{OH}^+\)), which remove trace gases from the atmosphere. The photolytic production of \(\text{OH}^+\) from \(\text{O}_3\) is shown in equations 2.12 and 2.13 (Tang et al., 1998; Connell, 2005).

\[
\text{O}_3 \xrightarrow{\text{hv}} \text{O}_2 + \text{O}
\] (2.12)

\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-
\] (2.13)

The interaction of \(\text{NH}_3\) with atmospheric hydroxyl radicals results in the formation of \(\text{NH}_2^+\). When \(\text{NH}_2^+\) reacts with \(\text{HNO}_3\) in the atmosphere, it is oxidised to \(\text{NO}\). It is because of this constant flux in \(\text{NH}_3\) concentrations that the long-range transport of \(\text{NH}_3\) is considered unlikely (Krupa, 2003).
2.3.3 Removal processes

Removal or sink processes refer to processes by which residence and aging times are influenced. Cloud formation can be considered as an example of a volume sink, while deposition mechanisms are considered to be area sinks. The advection of air masses to other layers in the atmosphere can also be considered to be a sink (Kneip & Lioy, 1980). One of the most important mechanisms by which gaseous species are removed from the atmosphere is through chemical reaction, during which the physical and chemical properties of the atmospheric species change (Josipovic et al., 2011). As shown in previous sections, gases and aerosols in the atmosphere can produce larger, longer-living aerosols through chemical reactions, which can be transported over long distances, including to other layers in the atmosphere.

Atmospheric gaseous species are removed from the atmosphere through deposition mechanisms, which provide essential nutrients to ecosystems (Waldman et al., 1992). Deposition can occur through wet and dry processes. Wet deposition is predominantly governed by two processes (Josipovic et al., 2011; Kajino & Aikawa, 2015), i.e. in-cloud scavenging involving the activation of aerosol CCN in clouds where conditions of super-saturation occur (termed rainout), and aerosol collection by hydrometeors (e.g. raindrops, fog droplets and snowflakes) below the cloud base (termed washout). Acidic and basic atmospheric compounds are water soluble, which are easily dissolved into rain-, fog- and cloud water (Waldman et al., 1992). The analysis of the chemical composition of such precipitation events assists in tracing the temporal and spatial evolution of atmospheric chemical compounds (Mphepya et al., 2006).

In addition to wet deposition and chemical transformation that are important mechanisms of removal of atmospheric trace gases, it is also important to consider the dry deposition of these species (Waldman et al., 1992). The dry deposition of gases is governed by the level of atmospheric turbulence, the nature of the deposition surface and the chemical properties (solubility and reactivity) of the depositing gas. Natural vegetation generally promotes dry deposition (Seinfeld & Pandis, 2006).
2.3.4 Impacts

The measurement that reflects the impacts of factors influencing the earth’s energy budget is termed radiative forcing (RF), which serves as an index of the importance of these factors as potential climate change mechanisms. In Figure 2.2, the estimated RFs for the most important atmospheric species are presented.

**Figure 2.2:** Average radiative forcing (RF) estimates and ranges for the most important atmospheric species (IPCC, 2007)

RF values are expressed in Watts per square meter (W.m\(^{-2}\)), with a positive value indicating a warming effect and a negative value a cooling effect on the atmosphere (IPCC, 2007). Well-known climate heating species include carbon dioxide (CO\(_2\)) and methane gas (CH\(_4\)), for which a high level of scientific understanding exists. These
species are considered to have a global impact on climate change. However, other trace gas species such as NO₂ and O₃ have a considerable regional impact on climate forcing (IPCC, 2007; Adon et al., 2010). Tropospheric O₃, on average, has an RF value of +0.35 W.m⁻² compared to +1.66 W.m⁻² for CO₂ and +0.48 W.m⁻² for CH₄. This means that although CO₂ and CH₄ have more significant global heating effects on the atmosphere, the regional heating associated with O₃ cannot be ignored (IPCC, 2007).

Exposure to high concentrations of NOₓ and SO₂ can have detrimental effects on human health. NO₂ is a very reactive species that is known to increase respiratory infections such as pneumonia and bronchitis, to impair lung growth in children and to weaken immune system functionality. SO₂ and other sulphur oxides are skin and mucosal membrane irritants and can aggravate heart and respiratory diseases such as emphysema (McGranahan & Murray, 2003; USNPS, 2013; USEPA, 2014).

NOₓ is essential for photosynthetic processes, as well as being building blocks for proteins, nucleic acids and other life sustaining substances in natural ecosystems. Plants derive their required nutrients from the atmosphere, precipitation and soils. Specific atmospheric concentrations of these nutrients are essential to sustain life. However, higher concentrations can be just as devastating as deficiencies thereof (Connell, 2005). Biological nitrogen is the limiting factor for the dynamics and productivity of terrestrial, marine, agricultural and forestry ecosystems (Galloway et al., 1995). Biomass production and accumulation are greatly increased by increased nitrogen availability, and consequently, the global carbon cycle is also altered. This results in an increase of atmospheric concentrations of CO₂, as well as a change in the response by ecosystems to such a change (Vitousek & Howarth, 1991; Schimel et al., 1995). The rates of nitrogen uptake and loss by ecosystems change as the biodiversity of affected ecosystems change, which generally decreases with increased nitrogen levels since these eutrophication and leaching processes disrupt the balance in soil and aquatic ecosystems (Tilman, 1987; Berendse et al., 1993; Aber et al., 1995; Fields, 2004; Abiodun et al., 2014). Nitrates (NO₃⁻), formed during the nitrogen cycle as discussed in section 2.3.2, leach into stream and groundwater through soil, removing minerals and acidifying the soil. As a result, downstream
freshwater and coastal ecosystems are affected (Liknes et al., 1996; Nixon et al., 1996).

NH$_3$ deposition also contributes to the nitrogen balance in soils, which together with NO$_x$ can lead to the critical load being exceeded. NH$_3$ readily reacts to form NH$_4^+$ aerosols that are converted to NO$_3^-$ in soil when deposited, while unreacted NH$_3$ can be recaptured by vegetation. However, vegetation in close proximity to the source of NH$_3$ emission can experience foliar damage (Sutton et al., 1998; Krupa, 2003). NH$_3$ serves to neutralise atmospheric acids such as H$_2$SO$_4$, HNO$_3$, HNO$_2$ and hydrochloric acid (HCl) through acid-based chemical reactions to form ammonium salts, which subsequently also remove gaseous NH$_3$ from the atmosphere.

Acidic precipitation can result in the adverse lowering of the pH of aquatic systems and consequently the release of toxic metals adsorbed on bottom sediments (Connell, 2005). The low pH and acid neutralising capability of natural waters coincide with relatively high concentrations of aluminium, SO$_4^{2-}$ and occasionally NO$_3^-$ and NH$_4^+$ (Bobbink et al., 1998). The decrease of the pH of soil and continental water facilitates the increase of the solubility and mobility of heavy metals such as iron (Fe$^{2+}$/Fe$^{3+}$) and manganese (Mn$^{2+}$), which can lead to the damage and death of aquatic life. Alkaline ions essential for plant growth, such as sodium (Na$^+$), potassium (K$^+$), calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$) are removed from soils, effectively inhibiting plant growth. The long-term effects of the acidification of soils include diminished buffer capacity, lower pH, increases of base cation leaching and elevated toxic metal concentrations, such as aluminium (Al). Nitrogen species concentration balances in the soil can also be altered (Breeman et al., 1982; Ulrich, 1983; Ulrich, 1991). Acid rain does not only adversely affect biological organisms and systems, but it can also have adverse economic effects, e.g. on agriculture. Infrastructure and architecture are also damaged (Atkins et al., 2006). Building materials containing limestone and calcium sulphate (CaSO$_4$), such as sandstone, are dissolved when exposed to acid rain (Ophardt, 2003).

Environmental impacts by O$_3$ include crop damage and associated harvest losses. Furthermore, O$_3$ has a detrimental effect on the respiratory system and causes throat and nose irritation that can lead to death (Ojumu, 2013). However, because O$_3$ is a strong oxidant, precautionary antioxidant intake can limit these symptoms.
The long-term effect of elevated O\textsubscript{3} exposure is still under investigation, but studies have shown the risk of chronic lung impairment (McGranahan & Murray, 2003). In addition, O\textsubscript{3} also participates in the production of HNO\textsubscript{3}, which contributes significantly to the acidification of the atmosphere and the photochemical production of other oxidants (Mauzerall & Wang, 2001; Adon et al., 2010). In 2004, HNO\textsubscript{3} contributed approximately 40% to the production of acid rain in North America, while SO\textsubscript{2} contributed approximately 50%. Atmospheric HNO\textsubscript{3} affects corrosion rates of metals such as aluminium (Al), since it is a strong acid (Dean, 1990; Abiodun et al., 2014). It also has an impact on the human respiratory system in much the same way as SO\textsubscript{2} and NO\textsubscript{2} (Abiodun et al., 2014).

2.4 Measurement techniques

2.4.1 Active techniques

Various photolytic processes, e.g. chemiluminescence, fluorescence and absorption, are employed in the continuous active monitoring of atmospheric trace gas species (Saltzman et al., 1993; Dhammapala, 1996; Skoog et al., 2004). Other active techniques include the use of annular denuders and non-dispersive infrared gas analysers (NDIR) (Martins, 2009). These highly sophisticated measurement instrumentation with their associated higher costs and logistical requirements are not always considered to be appropriate in monitoring networks where sites are often remote (Wesely & Hicks, 2000; Martins, 2009). In these types of measurement networks, simpler and cheaper methods, such as passive sampling, are often preferred.

2.4.2 Passive techniques

One of the many tools of modern atmospheric chemical research is the passive diffusive sampler, which provides a low cost and low maintenance means to measure key atmospheric gaseous pollutants (Carmichael et al., 2003; Martins et al., 2007). The European Committee for Standardization defines gaseous passive
sampling as the sampling of gases or vapours from the atmosphere at a species-specific diffusion rate through a membrane in the absence of active air movement through the sampler. Figure 2.3 depicts a schematic representation of the components of the passive sampler used in this study.

Figure 2.3: The passive sampler configuration and dimensions including the polypropylene snap-on casing, the ash-less hardened medium filter paper disc impregnated with an absorbing solution, a Teflon filter and a stainless-steel mesh (Adon et al., 2010)

The passive sampler assembly consists of a number of parts. The top assembly consists of a punched snap-on cap, used to hold a polytetrafluoroethylene (PTFE) filter and stainless steel mesh in place. A paper disc impregnated with a chemically selective absorbing solution is placed in another plastic snap-on cap indicated as the lower assembly in Figure 2.3. These top and bottom assemblies are snapped together with a polypropylene ring, which holds the sampler together. The passive sampler has a diameter of 25 mm and a height of 10 mm. The limited air volume
inside the sampler minimises the gas resistance time and transport distance to the filter paper disc containing the absorbing solution. The PTFE filter and stainless steel mesh serve to prevent active air movement through turbulent diffusion (Carmichael et al., 2003). The PTFE filter diameter is 25 mm and is 175 μm thick and it is 85% porous.

The working principle of passive samplers is based on physical (the laminar diffusion of pollutant gases through a membrane) and chemical processes (reaction of diffused pollutant trace gases with the absorbing solution on the filter). Diffusion rates of trace gases in the atmosphere into the sampler are governed by diffusion coefficients of these gases and adhere to Fick’s principles (Carmichael et al., 2003; Martins et al., 2007). The pollutant gas meets an ash-less medium filter paper disc impregnated with a chemical solution that reacts exclusively with a specific gas and quantitatively traps it on the filter. The filter paper disc provides a large surface area, while the absorbing solution is prepared using a volatile solvent. This ensures efficient and effective trapping of trace gas molecules (Ferm, 1991).

The chemical reaction between the trace gas and the absorbing solution creates a concentration gradient and a net flux between the atmosphere and the air at the surface of the sorbent (Carmichael et al., 2003; Aiuppa et al., 2004). Figure 2.4 shows the concentration profile of a gaseous pollutant in and around the sampler and illustrates the pathway followed by pollutant gas molecules from the inlet to the impregnated filter at the back of the sampler.
Using Fick's first law of diffusion, the net flux $\Phi$ (μg∙m$^{-2}$∙s$^{-1}$) of a pollutant gas can be calculated. The net flux is proportional to the concentration $C$ (μg m$^{-3}$) gradient along the path length $L$ (m) within the sampler, as illustrated by equation 2.13 (Ferm, 2001).

$$\phi = -D \left( \frac{dC}{dL} \right)$$

(2.13)

The proportionality constant $D$ (m$^2$∙s$^{-1}$) is referred to as the diffusion coefficient, while the term $(dC/dL)$ is the instantaneous pollutant concentration gradient in the direction of airflow. Flux $\Phi$ can also be defined as the amount of pollutant gas $dX$ (µg) that passes through a cross-sectional area $A$ (m$^2$) along the diffusion path in a given time $dt$ (s). This yields equation 2.14.

$$\phi = \left( \frac{dX}{dt} \right) / A$$

(2.14)

Combining equations 2.13 and 2.14, time integrating and rearranging yield equation 2.15 (Dhammapala, 1996).

$$C_{avg} = \left( \frac{X}{D \cdot t} \right) \cdot \left( \frac{L}{A} \right)$$

(2.15)

The term $L/A$ is the summation of the thickness ($L_X$) and area ($A_X$) of the plastic ring (R), the PTFE filter pores (F), the steel mesh (N) and the static layer (S). This is illustrated by equation 2.16.
\[
\frac{L}{A} = \left( \frac{L_R}{A_R} \right) + \left( \frac{L_F}{A_F} \right) + \left( \frac{L_N}{A_N} \right) + \left( \frac{L_S}{A_S} \right)
\] (2.16)

