

Wet deposition at a regional background site in South Africa – influence of air mass origin and rain intensity on chemical composition

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Abstract

The chemical composition of rainwater is an integral aspect of atmospheric chemistry. Wet deposition gives a good indication of the general ambient air quality and contributes to the understanding of the temporal and spatial evolution of atmospheric processes. There are numerous micro-physical, chemical and temporal processes that contribute to the eventual precipitation chemistry. In order to accurately assess the chemical contributions to rainwater, the environments where both the cloud formation and the rain event occurred need to be taken into account. In this study, wet deposition was measured at a regional background site in South Africa from December 2014 to July 2016. For this sampling period, two 10 month periods could be identified that represented two separate rain seasons. Ionic concentrations of nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), acetic acid (CH_3COO^-), formic acid (HCOO^-), oxalic acid ($\text{C}_2\text{O}_4^{2-}$), propionic acid ($\text{C}_3\text{H}_5\text{O}_2^-$), ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were analysed. In addition, the pH and electrical conductivity (EC) was also determined. A pilot method was developed to relate event-based cloud- and below-cloud air mass histories to the precipitation chemistry. In this method, back trajectory analysis was performed with the HYSPLIT v4.8 model using event-based parameters, i.e. cloud base height (CBH) and rain intensity measurements. The influence of major pollution point sources and source regions on the precipitation chemistry was investigated through event-based comparison of the chemical composition of the rainwater with the associated air mass histories.

The precipitation chemistry results indicated that SO_4^{2-} had the highest volume weighted mean (VWM) concentration, with NO_3^- , Ca^{2+} and NH_4^+ having the second, third and fourth highest VWMs, respectively. SO_4^{2-} concentrations were similar to industrially influenced South African DEBITS (Deposition of Biogeochemical Important Trace Species) sites, i.e. Amersfoort and Vaal Triangle, where previous precipitation chemistry studies have been conducted. The concentrations of NO_3^- and NH_4^+ were higher compared to concentrations thereof at the South African DEBITS sites. The mean pH of 4.65 indicated that precipitation was acidic. pH frequency distributions indicated that 88% of rain events had pH levels < 5.7 , i.e. the natural pH of rain. Source group contributions were estimated with Spearman correlations and empirical calculations. Fossil fuel combustion had the largest source contribution to the precipitation chemistry, while marine and terrigenous source groups had slightly lower contributions than fossil fuel. Agricultural source contributions were notable, with biomass burning contributions having the smallest influence. The ionic concentrations and pH of the rainwater increased over the dry austral winter months, which were attributed to prominent low-level inversion layers and anticyclonic recirculation of air masses. The

second drier sampling period indicated higher pH levels, which could be attributed to neutralisation by increased levels of Ca^{2+} and Mg^{2+} associated with wind-blown dust. In addition, Ca^{2+} was also indicated as the most important neutralising factor at Welgegund. Although a relatively small source contribution was determined from biomass burning, which was attributed to the veld fire season (June to mid-October) in South Africa not coinciding with the wet season (mid-October to April), the influence of veld fires was also indicated by the correlations between K^+ , Cl^- and organic acids.

The air mass histories associated with the CBH and below-cloud base level were related to the precipitation chemistry. Rain events with similar CBH- and below-cloud air mass histories indicated a prominent influence of point sources and/or source regions over which these air masses have passed. Rain events for which back trajectory sets for both the CBH and the below-cloud related air masses passed over the major pollution point source region east of Welgegund, indicated elevated concentrations of anthropogenic related pollutants (i.e. SO_4^{2-} , NO_3^-). In contrast, lower ionic concentrations were measured for rain events where both back-trajectory sets originated from the relatively cleaner western sector. The efficient scavenging and washout effect of rain was demonstrated for two rain events with similar air mass histories occurring on two consecutive days. The build-up of pollutants during winter was also indicated by the ionic concentrations measured for winter rain events. The influence of wildfires close to and distant from Welgegund was also indicated. The results obtained in this pilot study clearly highlighted the key influence of air mass history on rainwater chemistry. The method must be further developed by including more event-based parameters such as synoptic weather patterns, precipitation type and rain intensity. Long-term wet deposition studies will improve the statistical significance of the results presented in this study. Statistical analysis of a larger dataset, as well as the inclusion of meteorological parameters should allow greater insight into the relationships of the complex integrated processes that influence rainwater chemistry.