It is important to note that the inner diameter (21 mm) of the ring is used in calculations, as this is the diameter of the section through which diffusion takes place. According to Ferm (1991), the thickness of the static layer is on average 1.5 mm for non-indoor sampling. The \( \frac{L}{A} \) ratio for this configuration is therefore 35 m\(^{-1} \) (Dhammapala, 1996). The results of equation 2.15 are expressed in mixing ratios that translate to volume (mm\(^3\)) of pollutant gas per volume (m\(^3\)) of moist air under sampling conditions in order to eliminate pressure dependence (Schwartz & Warneck, 1995; Dhammapala, 1996). Applying the ideal gas law to equation 2.15 results in equation 2.17:

\[
C_{\text{avg}}(\text{ppb}) = \left( \frac{1000 \cdot X \cdot R \cdot T}{M_r \cdot D \cdot t} \right) \cdot \left( \frac{L}{A} \right)
\] (2.17)

Equation 2.17 is used to convert the determined leached pollutant concentration (ppb) to an average monthly atmospheric concentration \( C_{\text{avg}} \) where the absolute temperature is \( T \) (K) during the sampling period \( t \) (h). Firstly, the amount \( X \) (µg) of gaseous pollutant trapped on the filter is determined by multiplying the leached concentration (ppb = µg·dm\(^{-3}\)) by the leached volume (dm\(^3\)). The relative molar mass is represented by \( M_r \) and the gas constant by \( R \) (8.31 J·K\(^{-1}\)·mol\(^{-1}\)). The diffusion constants \( D_X \) for \( \text{SO}_2 \), \( \text{HNO}_3 \), \( \text{NO}_2 \), \( \text{O}_3 \) and \( \text{NH}_3 \), which are considered to be the major gaseous atmospheric pollutants and measured with passive diffusive samplers, are tabulated in Table 2.1 (Martins et al., 2007).
The measurement of gaseous concentrations in this study is based on the work conducted by the following people and institutions: Swedish Environment Research Institute (IVL) developed the measurement of SO\(_2\) and NO\(_2\) gaseous concentrations (Martins, 2009); O\(_3\) sampling is based on the work done by Koutrakis et al. (1993), while HNO\(_3\) monitoring is based on the work performed by Ferm (1991). Monitoring of NH\(_3\) is based on the method developed by Ferm and Rodhe (1997).

The chemical reactions in the equations presented below (equations 2.18 to 2.22) illustrate how SO\(_2\), HNO\(_3\), NO\(_2\), O\(_3\) and NH\(_3\) are chemically trapped and quantitatively collected with passive samplers (Martins, 2009).

\[
\begin{align*}
2\text{SO}_2 (g) + 4\text{OH}^- + \text{O}_2 &\rightarrow 2\text{H}_2\text{O} + 2\text{SO}_4^{2-} \quad (2.18) \\
\text{HNO}_3 (g) + \text{OH}^- &\rightarrow \text{NO}_3^- + \text{H}_2\text{O} \quad (2.19) \\
2\text{NO}_2 (g) + 3\text{I}^- &\rightarrow 2\text{NO}_2^- + \text{I}_3^- \quad (2.20) \\
\text{O}_3 (g) + \text{NO}_2^- &\rightarrow \text{NO}_3^- + \text{O}_2 \quad (2.21) \\
\text{NH}_3 (g) + \text{H}^+ &\rightarrow \text{NH}_4^+ \quad (2.22)
\end{align*}
\]

The unstable SO\(_3^{2-}\) ion is produced when SO\(_2\) reacts with OH\(^-\) (Equation 2.18). SO\(_3^{2-}\) ultimately forms SO\(_4^{2-}\) through the reaction with O\(_2\) and various other catalytic trace species in the atmosphere. The reaction between HNO\(_3\) and OH\(^-\) leads to the production of NO\(_3^-\) (Equation 2.19). As a result, two distinctly different species are
formed on the same filter. Therefore, SO$_2$ and HNO$_3$ are determined from the same passive sampler.

In order to effectively trap the unstable NO$_2^-$ ion \((\text{equation 2.20})\), the absorbent must be kept at a relatively high pH. NaOH is ideally used for this purpose where the pH is kept at 13 or higher. A pH of 12 or lower can result in NO$_2^-$ being oxidised to form NO$_3^-$. Atmospheric oxidants can be prevented from reacting with the reactive NO$_2^-$ through the addition of excess I$^-$, which serves to remove atmospheric oxidants by their reaction with this species to form I$_2$.

\textbf{Equation 2.21} shows the chemical reaction whereby O$_3$ can be efficiently trapped in order for concentrations to be monitored. It is also critical to control the pH of the absorbing surface as the reaction constant for this reaction is at a maximum when the pH is at 12. This is achieved by the addition of K$_2$CO$_3$. Another important factor in this reaction is the hygroscopicity of the sorbent crystals (NO$_2^-$). Their oxidation potential with O$_3$ is enhanced with an increase in hygroscopicity and consequently the collection efficiency is enhanced. The hygroscopicity is increased through the addition of glycerol and the use of different nitrite and carbonate salts to form sorbent crystals. Koutrakis \textit{et al.} (1993) speculate that the process of trapping O$_3$ is that of a homogenous phase reaction taking place in microscopic droplets of water at the surface of the filter. Although NO$_2^-$ can be oxidised by H$_2$O$_2$, the pH in the solution is too high for this to occur. The chemical reaction between HNO$_3$ and K$_2$CO$_3$ also forms NO$_3^-$, but due to the low ambient concentration of HNO$_3$ in comparison to O$_3$, this accounts for less than 5% of accumulated NO$_3^-$. In order to trap NH$_3$ effectively, citric acid is utilised as an absorbent \((\text{equation 2.22})\). Due to its high molecular mass and therefore its low volatility, citric acid is preferably used in this acid-based reaction. Although any alkaline pollutant can be trapped by this method, it is only NH$_3$ that is present in the atmosphere in any significant concentrations (Martins, 2009).
2.4.3 Dry deposition

The direct measurement of dry deposition in large networks is difficult because of the need for highly sophisticated instrumentation (Wesely & Hicks, 2000). Therefore, many monitoring networks, including DEBITS, employ the inferential technique in estimating dry deposition. This technique is based on the measurement of ambient aerosol and gas concentrations, which are multiplied by a modelled species-specific deposition velocity (Vet et al., 2014). The big leaf model is employed to calculate gaseous dry deposition velocities that are site specific (Zhang et al., 2003). This does result in substantial uncertainties in dry deposition values reported in literature; however, inferential dry deposition estimates remain invaluable for studying and assessing global and regional dry deposition (Wesely & Hicks, 2000; Vet et al., 2014).

2.5 Long-term measurement networks

Studying wet and dry deposition reveals the temporal and spatial evolution of the chemical composition of the atmosphere. Various monitoring networks have been established world-wide in order to perform these studies (Mphepya et al., 2006; Adon et al., 2013). The Deposition of Biogeochemically Important Trace Species (DEBITS) programme was first initiated in 1990 as part of the International Global Atmospheric Chemistry (IGAC)/International Geosphere-Biosphere Programme (IGBP) ‘core project’ specifically for the study of atmospheric deposition (Lacaux et al., 2003) in the tropical belt – a region for which very limited data was available. The large DEBITS network includes stations in the tropical belt of Africa, South America and Asia and is currently operated in the DEBITS II structure. The IDAF (IGAC/DEBITS/Africa) project was implemented in partnership with two French institutions, i.e. Institut National des Sciences de l’Univers (INSU) and Centre National de la Recherche Scientifique (CNRS), in 1994, as part of the French Environmental Research Observatory’s (ORE) networks (Galy-Lacaux et al., 2008; Adon et al., 2013).
IDAF endeavours to measure atmospheric deposition fluxes of trace gas and aerosol species and to identify the factors governing these fluxes. The IDAF mission also includes the identification of anthropogenic and natural sources of atmospheric trace gas and aerosol species, which is based on the high-quality long-term monitoring and measurement of precipitation, trace gas and aerosol chemical composition. Several studies relating to African precipitation chemical composition within the framework of IDAF have been conducted (Mphepya et al., 2004; Mphepya et al., 2006; Galy-Lacaux et al., 2008; Adon et al., 2013). In addition, trace gas concentrations and dry deposition studies were conducted within the IDAF network (Martins et al., 2007; Adon et al., 2010; Josipovic et al., 2010; Josipovic et al., 2011; Adon et al., 2013). As described previously, due to the difficulties associated with sophisticated direct active measurement methods, these trace gas studies were conducted by utilising passive samplers (Sutton et al., 2007; Wolff et al., 2010).

Although Africa is one of the most sensitive continents with regard to air pollution and climate change, it is also the least studied. In addition, South Africa, with the largest economy in Africa, is the only industrialised regional energy producer on the continent. Its continued economic growth has led to an increase in industrial activity. This, in turn, has led to higher electricity demand and an increase in fossil fuel combustion (Tiitta et al., 2014). The measurement of wet and dry deposition within the DEBITS framework is therefore very important for South Africa. Currently, there are five South African IDAF sites, which are Louis-Trichardt, Amersfoort, Skukuza, Vaal Triangle and Cape Point. Cape Point is the only marine site in the South African network, while the other four sites are impacted by the industrialised interior of South Africa.

2.6 Western Cape

2.6.1 Climatology

The Western Cape exhibits a Mediterranean climate with dry summers and increased rainfall during winter. Inland temperatures are generally higher than coastal temperatures by up to 5°C with average coastal maximum temperatures of
27°C during the summer months. Coastal winter temperatures typically range between 7 and 18°C. (www.southafrica.com, 2015). Winter months in the south-western Cape often see the occurrence of severe storms moving from the west to the east, resulting from cold front and low-pressure systems. During summer, gale-force winds are observed typically on clear, hot and sunny days and may blow for several consecutive days (CPT, 2014).

2.6.2 Geography

The topography of the Western Cape is quite varied. The southern coastline of the province is fringed with mountains, while the northern part of the Western Cape consists of a substantial portion of the Karoo plateau. The smallest of the six floral kingdoms world-wide, the Cape Floral Kingdom, is situated in the Western Cape. Although it is the smallest of the floral kingdoms and home to the Fynbos biome, it contains more species of flora than the entire Europe.

The cold Atlantic Ocean is located to the west of the Western Cape with the warm Indian Ocean on the southern coast. The Benguela current, considered the richest fishing grounds in the world, flows along the west coast, resulting in significant fishing activity (www.southafrica.info, 2015).

2.6.3 Cape Town ‘brown haze’

Cape Town is the capital city of the Western Cape. The Cape Town conurbation has the second highest population in South Africa and also holds a relatively large number of industrial activities. In order to show the impacts of pollutant species in this area, the formation of brown haze over Cape Town can be considered to be a good example. Brown haze is a phenomenon that occurs all over the world (Senaratne & Shooter, 2004; Abiodun et al., 2014). According to Jacobson (2002), the reddish brown colour of this haze is attributed to the presence of NO2, as well as UV/visible absorption of polycyclic aromatic hydrocarbons (PAH) and nitrogen aromatic compounds present in aerosols. This colour is also enhanced by the
presence of suspended soil and dust (Jacobson, 2002). This brown haze has been linked to foul odours, deteriorating health and impaired visibility. Cape Town regularly experiences high air pollution accumulation events, particularly during winter when stable atmospheric conditions are prevalent. The accumulation of atmospheric pollutants leading to this haze is driven by various meteorological and geographical processes. Cape Town is located at the most south-western tip of South Africa, where the city is bordered by Table Mountain to the south-west, Table Bay to the west and False Bay to the south. Stagnant anticyclonic air flow occasionally leads to calm conditions in the air masses above the city. Vertical dispersion of the atmosphere and pollutants is suppressed by the subsidence temperature inversion during most of the year, and is reinforced by the formation of a surface inversion layer due to radiative cooling at night (Abiodun et al., 2014). Furthermore, a surface inversion layer is induced by the cold Benguela current and South Atlantic anticyclone, which is strengthened over Cape Town (Preston-Whyte et al., 1977). The difference in temperature between the Benguela current and the warmer land results in sea breezes developing during the day time. This leads to pollutants being trapped in the Cape Town Basin. When high-pressure systems over Kwazulu-Natal and the Western Cape are observed, together with a cold front approaching the continent, berg winds are produced. These berg winds are conducive to the formation of brown haze over Cape Town, because the night-time dew-point temperature is reduced by the warm north-easterly winds (Jury et al., 1990). As a result, the months of April to September typically see Cape Town experiencing severe high-pollution events. During this period, this brown haze extends over the larger Cape Town area while it is forming and it will shift according to prevailing wind directions (Wicking-Baird et al., 1997).
Chapter 3

Experimental methods and materials

In this chapter, the atmospheric measurement site description, reagents and materials utilised, experimental procedures followed, and analytical techniques employed are presented.

3.1 Site description

In Figure 3.1, a map of the Cape Peninsula in South Africa is presented indicating Cape Point (CPT). The CPT Global Atmosphere Watch (CPT GAW) (34°21’S, 18°29’E) station is perched atop a cliff approximately 230 m above sea-level at the southernmost tip of the peninsula resulting in a 300° ocean view. The city of Cape Town is situated approximately 60 km north of the station. The nearby terrain is predominantly rocky and sparsely vegetated. Summer is associated with moderate temperatures and relatively low rainfall, as well as occasional biomass burning in the surrounding areas. Winter is associated with lower temperatures and increased rainfall. The predominant south-easterly to south-westerly winds carry air masses that are representative of clean maritime air from the hemispheric mid-latitudes. Winds from the north-northeast are also frequently recorded, typically during winter time, which transport air masses that are significantly influenced by anthropogenic emissions from various continental sources, including the greater Cape Town area (Brunke et al., 2004; Brunke et al., 2010).

Figure 3.1: Map of the Cape Peninsula (Brunke et al., 2010)
The site is managed by the South African Weather Service and provides a good platform for the measurement of atmospheric parameters on a continuous basis and for field campaigns to be conducted. The site is equipped with numerous instruments that conduct a large number of atmospheric measurements. The primary measurements of CPT GAW are the measurements of greenhouse gases, i.e. CO, CO₂, CH₄ and N₂O. Other continuous measurements include total gaseous mercury, ²²²Rn, solar radiation, precipitation chemistry and meteorological parameters. Passive sampling that measures monthly average gaseous concentrations of atmospheric SO₂, NO₂, O₃, NH₃ and HNO₃ is also performed, which is discussed in this investigation (Brunke et al., 2001; Baker et al., 2002; Brunke et al., 2004; Martins et al., 2007; Brunke et al., 2010; Brunke et al., 2012).

3.2 Reagents and materials

It is essential to use high purity chemical reagents in an atmospheric chemistry analytical laboratory. All chemicals used during the experimental procedures were analytical grade (AR), with the exception of a 3.5% sodium hypochlorite solution in the form of commercially available Javel. Chemicals were used without any further purification. Deionised water (18.2mΩ) was used in all experimental procedures, e.g. washing and rinsing of equipment, as well as in all aqueous solutions.

The following AR chemicals were used during the course of this investigation: sodium hydroxide (NaOH) (Rochelle Chemicals); methanol (CH₃OH) (Promark Chemicals); sodium nitrite (NaNO₂) (Associated Chemical Enterprises); potassium carbonate (K₂CO₃) (Saarchem); glycerol (C₃H₈O₃) (Sigma Aldrich); sodium iodide (NaI) (Saarchem); citric acid (C₆H₈O₇) (Saarchem); ortho phosphoric acid (H₃PO₄) (Promark Chemicals); sulphanilamide/4-Aminobenzenesulfonamide (C₈H₈N₂O₂S) (Saarchem); N-1-Naphthylethylenediamine dihydrochloride/NEDA (C₁₂H₁₄N₂.2HCl) (Sigma Aldrich); phenol (C₆H₆O) (Sigma Aldrich); sodium nitroprusside (Na₂[Fe(CN)₅NO]) (Sigma Aldrich) and di-ammonium hydrogen citrate (C₁₆H₁₄N₂O₇) (Saarchem).
Stock solutions used for the preparation of standard solutions for ion chromatography (IC) analysis were manufactured by SpectraScan and supplied by Industrial Analytical. These standards were certified to be 99.5% pure.

Materials for the preparation of passive samplers used in this investigation include ash-less hardened medium filter paper (EconoFilt) discs with a diameter of 25 mm, as well as PTFE filter membranes (EconoClear) with a pore size of 1 micron and a diameter of 25 mm. The filter paper discs and PTFE filter membranes were supplied by G.I.C. Scientific cc. The snap-on cap that houses the impregnated filter disc, the punched snap-on cap and the ring (refer to section 2.4.2) were manufactured to specification by the instrument makers of the North-West University on the Potchefstroom Campus (NWU-PC). The snap-on caps were manufactured from polypropylene tubes produced by Bellco Glass and supplied by The Scientific Group. The stainless steel mesh of the passive sampler (Figure 2.3) was also cut to specification and supplied by the NWU-PC instrument makers.

When measuring the concentrations of atmospheric trace elements with passive samplers, optimum laboratory cleanliness is essential during the preparation and analysis of these samplers. It is estimated that a sample error of up to 50% can be caused by contamination of as little as 20 nmol (Dhammapala, 1996). In order to prevent contamination, all sampler components, i.e. the polypropylene snap-on caps and rings, stainless steel mesh and reusable PTFE filter discs were cleaned prior to sampler preparation. The cleaning process started with the soaking of the components in 0.2% (v/v) o-H$_3$PO$_4$ for four to five hours, after which they were rinsed, and then soaked overnight in a 3% (v/v) EXTRAN MA O2 solution. After soaking overnight, the components were rinsed thoroughly and sonicated in deionised water. The rinsing process was repeated three times, after which the components were completely dried. The ash-less paper filters were also pre-treated in order to remove any debris that may be present. This was conducted by soaking the discs in methanol and sonicated in an ultrasonic bath for 30 minutes. This process was repeated four times, after which they were dried in a vacuum. After drying, the filter discs were sealed in air-tight bags for storage.

All glassware, containers and other laboratory equipment used in experimental procedures and analytical techniques were also washed by following a
comprehensive procedure to ensure no sample contamination. Firstly, all equipment was soaked in a diluted o-H₃PO₄ bath for a minimum of five hours, after which it was rinsed and soaked overnight in a soap solution (EXTRAN MA O2). Thereafter, glassware, containers and other laboratory equipment were rinsed up to ten times with deionised water and air dried in the preparation laboratory.

The preparation laboratory is equipped with air filtration units to ensure clean air in the laboratory. This also aids in a positive pressure being maintained in the laboratory keeping elements such as dust out. Furthermore, the preparation laboratory was kept at a constant 22°C, with relative humidity below 40%.

### 3.3 Sampling methods

#### 3.3.1 Passive sampler preparation and assembly

As mentioned in the previous section, paper filters were loaded with 50 µL absorbing solution that specifically reacts and traps the atmospheric gaseous species. All absorbing solutions were prepared in 100 mL volumetric flasks. SO₂ and HNO₃ react with the same sorbent and therefore the same sampler was used to determine these species. The absorbing solution for the SO₂/HNO₃ samplers was prepared by diluting 1.00 g NaOH in 100 mL methanol. For NO₂, the absorbing solution was prepared by firstly dissolving 0.88 g NaOH and 7.90 g NaI in 5 mL deionised water, after which the volumetric flask was filled with methanol. The absorbing solution for O₃ consisted of 1.00 g dried NaNO₂ (dried in an oven at approximately 70°C), 1.00 g K₂CO₃ and 2 mL glycerol that were dissolved in a 7:3 water-methanol mixture. The NH₃ absorbing solution was prepared by dissolving 2.0 g citric acid in 100 mL methanol.

A set of duplicate samples was prepared for each of the species measured at the CPT GAW. A schematic diagram of passive sampler used in this study is presented in Figure 2.3. Each passive sampler was prepared by placing an ash-less hardened filter disc in the bottom part of the sampler, which was then impregnated with 50 µL of the absorbing solution. A pre-assembled cap (top part of the sampler) containing a PTFE filter and a stainless steel mesh disc was then snapped on to the bottom part.
of the sampler by means of the plastic ring as indicated in Figure 2.3. The samplers were then sealed off in air-tight containers, which were sent via a courier service to the CPT GAW station for deployment and one-month exposure. A laboratory blank was also prepared each month for each gaseous species that was sealed in a container and stored in the laboratory.

### 3.3.2 Field exposure

Passive samplers were exposed for one month at the CPT GAW. These samplers were placed in a special housing unit that was positioned on a stand as presented in Figure 3.2.

![Figure 3.2: The aluminium stand (left) and the housing unit (right) wherein passive samplers were placed for exposure each month at the CPT GAW (Martins et al., 2007)](image)

The housing unit consisted of rails wherein the passive samplers were slid in with the steel mesh opening facing downwards for exposure each month. The housing unit was installed on a stand that was 1.5 m high. Both these components (housing unit and stand) consisted of aluminium and were constructed by the instrument makers at the NWU-PC (Martins et al., 2007). After one month, the exposed passive
samplers were removed and sealed-off in air-tight containers. Thereafter, new passive samplers were placed in the sampling stand. The exposed passive samplers were sent back to the laboratory of the Atmospheric Chemical Research Group (ACRG) at the NWU-PC. Received samples were logged and placed in a freezer for storage at 3°C up until analysis.

3.4 Analytical techniques

Prior to analysis, the exposed paper filters are removed from the passive sampler and placed in a container. The collected samples were then leached with 5 mL for SO$_2$/HNO$_3$, NO$_2$ and NH$_3$ samplers and in 25 mL deionised water for O$_3$ samplers. The samples were sonicated in an ultrasonic bath for 30 minutes. After December 2012, NH$_3$ and NO$_2$ samples were leached with 10 mL water due to a change in the analytical technique that will be discussed later in this section.

SO$_2$, HNO$_3$ and O$_3$ samplers collected during the entire sampling period were analysed with a suppressed ion chromatograph (IC), while NO$_2$ and NH$_3$ samples collected after December 2012 were also analysed with the IC. NO$_2$ and NH$_3$ samples collected prior to January 2013 were analysed with ultraviolet/visible (uv/vis) spectroscopy. Although the analysis of NO$_2$ and NH$_3$ samples with uv/vis spectroscopy is considered to be an acceptable analytical technique, this procedure required the use corrosive chemicals and relatively more complex sample preparation processes. This analytical procedure was followed in the past since the IC method utilised did not allow for the detection of these species or due to very long running times. However, improvements in the development of new columns and the use of eluent gradient methods allowed for the analysis of NO$_2$ and NH$_3$ samples with the IC.

A Dionex ICS-3000 IC system was utilised that has two flow lines with one flow line used for the detection of anion species, while the other flow line analyses cation species. The anion flow line (used for analysis of SO$_2$, HNO$_3$, O$_3$ and NO$_2$ samplers) was initially equipped (prior to January 2013) with 2 mm AS 18 analytical and 2 mm AG 18 guard columns, a 2 mm CRD 200 carbonate removal device and an ASRS
300 2 mm suppressor. An isocratic eluent programme was employed that kept the hydroxide (OH\(^-\)) eluent concentration constant at 18 mM, while the applied current was kept at 33 mA. In January 2013, the analytical and guard columns were replaced by 4 mm AS16 analytical and 4 mm AG16 guard columns. The 2 mm CRD 200 was also replaced by a 4 mm version and the suppressor was replaced by an AERS 500 4 mm suppressor. The eluent concentration and applied suppressor current were adapted to 10 mM and 30 mA, respectively, to accommodate the higher flow rate of 1.2 mL/min. A five-point calibration was performed with 0.1, 0.5, 1.0, 2.5 and 5.0 ppm standard solutions prepared from 1,000 ppm stock solutions. Analysis of the samples commenced only after the relative standard deviation of the calibration curve was below 5%.

The cation flow line (used for analysis of NH\(_3\)) was equipped with a CERS 500 2 mm suppressor. A set of 3 mm CS-16 analytical and 3 mm CG-16 guard columns were fitted and a constant methanesulphonic acid (MSA) eluent concentration of 35 mM was employed at a constant flow rate of 0.360 mL/min, while a suppressor current of 40 mA was applied. A five-point calibration was also performed with 0.1 ppm, 0.5 ppm, 1.0 ppm, 2.5 ppm and 5 ppm standard solution prepared from a 1,000 ppm NH\(_4^+\) stock solution. The samples were only analysed after the relative standard deviation of the calibration curve was below 5%.

NO\(_2\) and NH\(_3\) samples prior to January 2013 were analysed by a Cary 50 uv/vis spectrophotometer. A reagent solution was prepared for the analysis of NO\(_2\) samplers of uv/vis spectroscopy by adding 4 mL o-H\(_3\)PO\(_4\), 4 g C\(_6\)H\(_8\)N\(_2\)O\(_2\)S and 0.1 g C\(_{12}\)H\(_{16}\)Cl\(_2\)N\(_2\) in a 500 mL volumetric flask that was then filled with deionised water. After extraction of the samples, after leaching, 5 mL diazotising agent was added to every sample prior to uv/vis spectroscopic analyses at 540 nm. Standards for the analysis of NO\(_2\) samples were prepared from a 1 M NaNO\(_2\) stock solution, prepared by dissolving 0.069g NaNO\(_2\) in 1 L deionised water, from which 2, 5, 10 and 25 µM standards were prepared. A second solution was prepared for the standards by dissolving 0.1975 g sodium iodide (NaI) in 50 mL water. The diazotising and NaI solution was added to the standard solutions prior to analysis.

For the analysis of NH\(_3\) samples, two reagent solutions were prepared. One of the reagents was prepared by adding 10 g C\(_6\)H\(_5\)OH, and 0.05g Na\(_2\)(Fe(CN)\(_5\))NO\cdot2H\(_2\)O to
a 1 L volumetric flask that was filled with deionised water. The other reagent solution was also an aqueous solution prepared in a 1 L volumetric flask to which 5 mL NaOH and 40 mL 3.5% NaClO were added. After leaching of the samples, 10 mL of each reagent solution was added, while taking care to add the phenol solution first and allowing the sample mixture to reach equilibrium after an hour before adding the second reagent solution. The samples were then analysed at 633 nm. Standards were prepared from a 5 M C₆H₈O₇·2NH₃ solution, prepared by adding 0.113 g C₆H₁₄N₂O₇ to a 1 L flask and filling it with deionised water. From this stock solution, 10, 25, 50 and 100 µM standard solutions were prepared.

In all cases where methods were changed, samplers collected over a period of at least three months were analysed with both the previous and new method to ensure that the results from the methods were comparable.

Detection limits for the measurement procedures used for the various gaseous species, including sample preparation and analysis, were calculated using several laboratory blanks. The detection limit calculation was based on the method specified by the WMO in the bi-annual GAW laboratory inter-comparison study (LIS). This entailed the calculation of the standard deviation of the laboratory blank samples, which were multiplied by a factor of 3. The various detection limits were: 0.16 ppm (SO₂); 0.03 ppm (NO₂); 0.06 ppm (HNO₃); 0.12 ppm (NH₃) and 0.02 ppm (O₃). Only HNO₃ concentrations determined for April, June and July 2013 were below the detection limits of the analytical instrument for the passive samplers analysed in this study from 2005.