KEYWORDS: *Precipitation chemistry; Wet deposition; Ceilometer; Cloud base height; Air mass history; South Africa;*

Table of Contents

ACKNOWLEDGEMENTS	I
ABSTRACT	II
TABLE OF CONTENTS	IV
ABBREVIATIONS	VI
LIST OF FIGURES	IX
CHAPTER 3	IX
CHAPTER 4	X
CHAPTER 5	XI
LIST OF TABLES	XII
CHAPTER 4	XII
CHAPTER 5	XIII
1. INTRODUCTION AND OBJECTIVES	1
2. LITERATURE REVIEW	5
2.1 PRECIPITATION AND CLOUD PROCESSES	5
2.1.1 AN INTRODUCTION TO ATMOSPHERIC MOISTURE	5
2.1.2 CLOUDS AND CLOUD FORMATION	6
2.1.3 PRECIPITATION PROCESS	8
2.1.4 CLOUD BASE HEIGHTS AND LONG-RANGE TRANSPORTATION	10
2.1.5 METEOROLOGY OF THE SOUTH AFRICAN INTERIOR	12
2.2 PRECIPITATION CHEMISTRY	13
2.2.1 FUNDAMENTAL REACTIONS OF ANALYSED SPECIES	13
2.2.2 PH AND ACID RAIN	20
2.2.3 WET DEPOSITION	21
2.2.4 SOUTH AFRICAN PERSPECTIVE	23
2.3 LITERATURE CONCLUSION	24
3. EXPERIMENTAL	25
3.1 SITE DESCRIPTION	25
3.2 MATERIALS AND METHODS	27

3.2.1 RAINWATER SAMPLING	28
3.2.2 CHEMICAL ANALYSES OF RAINWATER	29
3.2.3 RAIN INTENSITY MEASUREMENTS	30
3.2.4 CLOUD BASE HEIGHT MEASUREMENTS	32
3.2.5 AIR MASS HISTORIES	34
3.2.8 DATA QUALITY OF THE CHEMICAL RAINWATER ANALYSES	35
3.2.9 STATISTICAL CALCULATIONS AND EVALUATION	36
4. RESULTS AND DISCUSSION:	40
PRECIPITATION CHEMISTRY AND WET DEPOSITION FLUXES	40
4.1 IONIC COMPOSITION OF WET DEPOSITION	40
4.2 ACIDITY	46
4.3 SOURCE CONTRIBUTION EVALUATION	48
4.4 TEMPORAL TRENDS	53
4.5 WET DEPOSITION FLUXES	55
4.6 CONTEXTUALISATION	56
5. RESULTS AND DISCUSSION:	57
AIR MASS ORIGIN AND RAIN INTENSITY	57
5.1 ANTHROPOGENIC CONTRIBUTION	60
5.2 A BACKGROUND EVENT	64
5.3 SCAVENGING EFFICIENCY OF TWO SUCCESSIVE EVENTS	65
5.4 BUILD-UP OF POLLUTANTS IN THE COLDER MONTHS	68
5.5 LONG-RANGE BIOMASS BURNING	71
5.6 SUMMER FIRES	73
6. CONCLUSION	77
7. PROJECT EVALUATION	79
BIBLIOGRAPHY	83

Abbreviations

ACRG	Atmospheric Chemistry Research Group
AE	Anionic equivalents
AGL	Above ground level
Al	Aluminium
APD	Avalanche photodiode
AQ	Air quality
ARL	Air Resource Laboratory
As	Arsenic
Ca ²⁺	Calcium
CaCO ₃	Calcium carbonate
CBH	Cloud base height
CCN	Cloud condensation nuclei
Cd	Cadmium
CE	Cationic equivalents
CEC	Cation exchange capacity
CH ₃ COO ⁻	Acetic acid
C ₃ H ₅ O ₂ ⁻	Propionic acid
CH ₃ SH	Methyl mercaptan
Cl ⁻	Chloride
CN	Condensation nuclei
CO ₂	Carbon dioxide
C ₂ O ₄ ⁻	Oxalic acid
CO	Carbon monoxide
COS	Carbonyl sulfide
CS ₂	Carbon disulfide
DAAC	Distributed Active Archive Centers
DEBITS	Deposition of Biogeochemical Important Trace Species
DMS	Dimethyl sulfide
EC	Electrical conductivity
EF	Enrichment factor
EOS	Earth Observation System
FMI	Finnish Meteorological Institute
GAW-PCP	Global Atmospheric Watch- Precipitation Chemistry Program
GDAS	Global Data Assimilation System
HCO ₃ ⁻	Bicarbonate

H_2CO_3	Carbonic acid
HCOO^-	Formic acid
Hg	Mercury
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
HONO	Nitrous acid
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IC	Ion chromatography
ID	Ion difference
IN	Ice nuclei
InGaAs	Indium gallium arsenide
IQR	Interquartile range
JHB-PTA	Johannesburg-Pretoria
K^+	Potassium
KCl	Potassium chloride
KOH	Potassium hydroxide
lidar	Light detection and ranging
LIS	Inter-laboratory comparison study
mA	Measured acidity
Mg^{2+}	Magnesium
MODIS	Moderate Resolution Imaging Spectrometer
MSA	Methane sulfonic acid
N	Nitrogen
Na^+	Sodium
NASA	National Aeronautics and Space Administration
NCEP	National Centre for Environmental Prediction
NF	Neutralisation factor
NH_3	Ammonia
NH_4^+	Ammonium
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulfate
NH_4HSO_4	Ammonium bisulfate
NH_4NO_3	Ammonium nitrate
NO_3^-	Nitrate
NO	Nitric oxide