3.5 Quality assurance and control

The passive samplers developed and used in this study have been verified through participation in various inter-comparison studies, which is a prerequisite for passive samplers used in the Deposition of Biogeochemical Important Trace Species (DEBITS) programme endorsed by the International Global Atmospheric Chemistry (IGAC) initiative. The first inter-comparison study was performed between 25 April 1995 and 10 May 1995, during which passive diffusive samplers from the
Commonwealth Scientific and Industrial Research Organisation (CSIRO) based in Australia, the IVL and the NWU-PC were compared to active measurements conducted by Eskom at Elandsfontein in the Mpumalanga Highveld of South Africa (Dhammapala, 1996). In 1997, a similar inter-comparison study was undertaken, where passive samplers were compared to active sampling monitors used in a more industrial region by Sasol (Van der Walt et al., 1998). Between May 1998 and December 2000, the remote site inter-comparison study was expanded to include three remote sites (Palmer, Elandsfontein and the CPT GAW) (Pienaar et al., 1999). In 2001, the passive samplers were also evaluated in an international study coordinated by the World Meteorological Organisation (WMO) GAW programme (Carmichael et al., 2003).

The most recent evaluation of the passive samplers used in this study was an inter-comparison study that was arranged by the National University of Singapore in 2008. In this investigation, the precision and accuracy of passive samplers used by different institutions internationally for the monitoring of $\text{SO}_2$ and $\text{NO}_2$ were determined. Passive samplers were compared to active samplers and to each other. The final report indicated that the passive samplers used by the NWU compared very well to active samplers and in most instances had better accuracy than similar samplers used by other institutions. The comparison of passive samplers utilised by the NWU-PC is also a continuous process, which is currently compared to active samplers at the Welgegund monitoring station (Jaars et al., 2014; Tiitta et al., 2014).

The IC analytical techniques were also verified by participating in the bi-annual LIS organised by the WMO, wherein a sample set of three laboratory-prepared rainwater samples are received and analysed, after which the results are reported and posted online. The results are visualised using ring diagrams, as presented in Figure 3.3. Measurements within the inter-quartile range (IQR), i.e. between the 25th and 75th percentiles, are considered good and are represented by a green hexagon, as indicated for example for sodium in Figure 3.3. Analytical results that are within the range defined by the median + IQR/1.349 are considered satisfactory and are represented by a Blue trapezoid, as indicated for example for nitrate in Figure 3.3. Unsatisfactory measurements fall outside of the range defined by the median + IQR/1.349 and are represented by a red triangle. Outward pointing trapezoids and
triangles indicate that the reported measurement is high, while inward pointing trapezoids and triangles indicate that the reported result is low. Measurements that are below the detection limit are represented by an open circle, as indicated for example for fluoride in Figure 3.3.

Figure 3.3: Example of ring diagrams used to visualise WMO LIS results (QASAC, 2014)

Example results obtained by the laboratory of the ACRG for three samples are presented in Figure 3.4. It is evident that the analytical processes and techniques applied by the ACRG for IC analyses are relatively good. During this specific round of inter-comparison (December 2014), some problems were experienced with the detection of NO$_3^-$ as indicated in Figure 3.4. These problems have since been resolved.

Figure 3.4: Results of WMO LIS 50: Samples 1, 2 and 3 are from left to right
3.6 Data processing

As mentioned in section 2.4.2, the gaseous species collect on passive samples as ionic species. IC analysis of the passive samplers reveals concentrations of these ionic species in the leached sample only. Therefore, the concentrations measured for these ionic compounds in aqueous solution have to be converted to average monthly atmospheric concentrations of gaseous SO₂, NO₂, HNO₃, NH₃ and O₃ by using equation 2.17 presented in section 2.4.2.

All sample duplicates were used to calculate average ambient concentrations for each of the gaseous species for each individual month. Long-term annual trends were assessed by calculating average annual concentrations, while seasonal trends were investigated by calculating monthly average concentrations. In both the aforementioned cases, the data was further refined by applying the Q-test with a 95% confidence threshold in order to reject possible outliers, which resulted in better defined trends.

3.7 Meteorology and fire frequencies

Ancillary meteorological data for Cape Point that include temperature, wind direction and speed, rainfall, humidity and ambient pressure were obtained from the South African Weather Services (SAWS). Wind roses were compiled using mathematical software (Matlab®) to create angular histograms of wind direction frequency.

Daily fire distribution data was derived from the National Aeronautics and Space Administration’s (NASA) Moderate Resolution Imaging Spectrometer (MODIS) satellite retrievals. MODIS is mounted on the polar-orbiting Earth Observation System’s (EOS) Terra spacecraft and globally measures, among others, burn scars, fire and smoke distributions. This dataset was retrieved from the NASA Distributed Active Archive Centers (DAAC) (Kaufman et al., 2003).
3.8 Back trajectory analysis

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model version 4.8 developed by the National Oceanic and Atmospheric Administration’s (NOAA) Air Resource Laboratory (ARL) was used to determine back trajectories of the air masses measured at Cape Point (Draxler & Hess, 2014). The Lagrangian approach is an atmospheric dispersion model that uses numerical methods to calculate the time history of air masses. In this model, advection and diffusion components are measured independently (Draxler & Hess, 1998). The meteorological data applied in this model was obtained from the Global Data Assimilation System (GDAS) archive of the United States National Weather Service’s (USNWS) National Centre for Environmental Prediction (NCEP). The hourly-arriving back trajectories were calculated backwards for a 96-hour period. The arrival height was set at 100 m to minimise error margins due to the less well-defined orography in the HYSPLIT model. Twenty-four individual hourly-arriving back trajectories were calculated for each day for the entire measurement period (1995 to 2013). Hereafter, the individual back trajectories were superimposed to show the statistical distribution by using mathematical software (Matlab®) to create a frequency map with a 0.2° x 0.2° resolution grid. The map had a colour index indicating the frequency of trajectories that pass over the coordinates.

3.9 Deposition calculations

The rate of gaseous dry deposition \( \varphi \) (flux) is calculated by the product of average ambient gas concentration \( (C_a) \) and the deposition velocity \( (u_d) \) (Vet et al., 2014) as shown by Equation 3.1:

\[
\varphi = (C_a \times u_d)
\]  

(3.1)

The units of \( C_a \) and \( u_d \) are \( \mu g.m^{-3} \) and \( m.s^{-1} \) respectively, resulting in the units of \( \varphi \) being \( \mu g.m^{-2}.s^{-1} \). As deposition \( \Phi \) is generally expressed in \( kg.ha^{-1}.yr^{-1} \), a conversion factor of 3.1536 is calculated as follows:

\[
\mu g.m^{-2}.s^{-1} = 10^{-9}kg.\left(10^{-2}ha\right)^{-1}.\left(3.1536\times10^{-7}yr\right)^{-1}
\]  

(3.2)
In this study \( u_d \) obtained from literature were utilised to estimate dry deposition, while it was also assumed that \( u_d \) was constant throughout the year. Annual deposition is calculated with \( C_a \) in **Equation 3.3** being the average annual ambient concentration. Monthly gaseous dry deposition was calculated with

\[
\Phi = \frac{3.1536}{12} (C_a \times u_d) \quad (3.4)
\]

where \( C_a \) was the average monthly concentration measured for the entire sampling period. Seasonal gaseous dry deposition were determined from these average monthly concentrations for the relevant months representing different seasons.

Elemental gaseous dry deposition is calculated by determining the fraction of the calculated deposition attributable to a specific element. For S, the molar percentage of S in \( \text{SO}_2 \) is 50%, from which it follows that the sulphur deposition (\( \Phi_S \)) is:

\[
\Phi_S = 0.5\Phi \quad (3.5)
\]

Total nitrogenous gaseous deposition (\( \Phi_N \)) is determined by the contributions of \( \text{NO}_2 \), \( \text{NH}_3 \) and \( \text{HNO}_3 \) to the amount of N deposited. The molar percentage of N in \( \text{NO}_2 \), \( \text{NH}_3 \) and \( \text{HNO}_3 \) are 36.8%, 82.4% and 22.2% respectively, from which it follows:

\[
\Phi_N = 0.368\Phi_{\text{NO}_2} + 0.824\Phi_{\text{NH}_3} + 0.222\Phi_{\text{HNO}_3} \quad (3.6)
\]
Chapter 4

Results and discussion

In this chapter, long-term inter-annual and seasonal trends of atmospheric inorganic gaseous species, which include SO₂, NO₂, NH₃, HNO₃ and O₃ measured at the CPT GAW, are discussed and compared to other IDAF measuring stations. Air mass movement, meteorology and fire event frequencies are explored in an attempt to estimate the origins of the measured gaseous concentrations. In addition, the gaseous dry deposition fluxes of these species are calculated and discussed.

4.1 Long-term measurement of atmospheric inorganic gaseous species

4.1.1 Inter-annual variability of gaseous species

Atmospheric gaseous concentrations of sulphur dioxide (SO₂), nitrogen dioxide (NO₂), ammonia (NH₃) and ozone (O₃) were measured at the Cape Point Global Atmosphere Watch (CPT GAW) atmospheric monitoring station with passive diffusive samplers from 1995 to 2013, while passive sampling of nitric acid (HNO₃) commenced in 2003 at the CPT GAW. Samplers were exposed for one month from which monthly average concentrations of these gaseous species could be determined. In Figures 4.1 (a) to (e), the measured gaseous concentrations are presented for each sampling year with box and whisker plots indicating the mean, median, 25th and 75th percentiles, while the whiskers indicate ±2.7σ (with σ the standard deviation). NH₃ concentrations measured from 2012 to 2013 were excluded due to problems experienced with the analytical instrument used for analysis of these samples during this period. Inter-annual variability can be ascribed to various factors, which include inter-annual changes in meteorology and sources of species. A few instances are observed where the average annual concentrations were similar or exceed the 75th and 25th percentiles. These occurrences were attributed to individual monthly concentrations being much higher (or lower) for that
specific year, which were, however, not identified as outliers by the Q-test applied to the dataset to verify the statistical significance of differences in concentrations.

(a)

(b)
Chapter 4: Results and discussion
Figure 4.1: Annual SO$_2$ (a), NO$_2$ (b), NH$_4$ (c), HNO$_3$ (d), and O$_3$ (e) concentrations from 1995 to 2013 (2012 to 2013 NH$_3$ measurements were excluded due to uncertainties associated with analytic procedures during this period). The red line of each box represents the median, the top and bottom edges of the box the 25$^{th}$ and 75$^{th}$ percentiles, respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution) and the black dots the averages. The maximum concentrations and the number of measurements (N) are presented at the top.

Small inter-annual variability is observed for SO$_2$ from 1995 to 2004 with average annual concentrations ranging between 0.30 and 1.82 ppb. However, from 2005 to 2009, a steady increase in average annual SO$_2$ concentrations is observed between each of the years, with SO$_2$ levels reaching an annual average maximum of 4.83 ppb in 2009. After 2009, a decrease in average annual SO$_2$ concentrations was observed up until 2013. Although an SO$_2$ peak is observed in 2009, a slight overall increase is observed in SO$_2$ after 2004. In Figure 4.2, moving averages of SO$_2$ concentrations are presented from 1995 to 2013. A slight decline in SO$_2$ concentrations is observed from 1996 to 2002, followed by an increase in SO$_2$ levels up until 2009. Although this increase between 2003 and 2009 is evident, distinct conclusions with regard to long-term gaseous SO$_2$ concentration trends cannot be...
made, since the increase indicated by the moving averages could possibly only be attributed to the peak observed in 2009. Continued monitoring at the CPT GAW is required in order to get greater certainty about long-term trends, e.g. for decadal trends.

Figure 4.2: Three-year moving averages and medians of SO$_2$ gaseous concentrations at the CPT GAW station for the measurement period 1995 to 2013

A small inter-annual variability is observed for NO$_2$, with the exception of 2011 and 2012 that had higher annual mean NO$_2$ concentrations coinciding with a larger spread of NO$_2$ concentrations. The average annual concentrations ranged between 0.28 and 2.75 ppb. However, in general, a slight decrease in NO$_2$ levels is observed from 1999 up until 2002, followed by an increase in NO$_2$ concentrations. The three-year moving averages of NO$_2$ presented in Figure 4.3 indicate a decrease in NO$_2$ levels from 1996 to 2001, followed by an increase in NO$_2$ concentrations, which is similar to the SO$_2$ long-term trend observed. A decrease in SO$_2$ and NO$_2$ concentrations up until 2001/2002, followed by a steady increase up until 2009, is evident. The observed increase in SO$_2$ and NO$_2$ levels can be attributed to two possible explanations, i.e. changes in meteorological conditions and/or an increase
in sources e.g. economic growth with associated higher energy demand and a larger vehicle fleet.

Figure 4.3: Three-year moving averages and medians of NO$_2$ gaseous concentrations at the CPT GAW station for the measurement period 1995 to 2013

Ojumu (2013) and Abiodun et al. (2014) recently reported the long-range transport of atmospheric pollutants from the industrialised Highveld in the interior of South Africa to Cape Town. The major pollutant sources in the industrialised Highveld included nine coal-fired power stations, petrochemical industries, pyro-metallurgical smelters, mining activities, as well as the Johannesburg-Pretoria conurbation. Overlay back trajectories presented in section 4.1.2 (Figure 4.9 and Figure 4.10) also indicate that the CPT GAW station is affected by air masses passing over the industrialised interior of South Africa, especially from May to October, i.e. late spring, winter and early-mid spring. Therefore, trends observed for SO$_2$ and NO$_2$ concentrations could be ascribed to periods where the CPT GAW station is more frequently affected by air masses passing over the industrialised interior of South Africa. Furthermore, monthly SO$_2$ and NO$_2$ measurements conducted in the DEBITS project at sites in the north-eastern interior of South Africa, which include sites within the industrialised
Highveld, also indicate increases in SO$_2$ and NO$_2$ levels from 2001/2002 that are attributed to the increase in economic growth and higher energy demand. In addition to the long-range transport of pollutant species, wind roses compiled for the CPT GAW also indicated the impact of local pollution from Cape Town, especially during certain periods of the year. Therefore, changes in local meteorological conditions can also have an impact on the SO$_2$ and NO$_2$ trends observed, i.e. instances of air masses passing over Cape Town affecting the CPT GAW. Furthermore, any changes in local sources could also contribute to the trends observed. These impacts of meteorological conditions and source contributions on inorganic gaseous species will be discussed in detail in the subsequent section.

More significant inter-annual variability is observed for NH$_3$ concentrations, which can be attributed to the inter-annual fluctuations in the presence of animals and sea birds at the CPT GAW station that is situated in a national conservation park. Between 1995 and 2011, the NH$_3$ levels ranged from 0.85 to 2.67 ppb. No distinct long-term trend is observed for NH$_3$ concentrations from 1995 to 2011.

Small variations in the average annual HNO$_3$ concentrations at the CPT GAW were observed. The average annual HNO$_3$ concentrations ranged between 0.13 and 1.19 ppb. The highest HNO$_3$ concentrations were measured in 2009, which coincided with the SO$_2$ peak observed. Although this peak is observed in 2009, followed by a decrease in subsequent years, no clear annual trends are observed.

Small inter-annual variability was observed for O$_3$ concentrations from 1995 to 2013, with the exception of 1999 to 2001, which exhibited lower annual average O$_3$ concentrations. Average annual O$_3$ levels ranged between 17.93 and 38.27 ppb. O$_3$ levels exhibit a cyclic trend with values increasing and decreasing between certain periods. In general, average annual O$_3$ concentrations remained similar revealing no distinct annual trend.
4.1.2 Seasonal trends of atmospheric gaseous concentrations

In Figure 4.4 (a) to (e), the statistical spread of monthly concentrations for each of the gaseous species measured for the entire sampling period are presented in order to assess seasonal variability. Similar to the annual concentrations, a few instances are observed where the average monthly concentrations were similar or exceeded the 75th and 25th percentiles. These occurrences were attributed to monthly concentrations for certain years being much higher (or lower) for that specific year, which were not identified as outliers by the Q-test.
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(b) 

(c) 

NO\textsubscript{2} concentration (ppb)

NH\textsubscript{3} concentration (ppb)

Jan  Feb  Mar  Apr  May  Jun  Jul  Aug  Sept  Oct  Nov  Dec

2.33  2.01  2.09  3.44  4.81  3.56  4.95  3.29  1.99  2.03  1.24  2.10
16     16     15     16     16     17     16     17     17     15     16     18

Max

N

2.99  2.48  4.25  3.07  5.17  6.85  4.70  4.06  3.96  3.02  3.88  4.83
14     15     15     16     15     14     14     15     16     16     16     16
Figure 4.4: Monthly averaged SO$_2$ (a), NO$_2$ (b), NH$_4$ (c) HNO$_3$ (d), and O$_3$ concentrations from 2003 to 2013. The red line of each box represents the median, the top and bottom edges of the box the 25$^{th}$ and 75$^{th}$ percentiles, respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution) and the black dots the averages. The maximum concentrations and the number of measurements (N) are presented at the top.
Higher SO$_2$ concentrations were observed during two periods in the year i.e., January to February, and July to August. More distinct seasonal patterns were observed for NO$_2$ and O$_3$. Higher NO$_2$ levels occurred from April to August with NO$_2$ concentrations peaking in July, while O$_3$ had higher concentrations between July and October. There were no distinct seasonal patterns observed for NH$_3$ and HNO$_3$. In an effort to explain these seasonal patterns observed, seasonal changes in source contributions, meteorological conditions and ecological process were considered.

The CPT GAW station is situated in the Western Cape of South Africa. This region is associated with a distinct wet season occurring from April to September and a dry season from October to March, i.e. a wet winter and a dry summer season. In Figure 4.5, the average monthly rainfall for the period January 2004 to December 2013 is presented, which clearly indicates the prominent wet and dry seasons in this region. This is in contrast to wet and dry seasons observed in the northern interior of South Africa, where the dry season occurs from May to September and the wet season from October to May (SAWS, 2015). The northern interior of South Africa is usually associated with elevated levels of SO$_2$ and NO$_2$ during the dry winter (June to August), while O$_3$ levels peak in the late winter, early spring (August to October) (Tiitta et al., 2014). Higher SO$_2$ and NO$_2$ concentrations in the interior are usually attributed to more pronounced inversion layers trapping pollutant species near the surface of the earth, as well as increased occurrences of household combustion for space heating and biomass burning (Gadi et al., 2003; Galy-Lacaux et al., 2008; Lourens et al., 2011; Venter et al., 2012). The increase of O$_3$ concentrations is usually ascribed to the increase in photochemical activity and the regional increase in biomass burning from August to October. Since the source contributions and meteorological conditions are different at the CPT GAW compared to the interior of South Africa, source contributions, meteorological conditions and ecological processes were assessed specifically for the CPT GAW station.
Figure 4.5: Monthly average precipitation measured at the CPT GAW during the period January 2004 to December 2013

In Table 4.1, the average gaseous concentrations measured during the wet- and dry season are presented. Although the standard deviations of the average concentrations presented for the wet and dry season in Table 4.1 are relatively large, some differences are observed differences for the two seasons. The average \( \text{SO}_2 \) and \( \text{HNO}_3 \) were higher during the dry season, while average \( \text{NO}_2 \) and \( \text{O}_3 \) concentrations were higher during the wet season. \( \text{NH}_3 \) concentrations are marginally higher during the wet season.
Table 4.1: Average annual, wet- (April to September) and dry (October to March) seasonal gaseous concentrations (ppb) with the associated standard deviations (±σ) of SO₂, NO₂, NH₃, HNO₃ and O₃ measured at CPT GAW from 1995 to 2013

<table>
<thead>
<tr>
<th></th>
<th>Annual</th>
<th>Wet season</th>
<th>Dry season</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>1.27±1.07</td>
<td>1.14±0.94</td>
<td>1.45±1.44</td>
</tr>
<tr>
<td>NO₂</td>
<td>1.32±0.60</td>
<td>1.74±0.84</td>
<td>0.89±0.38</td>
</tr>
<tr>
<td>NH₃</td>
<td>1.66±0.47</td>
<td>1.58±0.69</td>
<td>1.71±0.49</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.71±0.27</td>
<td>0.66±0.31</td>
<td>0.75±0.38</td>
</tr>
<tr>
<td>O₃</td>
<td>26.61±4.93</td>
<td>29.98±6.36</td>
<td>23.08±4.83</td>
</tr>
</tbody>
</table>

A wind rose was compiled for the entire sampling period, which was separated into two wind roses for the wet (April to September) and dry (October to March) seasons from 1995 to 2013, which are presented in Figure 4.6. It is evident that the CPT GAW experiences predominantly east-south-easterly to south-easterly winds throughout the year (Figure 4.6 (a)). A similar wind rose is obtained for the dry season in Figure 4.6(c), also indicating predominant wind flow from the same region, which indicates mainly marine air masses. However, during the wet season, the frequency of winds originating from the north-north-western to western sector increases, as indicated in Figure 4.6(b). This denotes that the CPT GAW station is affected more frequently by air masses passing over the Cape Town conurbation. Therefore, the higher SO₂ concentrations observed in July and August, as well as the higher NO₂ levels occurring from April to August, could be partially attributed to an increase of air masses moving over Cape Town to the CPT GAW. Typical sources of SO₂ and NO₂ in the Cape Town conurbation include industrial activities, vehicular emissions, as well as household combustion for cooking and space heating (Ojumu, 2013). In addition, household combustion for space heating will increase during the colder winter months, while lower occurring inversion layers will trap pollutant species near the surface that will lead to higher concentrations of pollutant species in the Cape Town conurbation during winter.
Figure 4.6: Angular histograms of wind direction frequency (wind roses) at the CPT GAW station from 1995 to 2013 (a), during the annual wet seasons (April to September) from 1995 to 2013 (b), and during the annual dry seasons (October to March) from 1995 to 2013 (c)

The beginning of the increase in $\text{NO}_2$ concentrations also coincides with the onset of the wet season in April. This indicates that $\text{NO}_2$ levels can partially be associated with the emissions of biogenic nitrogen (N) accumulated in the soil (predominantly as ammonium and nitrate) (Adon et al., 2010). CPT GAW is situated in a nature reserve with relatively large populations of grazing animals and sea birds. The excrement of these animals in the dry season will contribute to the accumulation of
the N species in the dry season. After the first rain event occurs, bacterial nitrification is activated, which leads to N consumption that causes the release of large pulses of NO (Ludwig et al., 2001; Laville et al., 2005; Adon et al., 2010) that is rapidly oxidised to NO\textsubscript{2}. The microbial emissions of NO\textsubscript{X} (N\textsubscript{2}O, NO, NO\textsubscript{2}) can be considered to be a significant source of NO\textsubscript{2} measured at the CPT GAW. Another natural source of NO\textsubscript{2} during the wet season is the generation of NO\textsubscript{X} through thunder storms, which are a common natural source of NO\textsubscript{X} (Seinfeld & Pandis, 2006). It is estimated that NO\textsubscript{X} produced by lightning accounts for approximately 10 – 20 % of NO\textsubscript{X} sources worldwide, while it is the single most dominant source in the upper troposphere (Galloway et al., 2004).

As mentioned, O\textsubscript{3} exhibited a similar trend as NO\textsubscript{2}, with O\textsubscript{3} concentrations also gradually starting to increase with the onset of the wet season in April. Atmospheric O\textsubscript{3} is a secondary pollutant that is formed through the photochemical oxidation of NO\textsubscript{2}. Therefore, the production is driven by the emissions of NO\textsubscript{2} into the atmosphere (Connell, 2005). As mentioned, the NO\textsubscript{2} concentrations increase during the onset of the wet season. Therefore, there is an increase in precursor species of O\textsubscript{3} that leads to an increase in O\textsubscript{3} formation, i.e. higher tropospheric O\textsubscript{3} concentrations are associated with higher NO\textsubscript{2} levels in the atmosphere. Stewart et al. (2008) also estimated a relatively high O\textsubscript{3} production rate as a result of high NO\textsubscript{X} concentrations during the AMMA experiment in the Sahel. However, this is an oversimplification that does not account for titration of O\textsubscript{3} with NO\textsubscript{x}. Although the highest O\textsubscript{3} levels coincide with the highest NO\textsubscript{2} concentrations, NO\textsubscript{2} concentrations decrease, while O\textsubscript{3} levels are still relatively high during this period at the end of the wet season during August and September. This can partially be ascribed to lower concentrations of atmospheric NO\textsubscript{x} during these months that causes reduced O\textsubscript{3} titration. In addition, August and September are also associated with increased photochemical oxidation due to longer daylight hours in spring. During the summer months, daylight hours are even longer, but the O\textsubscript{3} concentrations remain relatively low due to fewer precursor species in the atmosphere. Adon et al. (2010) indicated a similar observation for dry (semi-arid) savannahs in West Africa where NO\textsubscript{2} and O\textsubscript{3} levels were also higher during the wet season. Photochemical processes and the exchange between free troposphere and terrestrial surfaces were considered to be
the major sources of \( O_3 \) in the absence of biomass burning in these parts of West Africa.

The photochemical reactions of VOCs with \( \text{NO}_2 \) also produce \( O_3 \) – a major component of smog. During winter, Cape Town is frequented by the occurrence of smog, termed brown haze, which has been linked to impaired visibility, deteriorating health and unpleasant odours (Abiodun et al., 2014). The formation and prevalence of this brown haze are brought about by various topographical and meteorological factors, and it shifts according to the prevailing wind direction (Ojumu, 2013). The prevailing north to west-north-west winds will therefore shift this haze towards Cape Point, increasing pollutant concentrations measured here.

\( \text{NH}_3 \) levels can be attributed to the presence of animal and especially sea bird species being relatively constant throughout a one-year period. Adon et al. (2010) indicated that \( \text{HNO}_3 \) corresponded to higher \( \text{NO}_2 \) concentrations in wet seasons in wet and dry ecosystems, which is not observed at the CPT GAW. However, slightly lower \( \text{HNO}_3 \) levels observed during the wet season (May-September) can be attributed to high \( \text{HNO}_3 \) solubility in water, i.e. leading to higher wet scavenging or removal.

Biomass burning is considered to be a major source of pollutant species (e.g. \( \text{SO}_2 \), \( \text{NO}_2 \) and \( O_3 \)) in the interior of South Africa. Therefore, the impacts of local and regional biomass burning on the concentrations of the gaseous species measured were also investigated. In Figure 4.7, the temporal burn frequency for South Africa from 2008 to 2012, as well as the burn frequency within a 400 km radius from the CPT GAW for the same period obtained from MODIS satellite data is presented. It is evident that the burn frequency is generally higher from June to October in South Africa, peaking in September, which is associated with the dry season in the interior of South Africa. However, limiting the burn frequency within a 400 km radius of the CPT GAW indicates higher burn frequencies coinciding with the dry season in the Western Cape.
As mentioned previously, relatively higher SO$_2$ concentrations were also measured during January and February, while none of the other gaseous species had elevated levels during the dry season. Therefore, it seems that biomass burning is most likely a source of SO$_2$ measured at the CPT GAW during summer. In Figure 4.8, a wind rose compiled from November to April, which are the months with the highest burn frequencies, is presented with a map indicating the 400 km radius surrounding CPT GAW. It is evident that winds arriving at the CPT GAW during this period originate from air masses passing over the Overberg district, which is a large area covered by natural vegetation. This area also houses two South African national parks, i.e. the Agulhas- and Bontebok National Parks. Therefore, this area is susceptible to biomass burning occurring during the dry season, which could have an impact on SO$_2$ concentrations measured at CPT GAW as indicated by the SO$_2$ peak in January and February. However, the emissions of SO$_2$ from biomass burning is not well quantified for the Western Cape. Adon et al. (2010) observed a second NO$_2$ peak in the dry season in dry savannahs in western Africa, which was attributed to biomass burning. However, in this study, an NO$_2$ peak coinciding with biomass burning is not observed at CPT GAW.
As mentioned previously, Ojumu (2013) and Abiodun et al. (2014) reported the long-range transport of atmospheric pollutants from the industrialised Highveld in the interior of South Africa to Cape Town. Therefore, in an effort to establish the influence of the long-range transport of inorganic gaseous species measured at the CPT GAW station, hourly 96-hour overlay back trajectories from 1995 to 2013 were compiled for the periods May to July (highest NO$_2$ concentrations during the wet season) and August to April (lower NO$_2$ concentrations during the mostly dry season), which are presented in Figure 4.9. Although it is understood that the atmospheric lifetimes of species can be shorter than 96 hours, such as SO$_2$, the atmospheric lifetimes does depend on the atmospheric conditions. SO$_2$, for instance will have a longer lifetime in a dry atmosphere since the removal thereof depends on the availability of water to form H$_2$SO$_4$. Furthermore, secondary pollutants such as O$_3$ will only be present in aged air masses. In addition, trajectory analysis performed in other studies indicated that 96-hour trajectories generally represent long-range transport of air masses. 96-hour trajectories can therefore be considered to be representative of the long-range transport of atmospheric pollutants in southern Africa. The colour code indicates the percentage of trajectories passing over 0.2° x 0.2° grid cells; with red being the highest percentage of trajectories passing over a specific cell and dark blue the lowest percentage.
It is evident that during May to July (Figure 4.9 (a)) the CPT GAW station is in more instances affected by air masses moving over the interior of South Africa, which includes the Bushveld Igneous Complex, the Mpumalanga Highveld and the Johannesburg-Pretoria conurbation pollutant source regions (Jaars et al., 2014; Sundström et al., 2015). During this period, concentrations of pollutant species are also higher due to the presence of more pronounced inversion layers trapping pollutants near the surface. In addition, air masses in this part of the interior of South Africa tend to recirculate anti-cyclonically in a persistent high pressure system, which leads to increases in atmospheric pollutant species and the formation of secondary pollutant species. Therefore, the long-range transport of atmospheric species could contribute to the higher concentrations of the inorganic gaseous species measured at the CPT GAW. The relatively higher SO₂, NO₂ and O₃ measured during months in the wet season could also be partially attributed to the CPT GAW station being affected by aged air masses passing over the interior of South Africa (Figure 4.10 (a)).

These overlay back trajectories also indicate that inorganic gas concentration measurements during the dry season (Figure 4.10 (b)) can be considered to be indicative of Southern Hemispheric background trace gas concentrations, which is also reflected by the wind rose presented in Figure 4.6(c). Furthermore, the
continental flow of air masses during the dry season also indicated the impact of biomass burning (Figure 4.7) on SO₂ concentrations as observed in January and February. In addition, the higher frequency of air masses passing over the Cape Town conurbation during the wet season indicated in Figure 4.6(b) is also reflected in the overlay back trajectories shown in Figure 4.10 (a).

Figure 4.10: Hourly-arriving calculated four-day back overlay trajectories for the CPT GAW station during (a) the wet season (annually from April to September), and (b) the dry season (annually from October to March) for the period 1995 to 2013 at CPT GAW

4.1.3 Contextualisation of gaseous concentrations

In Table 4.2, the averages of the atmospheric gaseous concentrations measured at Cape Point from 1995 to 2013 are compared to local and international IDAF (IGAC DEBITS AFrica) sites in tropical regions. With the exception of Amersfoort that is in close proximity of industrial sources, all the sites listed in Table 4.2 are considered to be background sites with no local sources of pollutants.
The average SO$_2$ concentration of 1.3±1.1 ppb measured at Cape Point compares to the average SO$_2$ level determined at Agoufou (1.0±0.2 ppb), while it is slightly higher than the 0.8±0.3 ppb measured at Djougou and Lamto, and the 0.8±0.7 ppb at Louis Trichardt. Biomass burning is considered the main source of SO$_2$ at Agoufou and Djougou, with Lamto experiencing lower impacts of biomass burning (Adon et al., 2010). Biomass burning is also the major source of SO$_2$ at Louis Trichardt (Martins et al., 2007). The average SO$_2$ concentration at Cape Point is approximately half of the SO$_2$ level measured at the industrially impacted Amersfoort. Much lower SO$_2$ concentrations are measured in Bomassa and Okaukuejo, which represent forest and arid regions, respectively. Reported SO$_2$ concentrations at Katibougou and Banizoumbou are ~50% of that measured at Cape Point (≤ 0.6±0.2 ppb).
The average \( \text{NO}_2 \) concentration (1.3±0.6 ppb) measured at Cape Point is close to the \( \text{NO}_2 \) levels determined in the wet savannahs, i.e. 1.2±0.1 ppb at Djougou and 1.0±0.3 ppb measured, as well as in the forest at Bomassa, i.e. 1.4±0.4 ppb. The average \( \text{NO}_2 \) concentrations of 2.5±1.0 ppb at the anthropogenically impacted Amersfoort are approximately two times higher compared to \( \text{NO}_2 \) measured at Cape Point. The average \( \text{NO}_2 \) concentration of 0.7±0.4 ppb at Louis Trichardt is approximately half of the Cape Point \( \text{NO}_2 \) levels. Louis Trichardt is situated in a very dry region in South Africa with low microbial activity causing \( \text{NO}_2 \) emissions form soil. Louis Trichardt is also removed from industrial activities with no large local pollutant sources. Therefore, Cape Point is also more likely to be impacted from emission sources in the relatively nearby Cape Town conurbation, while there are no anthropogenic sources nearby Louis Trichardt. \( \text{NO}_2 \) levels measured for the dry savannah (Agoufou, Katibougou and Banizoumbou) were higher (1.8±0.4, 1.9±0.3 ppb and 2.4±0.4 ppb, respectively) than \( \text{NO}_2 \) measured at Cape Point. The \( \text{NO}_2 \) levels at these sites, which are comparable to \( \text{NO}_2 \) concentrations measured at Amersfoort, were attributed to the impacts of biomass burning (Adon et al., 2010). Much lower \( \text{NO}_2 \) concentrations are observed for the arid Okaukuejo site, which can be attributed to low microbial activity and anthropogenic sources.

The average \( \text{O}_3 \) concentration measured at Cape Point (26.6±4.9 ppb) was similar to \( \text{O}_3 \) levels at all the southern African sites, with a relatively higher \( \text{O}_3 \) concentration at Louis Trichardt (35±8.6 ppb). These average \( \text{O}_3 \) levels measured at the southern African sites are approximately two times higher than the \( \text{O}_3 \) concentrations measured at dry savannahs, i.e. 12.2±2.6, 12.6±2.2 and 11.9±2.3 ppb at Agoufou, Katibougou and Banizoumbou, respectively, as well as wet savannahs, i.e. 14±0.2 and 10.9±1.8 ppb at Djougou and Lamto. Much lower \( \text{O}_3 \) concentrations were measured for forest ecosystems in central Africa, 4.0±0.4 ppb at Bomassa and 4.8±1.0 ppb at Zoetele. \( \text{O}_3 \) concentrations in South Africa can be attributed to the regional impacts of industrial, vehicular, and domestic- and biomass burning emissions experienced in southern Africa, which are re-circulated through anti-cyclonic air mass recirculation. The higher \( \text{O}_3 \) concentration measured at Louis Trichardt can be ascribed to the additional influence of trans-boundary impacts from biomass burning events in sub-Saharan Africa, especially Zambia, Zimbabwe and Angola (Tiitta et al., 2014).
The average HNO\textsubscript{3} concentration of 0.7±0.3 ppb at Cape Point was slightly lower compared to the average HNO\textsubscript{3} level of 0.9±0.5 ppb at Amersfoort (industrialised dry savannah), while it was slightly higher than the averages of 0.5±0.1, 0.4±0.1 and 0.5±0.2 ppb HNO\textsubscript{3} measured at Agoufou, Katibougou and Banizoumbou, respectively (dry savannahs). The average HNO\textsubscript{3} measured at all the other southern, western and central African sites was much lower than the HNO\textsubscript{3} measured at Cape Point, with Louis Trichardt recording the lowest HNO\textsubscript{3} concentration of 0.2±0.1 ppb.

The average NH\textsubscript{3} concentration at Cape Point of 1.7±0.5 ppb is relatively higher compared to the average NH\textsubscript{3} levels measured at the other southern African sites (1.2±0.7 ppb at Louis Trichardt and Amersfoort, 1.5±0.7 ppb at Okaukuejo). However, the NH\textsubscript{3} concentrations at Cape Point were approximately between three and six times lower compared to the NH\textsubscript{3} concentrations measured at the western and central African sites, which ranged between 3.9 ppb at Djougou and 7.4 ppb at Agoufou. The relatively high concentrations at the western and central African sites can be attributed to high NH\textsubscript{3} concentrations from agricultural activities, livestock and the use of biofuels (e.g. animal dung) (Carmichael \textit{et al.}, 2003). The major source of NH\textsubscript{3} at Cape Point could be considered to be guano from sea birds at this coastal site, as well as other animals in the nature reserve wherein the CPT GAW is situated.

4.2 Dry deposition

Dry deposition velocity is specific for each atmospheric gaseous species and each region (Vet \textit{et al.}, 2014). As mentioned in Chapter 2, direct and indirect methods are available to determine dry deposition fluxes. It was decided within the DEBITS project that an indirect approach will be followed at the tropical and sub-tropical sites due to the difficulties associated with operating sophisticated direct flux measurement at remote sites (Sutton \textit{et al.}, 2007; Wolff \textit{et al.}, 2010). Therefore, an inferential technique was utilised in this study to estimate dry deposition fluxes from the atmospheric gas concentrations measured and modelled dry deposition velocities (Wesely & Hicks, 2000; Zhang \textit{et al.}, 2005; Shen \textit{et al.}, 2009; Delon \textit{et al.},
2010; Adon et al., 2013). Zhang et al. (2003) and Vet et al. (2014) presented modelled dry deposition velocities for different land use categories (LUCs). These calculations of gaseous dry deposition velocities involved the estimation of the aerodynamic resistance, quasi-laminar sub-layer resistance and the canopy resistance. The dry deposition velocities presented for deciduous shrub and thorn shrub by Zhang et al. (2003) and Vet et al. (2014) were considered to be relatively good estimations for the Fynbos biome wherein the CPT GAW is situated, since no deposition velocity was determined specifically for this unique LUC. The uncertainties associated with using these estimated dry deposition velocities for other LUCs are understood. However, since there are no measured or modelled deposition velocities available in literature for the Fynbos biome, these rough estimates will at least provide an indication of dry deposition at the CPT GAW. Furthermore, the seasonal fluctuations associated with deposition velocities were also not considered. Therefore, the gaseous dry deposition velocities used in this study for each of the gaseous species are presented as ranges of deposition velocities (minimum and maximum), as indicated in Table 4.3.

<table>
<thead>
<tr>
<th>Table 4.3: Gaseous dry deposition velocities $u_5$ (cm·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_2^\dagger$</td>
</tr>
<tr>
<td>$NO_2^\dagger$</td>
</tr>
<tr>
<td>$HNO_3^\dagger$</td>
</tr>
<tr>
<td>$NH_3^\dagger$</td>
</tr>
<tr>
<td>$O_3^\dagger$</td>
</tr>
</tbody>
</table>

($^\dagger$Zhang et al., 2003; $^\ddagger$Vet et al., 2014)

It must also be noted that in order to calculate total dry deposition, both particulate and gaseous dry deposition fluxes must be determined (Vet et al., 2014). Since the focus of this study was the measurement of the concentrations and deposition of gaseous species at the CPT GAW, only the gaseous dry depositions are presented and discussed in the subsequent sections. The annual average gaseous dry depositions of each of the gases calculated in this study are listed in Table 4.4.
together with dry deposition fluxes determined at other IDAF measurement sites. The results presented in Table 4.4 are discussed in subsequent sections.

4.2.1 Sulphur dioxide (SO$_2$)

Annual average SO$_2$ fluxes ranged between 0.6±0.5 and 1.4±1.2 kg S.ha$^{-1}$.yr$^{-1}$ at the CPT GAW (Table 4.4), which compares well with the S dry deposition fluxes in the dry savannahs of west and central Africa, ranging from 0.5±0.2 kg S.ha$^{-1}$.yr$^{-1}$ at Banizoumbou to 0.7±0.3 kg S·ha$^{-1}$.yr$^{-1}$ at Katibougou and Agoufou, which can be compared to lower estimated SO$_2$ fluxes at the CPT GAW. The wet savannahs of Djougou and Lamto (0.9±0.2 kg S·ha$^{-1}$.yr$^{-1}$ and 0.8±0.4 kg S·ha$^{-1}$.yr$^{-1}$ respectively), and forests of Bomassa and Zoetele (1.0±0.5 kg S·ha$^{-1}$.yr$^{-1}$ and 0.8±0.3 kg S·ha$^{-1}$.yr$^{-1}$ respectively) exhibited relatively higher gaseous sulphur dry deposition that compares well to the higher end range of SO$_2$ fluxes estimated at the CPT GAW. Comparison of the S flux measured at CPT GAW to the southern African sites indicates that S fluxes at Louis-Trichardt (1.1±0.7 kg S·ha$^{-1}$.yr$^{-1}$) were similar than the higher S fluxes estimated, while the rate of sulphurous dry deposition at Amersfoort (2.4±0.9 kg S·ha$^{-1}$.yr$^{-1}$) was two times higher. The higher deposition at Amersfoort can be expected due to the high SO$_2$ concentrations measured at Amersfoort that are related to its proximity to the industrialised Highveld, as previously mentioned. It is interesting to note that even though Louis Trichardt exhibited lower annual SO$_2$ concentrations (Table 4.1) than the CPT GAW, the rate of sulphurous deposition was higher at Louis Trichardt, which can be attributed to higher deposition velocities estimated for Louis Trichardt. The lowest S dry deposition flux in the IDAF network was reported for Okaukuejo, i.e. 0.3±0.2 kg S·ha$^{-1}$.yr$^{-1}$. 
<table>
<thead>
<tr>
<th>Location</th>
<th>Ecosystem</th>
<th>( \text{SO}_2 ) (S) (^\dagger)</th>
<th>( \text{NO}_2 ) (N) (^\ddagger)</th>
<th>( \text{HNO}_3 ) (N) (^\ddagger)</th>
<th>( \text{NH}_3 ) (N) (^\ddagger)</th>
<th>Total N (^\ddagger)</th>
<th>( \text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Point, SA (1995-2013)</td>
<td>Marine / Coastal</td>
<td>0.6±0.5 — 1.4±1.2</td>
<td>0.6±0.3 — 0.8±0.3</td>
<td>2.2±0.6 — 2.6±0.7</td>
<td>3.1±1.0 — 4.0±1.3</td>
<td>11.7±2.2 — 57.1±10.6</td>
<td></td>
</tr>
<tr>
<td>Louis Trichardt, SA (1995-2005)</td>
<td>Dry savannah</td>
<td>1.1±0.7</td>
<td>0.5±0.2</td>
<td>1.0±0.3</td>
<td>1.0±0.6</td>
<td>2.5±1.1</td>
<td>87±21</td>
</tr>
<tr>
<td>Amersfoort, SA (1997-2005)</td>
<td>Dry savannah</td>
<td>2.4±0.9</td>
<td>0.6±0.2</td>
<td>0.9±0.5</td>
<td>0.5±0.3</td>
<td>2.0±1.2</td>
<td>23±5</td>
</tr>
<tr>
<td>Okaukuejo, Namibia (1994-2005)</td>
<td>Desert</td>
<td>0.3±0.2</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.2±0.1</td>
<td>0.4±1.6</td>
<td>25±7</td>
</tr>
<tr>
<td>Agoufou, Mali (2005-2007)</td>
<td>Dry savannah</td>
<td>0.7±0.3</td>
<td>0.4±0.1</td>
<td>0.7±0.3</td>
<td>2.9±0.4</td>
<td>4.0±0.9</td>
<td>11.2±3.3</td>
</tr>
<tr>
<td>Katibougou, Mali (1998-2007)</td>
<td>Dry savannah</td>
<td>0.7±0.3</td>
<td>0.7±0.1</td>
<td>0.8±0.2</td>
<td>3.9±0.6</td>
<td>5.4±0.7</td>
<td>17.2±2.7</td>
</tr>
<tr>
<td>Banizoumbou, Niger (1998-2007)</td>
<td>Dry savannah</td>
<td>0.5±0.2</td>
<td>0.6±0.1</td>
<td>0.7±0.3</td>
<td>2.7±0.9</td>
<td>4.0±1.0</td>
<td>12.7±2.4</td>
</tr>
<tr>
<td>Djougou, Benin (2005-2007)</td>
<td>Wet savannah</td>
<td>0.9±0.2</td>
<td>0.4±0.1</td>
<td>0.7±0.2</td>
<td>2.2±0.7</td>
<td>3.3±0.9</td>
<td>16.9±3.2</td>
</tr>
<tr>
<td>Lamto, Ivory Coast (1998-2007)</td>
<td>Wet savannah</td>
<td>0.8±0.4</td>
<td>0.4±0.1</td>
<td>0.7±0.1</td>
<td>3.5±1.0</td>
<td>4.6±0.8</td>
<td>19.3±3.4</td>
</tr>
<tr>
<td>Bomassa, Congo (1998-2006)</td>
<td>Forest</td>
<td>1.0±0.5</td>
<td>0.8±0.2</td>
<td>1.0±0.3</td>
<td>10.0±3.3</td>
<td>11.8±0.9</td>
<td>10.6±0.7</td>
</tr>
<tr>
<td>Zoetele, Cameroon (1998-2007)</td>
<td>Forest</td>
<td>0.8±0.3</td>
<td>0.5±0.1</td>
<td>1.0±0.3</td>
<td>9.7±2.2</td>
<td>11.2±0.9</td>
<td>13.2±2.9</td>
</tr>
</tbody>
</table>

(Martins, 2009; Adon et al., 2013); \(^\dagger\) kg S ha\(^{-1}\) yr\(^{-1}\); \(^\ddagger\) kg N ha\(^{-1}\) yr\(^{-1}\)
In Figure 4.11, the average monthly rate of deposition of SO$_2$ measured for the entire sampling period is presented in order to assess seasonal variability. As expected, a similar trend is observed compared to the trend indicated for atmospheric SO$_2$ concentrations, i.e. two periods with higher S dry deposition fluxes in January to February, and July to August. As mentioned previously, these higher levels coincided with peak biomass burning periods around the CPT GAW area and the impacts of higher SO$_2$ levels present during winter (June to August). The rate of S dry deposition during the wet season (April to September) at the CPT GAW is estimated to be between 0.52±0.43 kg S.ha$^{-1}$.yr$^{-1}$ and 1.28±1.05 kg S.ha$^{-1}$.yr$^{-1}$, while the S dry deposition flux is estimated to be between 0.66±0.66 kg S.ha$^{-1}$.yr$^{-1}$ and 1.62±1.61 kg S.ha$^{-1}$.yr$^{-1}$ during the dry season (October to March).

Figure 4.11: The lower and upper limits of the calculated dry deposition are given for each month. Seasonal SO$_2$ gaseous dry deposition is calculated for the period 1995 to 2013. The red line of each box represents the median, the top and bottom of the box the 25$^{th}$ and 75$^{th}$ percentiles, respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution), the black dots the averages and the crosses the maximum gaseous dry deposition. The maximum gaseous dry deposition and the number of measurements (N) are presented at the top.
4.2.2 Nitrogen dioxide (NO₂)

The gaseous nitrogen dry deposition resulting from NO₂ flux calculated for CPT GAW is compared with other IDAF sites in Table 4.4. The annual average NO₂ fluxes were estimated to be 0.6±0.3 kg N.ha⁻¹.yr⁻¹. From Table 4.4, it is evident that the NO₂ fluxes measured at all the IDAF sites were comparable to each other with the exception of Okaukuejo, which exhibited the lowest rate of N deposition (0.1±0.1 kg N.ha⁻¹.yr⁻¹). Annual average NO₂ fluxes measured at the other South African sites at Louis Trichardt and Amersfoort were 0.5±0.2 kg N.ha⁻¹.yr⁻¹ and 0.6±0.2 kg N.ha⁻¹.yr⁻¹, respectively. The west and central African dry savannah NO₂ dry deposition rates ranged from 0.4±0.1 kg N.ha⁻¹.yr⁻¹ to 0.7±0.1 kg N.ha⁻¹.yr⁻¹ at Agoufou and Katibougou, respectively, while the wet savannah NO₂ fluxes ranged between 0.4±0.1 kg N.ha⁻¹.yr⁻¹ at Djougou and Lamto to 0.6±0.1 kg N.ha⁻¹.yr⁻¹ at Banizoumbou. The forest regions of Bomassa and Zoetele exhibited NO₂ dry deposition rates of 0.8±0.2 kg N.ha⁻¹.yr⁻¹ and 0.5±0.1 kg N.ha⁻¹.yr⁻¹ respectively.

From Figure 4.12, it is evident that NO₂ fluxes were higher during April to August, which correlates with the seasonal pattern observed for atmospheric NO₂ concentrations, i.e. higher N fluxes associated with higher NO₂ concentrations. As discussed previously, these elevated levels of the rate of N deposition can be attributed to an increase in impacts of the long-range transport of air masses from higher pollutant levels from the industrialised interior of South Africa at the CPT GAW, increased influence from air masses passing over the Cape Town conurbation and increases in microbial activity with the onset of the wet season. Wet seasonal nitrogen dry deposition rate at the CPT GAW associated with NO₂ deposition is estimated to be between 0.77±0.37 kg N.ha⁻¹.yr⁻¹ and 0.85±0.41 kg N.ha⁻¹.yr⁻¹, while dry seasonal N flux is estimated to range between 0.39±0.17 kg N.ha⁻¹.yr⁻¹ and 0.43±0.18 kg N.ha⁻¹.yr⁻¹ that is almost half of the N flux determined during the wet season.
Figure 4.12: The lower and upper limits of the calculated dry deposition are given for each month. Seasonal NO$_2$ gaseous dry deposition is calculated for the period 1995 to 2013. The red line of each box represents the median, the top and bottom of the box the 25$^{th}$ and 75$^{th}$ percentiles respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution), the black dots the averages and the crosses the maximum gaseous dry deposition. The maximum gaseous dry deposition and the number of measurements (N) are presented at the top.

4.2.3 Ammonia (NH$_3$)

Annual average NH$_3$ fluxes at the CPT GAW ranged between 2.2±0.6 kg N.ha$^{-1}$.yr$^{-1}$ and 2.6±0.7 kg N.ha$^{-1}$.yr$^{-1}$ as indicated in Table 4.4. These NH$_3$ fluxes were much higher compared to the other South African sites, i.e. approximately five times higher compared to the annual rate of NH$_3$ deposition at Amersfoort and approximately 2.5 times higher compared to NH$_3$ flux levels determined at Louis Trichardt. The CPT GAW NH$_3$ annual deposition was similar to NH$_3$ fluxes determined at Banizoumbou (2.7±0.9 kg N.ha$^{-1}$.yr$^{-1}$), Agoufou (2.9±0.4 kg N.ha$^{-1}$.yr$^{-1}$) and Djougou (2.2±0.7 kg N.ha$^{-1}$.yr$^{-1}$). The forests in Bomassa and Zoetele exhibited substantially higher annual rates of NH$_3$ dry deposition, i.e. 10.0±3.3 kg N.ha$^{-1}$.yr$^{-1}$ and 9.7±2.2 kg N.ha$^{-1}$.
Okaukuejo revealed the lowest NH$_3$ dry deposition of 0.2±0.1 kg N.ha$^{-1}$.yr$^{-1}$.

In Figure 4.13, the average monthly NH$_3$ fluxes determined are presented, which indicate no distinct seasonal trend. The average NH$_3$ deposition rate during the wet season (April to September) is estimated to range between 2.13±0.93 kg N.ha$^{-1}$.yr$^{-1}$ and 2.46±1.07 kg N.ha$^{-1}$.yr$^{-1}$, which is slightly lower compared to the average NH$_3$ determined during the dry season (October to March) that ranged between 2.31±0.67 kg N.ha$^{-1}$.yr$^{-1}$ and 2.67±0.77 kg N.ha$^{-1}$.yr$^{-1}$.

**Figure 4.13** The lower and upper limits of the calculated dry deposition are given for each month. Seasonal NH$_3$ gaseous dry deposition is calculated for the period 1995 to 2011. The red line of each box represents the median, the top and bottom of the box the 25$^{th}$ and 75$^{th}$ percentiles respectively, the whiskers ±2.7$\sigma$ (99.3% coverage if the data has a normal distribution), the black dots the averages and the crosses the maximum gaseous dry deposition. The maximum gaseous dry deposition and the number of measurements (N) are presented at the top.
4.2.4 Nitric acid (HNO₃)

Dry HNO₃ deposition at CPT GAW annually deposits N at deposition rates ranging between 0.3±0.1 kg N.ha⁻¹.yr⁻¹ and 0.8±0.3 kg N.ha⁻¹.yr⁻¹ (Table 4.4). With the exception of HNO₃ flux determined at Okaukuejo, the lower estimated rate of HNO₃ deposition at CPT GAW is lower compared to all the other southern, western and central African IDAF sites. However, the higher estimated HNO₃ flux compared relatively well with all the IDAF sites and is within the same range compared to the other South African sites.

No HNO₃ dry deposition seasonality is observed at the CPT GAW for the period 2003 to 2013, as shown in Figure 4.14. Wet seasonal N dry deposition rates due to HNO₃ deposition are estimated to be between 0.27±0.13 kg N.ha⁻¹.yr⁻¹ and 0.77±0.36 kg N.ha⁻¹.yr⁻¹, which are similar to the dry seasonal N dry deposition flux ranging between 0.31±0.16 kg N.ha⁻¹.yr⁻¹ and 0.88±0.44 kg N.ha⁻¹.yr⁻¹.

Figure 4.14: The lower and upper limits of the calculated dry deposition are given for each month. Seasonal HNO₃ gaseous dry deposition is calculated for the period 2003 to 2013. The red line of each box represents the median, the top and bottom of the box the 25th and 75th percentiles respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution), the black dots the averages and the crosses the maximum gaseous dry deposition. The maximum gaseous dry
deposition and the number of measurements \((N)\) are presented at the top.

### 4.2.5 Total nitrogen \((N)\)

The annual total gaseous nitrogen dry deposition fluxes, comprising \(\text{NO}_2\), \(\text{HNO}_3\) and \(\text{NH}_3\) fluxes, are estimated to range between 3.1±1.0 and 4.0±1.3 kg N ha\(^{-1}\) yr\(^{-1}\). The total N deposition fluxes at the CPT GAW are higher compared to the two other South African dry savannah sites, i.e. 2.5±1.1 kg N ha\(^{-1}\) yr\(^{-1}\) at Louis Trichardt and 2.0±1.2 kg N ha\(^{-1}\) yr\(^{-1}\) at Amersfoort. The total N fluxes are similar to total N fluxes determined at Agoufou (4.0±0.9 kg N ha\(^{-1}\) yr\(^{-1}\)), Banizoumbou (4.0±1.0 kg N ha\(^{-1}\) yr\(^{-1}\)) and Djougou (3.3±0.9 kg N ha\(^{-1}\) yr\(^{-1}\)). Total N deposition fluxes in the forests of Bomassa and Zoetele were 11.2±0.9 and 11.8±0.9 kg N ha\(^{-1}\) yr\(^{-1}\), respectively, which are substantially higher compared to all the IDAF sites. The high total N deposition in a forest ecosystem can mainly be attributed to high \(\text{NH}_3\) fluxes (Adon et al., 2013).

It is estimated that annual average \(\text{NO}_2\) flux contributes to approximately 17.2%, annual average \(\text{NH}_3\) flux approximately 68% and dry \(\text{HNO}_3\) deposition to approximately 14.8% of the total annual N flux at the CPT GAW. At the West and central African sites, \(\text{NH}_3\) also has the highest contribution to the total N flux (Table 4.4). However, at the other two South African sites, larger contributions from the other N species are observed. At Amersfoort, the largest contributor to total N flux is \(\text{HNO}_3\) (45%), while at Louis Trichardt the highest contributions are from both \(\text{HNO}_3\) (40%) and \(\text{NH}_3\) (40%).

### 4.2.6 Ozone \((O_3)\)

\(O_3\) dry deposition at CPT GAW ranged between 11.7±2.2 kg ha\(^{-1}\) yr\(^{-1}\) and 57.1±10.6 kg ha\(^{-1}\) yr\(^{-1}\) depending on the two \(u_d\) used in the calculation. The large difference in the two estimated \(O_3\) fluxes can be attributed to the difference between the two deposition velocities used. The lower estimated are similar to \(O_3\) deposition at two dry savannah sites, i.e. Agoufou (11.2±3.3 kg ha\(^{-1}\) yr\(^{-1}\)) and Banizoumbou (12.7±2.4 kg ha\(^{-1}\) yr\(^{-1}\)) in western Africa, as well as the \(O_3\) deposition at the two forest sites in
The higher O$_3$ deposition velocities in forests can be attributed to higher O$_3$ rates of deposition in relation to the low O$_3$ levels measured at these sites. The higher estimated O$_3$ flux at the CPT GAW can be considered to be very high deposition and, although not completely similar, can be compared to the high O$_3$ flux determined at Louis Trichardt (87±21 kg.ha$^{-1}$.yr$^{-1}$). As mentioned previously, Louis Trichardt is a regional background sites that is impacted by aged air masses passing over the industrialised interior of South Africa leading to elevated O$_3$ levels. O$_3$ concentrations at Louis Trichardt are also higher compared to O$_3$ levels at Amersfoort, which is in close proximity to the industrialised region, which also has an associated lower O$_3$ flux (23±5 kg.ha$^{-1}$.yr$^{-1}$). Furthermore, Louis Trichardt is situated in a different LUC than Amersfoort that has higher deposition velocities. Relatively high O$_3$ flux (25±7 kg.ha$^{-1}$.yr$^{-1}$) was also determined in the desert southern African site, Okaukuejo, which reflects the regional elevated O$_3$ levels in southern Africa.

As expected, a similar trend is observed for the average monthly O$_3$ dry deposition fluxes presented in Figure 4.15 than the trend observed for average monthly concentrations (Figure 4.4), i.e. higher O$_3$ concentrations associated with higher O$_3$ fluxes. As mentioned previously, the months with higher O$_3$ dry deposition can be attributed to increased impacts of aged air masses passing over the polluted interior of South Africa, as well as an increase in impacts of air masses passing over the Cape Town conurbation. O$_3$ dry deposition during the wet season (April to September) at the CPT GAW was calculated to range between 13.24±2.81 kg.ha$^{-1}$.yr$^{-1}$ and 64.29±13.63 kg.ha$^{-1}$.yr$^{-1}$, which is significantly higher compared to the estimated O$_3$ dry deposition during the dry season (October to March) that was determined to be between 10.19±2.13 kg.ha$^{-1}$.yr$^{-1}$ and 49.49±10.36 kg.ha$^{-1}$.yr$^{-1}$.
Figure 4.15: The lower and upper limits of the calculated dry deposition are given for each month. Seasonal O₃ gaseous dry deposition is calculated for the period 1995 to 2013. The red line of each box represents the median, the top and bottom of the box the 25th and 75th percentiles respectively, the whiskers ±2.7σ (99.3% coverage if the data has a normal distribution), the black dots the averages and the crosses the maximum gaseous dry deposition. The maximum gaseous dry deposition and the number of measurements (N) are presented at the top.
Chapter 5

Project evaluation and future perspectives

In this chapter, the study is evaluated according to the successes achieved and the shortcomings of the study. Future recommendations are also proposed.

5.1 Project evaluation

The general aim of this study was to establish long-term annual and seasonal trends for atmospheric inorganic gaseous species measured at the Cape Point Global Atmosphere Watch (CPT GAW) station, to determine the most important sources of these species and to estimate the gaseous dry deposition of these atmospheric inorganic gaseous compounds. Specific objectives listed in Chapter 1 were identified in order to obtain these aims. The investigation is evaluated in view of successes and shortcomings by evaluating each specific objective in the subsequent sections.

5.1.1 Objective 1

Long-term sampling of SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ with passive samplers at CPT GAW station

**Successes**

Passive sampling of SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ concentrations commenced in 1995 at the CPT GAW and it is presently still on going. Together with another Deposition of Biogeochemical Important Trace Species (DEBITS) site, i.e. Louis Trichardt, this is largest continuous long-term dataset that exists for these inorganic gaseous species in southern Africa. Passive samplers were successfully prepared by the Atmospheric Chemistry Research Group (ACRG) at the North-West University’s Potchefstroom Campus (NWU-PC), as well as deployed and collected by the personnel of South African Weather Service (SAWS) operating the CPT GAW...
station. The logging system utilised by the ACRG during this entire sampling period indicated a few instances where exposed samplers were not acceptable due to logistical problems and contamination, e.g. getting wet during a rain event. The collection efficiency was very good.

**Shortcomings**

Apart from the few instances where samplers could not be analysed due to problems encountered during the shipment, deployment and collection of samplers, no other shortcomings were encountered with the passive sampling procedure. However, the shortcomings with applying passive samplers compared to the use of continuous or active sampling methods (section 2.4) are realised. A major deficiency associated with the use of passive samplers is that only monthly atmospheric inorganic gaseous concentrations can be determined and instantaneous peaks of pollutant concentrations cannot. However, passive sampling can still be considered a simple and cost-effective method of sampling.

**Future perspectives**

The use of continuous active samplers to monitor these atmospheric inorganic species in future is recommended. Active measurements must also be compared to passive samplers at the CPT GAW in order to continue with the long-term trend measured at this site.

### 5.1.2 Objective 2

Analysis of passive samplers with appropriate analytical techniques that comply with international analytical guidelines, and processing the analytical results to determine atmospheric concentrations of inorganic gaseous species

**Successes**

Analyses of all SO₂, HNO₃ and O₃ samples were successfully performed using ion chromatography (IC) techniques. Ultraviolet/visible (uv/vis) spectrometry was conducted to analyse NO₂ and NH₃ samplers up until the end of December 2012,
after which IC techniques were established for the analysis of these two species. This can be considered to be a major achievement, since this allowed for more accurate analyses and also led to more time efficient analyses of the passive samplers. The use of corrosive chemicals was also excluded. The IC system was successfully optimised and programmed to perform analyses of all five ionic species associated with the relevant inorganic gases within a reasonable running time and also achieving good accuracy. Participation in the World Meteorological Organisation (WMO) bi-annual laboratory inter-comparison study (LIS) programme ensured external verification of the analytical procedure applied.

Analytical concentrations with ionic concentrations in aqueous solution were successfully converted to determine atmospheric concentrations of the inorganic gaseous species. Effective statistical identification of outlier concentrations was also performed. Mathematical programming software was successfully applied for further processing of the dataset.

**Shortcomings**

In some of the samples analysed during the WMO LIS study, there were instances where some of the detected species were not within acceptable concentration ranges. Additionally, by applying the Q-test, it was also established that several NH₃ samples exhibited concentrations much higher for the period May 2011 to June 2013, which was attributed to analytical errors. This data was removed from the dataset and not used further.

**Future perspectives**

Although major improvements were made on the analytical technique employed, the WMO LIS did indicate a few unsatisfactory results. Therefore, it is recommended that the IC procedures employed are further improved.
5.1.3 Objective 3

Assess seasonal and inter-annual atmospheric concentrations of inorganic gaseous compounds at the CPT GAW station and compare annual average concentrations with other sites.

Successes

Inter-annual variability and seasonal trends were successfully assessed in this study. Inter-annual variability could be attributed to changes in meteorology and impacts of sources was observed for all species considered in this investigation. Small inter-annual variability were observed for O₃, NH₃ and HNO₃. However, SO₂ and NO₂ indicated distinct decreases from 1995 to 2002, followed by a period of increase in annual average concentrations after 2002. Distinct seasonal patterns were observed for SO₂, NO₂ and O₃. NO₂ peaked from April to August, while O₃ revealed elevated levels from July to October. SO₂ had higher concentrations during two periods of the year, i.e. January to February, and July to August. The annual average concentrations of the inorganic gaseous species were also compared to other sites in the IGAC DEBITS Africa (IDAF) network.

Shortcomings

Although the inter-annual variability for SO₂ and NO₂ indicated two periods with distinct tendencies, more data is required to substantiate decadal trends. No deductions could be made from long-term NH₃, HNO₃ and O₃ concentrations.

Future perspective

It is recommended that quantitative trend analysis is performed on the datasets in order to determine long-term trends.

5.1.4 Objective 4

Determine possible sources of atmospheric inorganic species at the CPT GAW station by exploring air mass movement, meteorology and fire event frequencies.
Successes

Natural and anthropogenic sources could be identified as possible sources of the species considered by contributing to inter-annual variability and seasonal patterns. Back trajectory analysis was successfully applied to determine predominant air mass movement during different periods of the year. Back trajectories were determined with the HYSPLIT model and processed in Matlab®. Meteorological data was also obtained from the SAWS, while fire event frequencies were acquired from satellite retrievals of the MODIS collection 5 burned area product. The SO$_2$, NO$_2$ and O$_3$ peaks observed during the winter months (June to August) could at least partially be attributed to an increase in the long-range transport of pollutant species as indicated by the increase in air mass movement from the industrialised interior of South Africa arriving at the CPT GAW. Back trajectory analysis and meteorological data also indicated the impacts of more air masses passing over the Cape Town conurbation. Fire event frequencies indicated that increased burning during January and February could contribute to elevated SO$_2$ concentrations measured during these two months. An increase in NO$_2$ concentrations during the wet season was also attributed to increased microbial activity.

Shortcomings

Although sources of SO$_2$, NO$_2$ and O$_3$ could be determined, no distinct source could be determined for NH$_3$ and HNO$_3$. Stratospheric injection of O$_3$ was not considered during the processing of air mass back trajectories.

Future perspectives

Although back trajectory analysis, meteorological data and fire events could be successfully used to identify possible sources SO$_2$, NO$_2$ and O$_3$, higher resolution data obtained from active measurements would allow for more conclusive evidence of different sources of these species, as well as determine the sources of NH$_3$ and HNO$_3$. Statistical analyses, such as principle component analysis, could be used to further substantiate sources of these species. In addition, modelling studies must also be conducted in order or assist with identifying sources.
5.1.5 Objective 5

Determine dry deposition of atmospheric inorganic gaseous compounds

Successes

Gaseous deposition velocities for SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ were obtained from literature from which the average annual sulphur (S) and nitrogen (N), as well as O$_3$ dry deposition could be calculated. The total N (NO$_2$ + NH$_3$ + HNO$_3$) deposition was also determined. Dry deposition fluxes were contextualised by comparing them to dry depositions measured at other IDAF sites in southern, western and central Africa. Estimated S dry deposition at the CPT GAW compared well with the other IDAF sites, with the exception of the industrially impacted Amersfoort where S deposition was two times higher. NO$_2$ and HNO$_3$ dry N depositions were within the same range at all the IDAF sites. Relatively large differences were observed for N deposition associated with NH$_3$. NH$_3$ fluxes at the CPT GAW were higher compared to other southern African sites, but lower compared to NH$_3$ deposition at sites in forests in central Africa. NH$_3$ had the highest contribution to total N deposition fluxes measured at the CPT GAW.

The seasonal patterns determined for dry deposition of SO$_2$, NO$_2$, NH$_3$, HNO$_3$ and O$_3$ coincided with seasonal trends observed for atmospheric gaseous species, i.e. higher concentrations of these species associated with higher deposition. This could be attributed to the deposition velocities used in this study, which were kept constant for each of the months throughout the year.

Shortcomings

One of the major deficiencies of the dry deposition calculated in this study was attributed to the use of modelled deposition velocities determined for land use categories (LUC) that was considered to be similar to the unique Fynbos biome where the CPT GAW is situated (Zhang et al., 2003). There were no deposition velocities available in literature specifically for this distinctive LUC. Modelling of deposition velocities was beyond the scope of this study. Modelling would have allowed the determination of different deposition velocities for each month of the year, which would have indicated seasonality associated with deposition better
(Adon et al., 2013). The direct measurement of deposition fluxes is very sophisticated and currently there is only one instrument that measures SO$_2$ and NO$_2$ fluxes in South Africa, which only commenced in 2015.

**Future perspectives**

It is recommended that gaseous dry deposition velocities for the Fynbos LUC are specifically determined for each of the gaseous species by utilising an appropriate model, e.g. inferential modelling. This would increase the accuracy of the dry deposition fluxes calculated for the CPT GAW. Furthermore, seasonal patterns, i.e. deposition velocities for each month, can be calculated. It is also recommended that modelled deposition fluxes are compared to the SO$_2$ and NO$_2$ fluxes measured directly at Welgegund in South Africa, which will further improve the estimates of gaseous dry deposition calculated at CPT GAW, as well as for dry gaseous deposition fluxes determined in general for southern Africa.

In this study, the dry deposition associated only with gaseous species was considered. In order to establish total dry deposition, aerosol deposition must also be determined. Furthermore, total deposition must also be established by combining the wet deposition with total dry deposition.
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