NO ₂	Nitrogen dioxide
N ₂ O ₅	Dinitrogen pentoxide
NO•	Nitrate radical
NOAA	National Oceanic and Atmospheric Administration
nSSF	Non-sea salt fraction
NWU	North-West University
O ₃	Ozone
OA	Organic acids
OA*	Dissociated organic acids
OH•	Hydroxyl radical
pA	Acidic potential
Pb	Lead
PBL	Planetary boundary layer
PM ₁	Particulate matter (diameter less than 1 µm)
PO ₄ ²⁻	Phosphate
ppb	Parts per billion
RF	Radiative forcing
S	Sulfur
SO ₄ ²⁻	Sulfate
SO ₂	sulfur dioxide
SSF	Sea salt fraction
TOC	Total organic carbon
UH	University of Helsinki
VOC	Volatile organic compound
VWM	Volume weighted mean
WHO	World Health Organization
WMO	World Meteorological Organization

List of Figures

Chapter 3

Figure 3.1:	Map of southern Africa with a zoomed insert showing the Welgegund atmospheric research station with a red star, relative to major pollution sources indicated with black dots, and the grey shaded area representing the JHB-PTA metropolitan	26
Figure 3.2:	The Welgegund atmospheric measurement station with the <i>Vaisala</i> and <i>Casella</i> (a) rain intensity instruments indicated along with the (b) <i>Vaisala</i> CT25K ceilometer (Photo credit: Paul Beukes)	26
Figure 3.3:	The wet-only sampler (<i>NWU Instrument Makers</i>). The light-refracting sensor is visible at the foremost corner of the instrument. The instrument is in the “open” position (Photo credit: Micky Josipovic)	28
Figure 3.4.1:	The <i>Dionex</i> ICS-3000 ion chromatographic system utilised for the ionic content analysis	30
Figure 3.4.2:	The <i>Hanna Instruments</i> combined EC and pH meter	30
Figure 3.5:	The <i>Vaisala</i> QMR102 and <i>Casella</i> 0.1 mm tipping bucket rain intensity instruments as installed at the Welgegund measurement station (Photo credit: Micky Josipovic)	31
Figure 3.6:	The <i>Vaisala</i> CT25K ceilometer (Photo credit: Micky Josipovic)	33
Figure 3.7:	The ring diagram results from the LIS 54 study conducted in 2016. The ion legend is shown below the three sample results. The following explanation of the legend is applicable. A green hexagon represents a good result (within the interquartile range (IQR)); a blue trapezoid indicates a satisfactory result (within the range of the median $\pm$ IQR/1.349, also known as the pseudo-standard deviation); unsatisfactory results (outside of the satisfactory range) are represented by a red triangle (QA/SAC-Americas, 2016)	36

Chapter 4

Figure 4.1:	The typical anticyclonic recirculation pattern is evident in the hourly arriving back trajectories calculated for 96 hours backwards and arriving at 100 m (AGL), which were overlaid for the entire sampling period (Dec 2014 – Jul 2016). The frequency of trajectories passing over 0.2 x 0.2 grid cells are shown as percentage indicated with a colour index	44
Figure 4.2:	The monthly number of fire pixels within a 100, 250 and 500 km radius from Welgegund. The amount of rain events sampled monthly is indicated in blue at the top of the figure	45
Figure 4.3:	The pH frequency distribution measured for precipitation collected at Welgegund from December 2014 to July 2016	46
Figure 4.4:	Spearman correlations between the ionic species in rainwater. Red indicates a good correlation with a correlation coefficient close to 1 and blue indicates a weaker or negative correlation	49
Figure 4.5:	Apportioned estimated source contributions to the ionic composition of rainwater collected at Welgegund as calculated through the methods described in Section 3.2.9.2	51
Figure 4.6:	The monthly total VWM ionic content (in $\mu\text{eq.L}^{-1}$) of the Welgegund precipitation for the entire sampling period. The mean monthly rainfall depth (in mm) is indicated by a blue line	54
Figure 4.7:	The monthly averaged pH values for Welgegund over the entire sampling period	55

Chapter 5

Figure 5.1:	A map of southern Africa with the population density obtained from CIESIN (2010) indicated with a colour index, with an increase in population density indicated with an increase from green to yellow. The Welgegund atmospheric research station is indicated with a red star, whereas major pollution point sources in the interior of South Africa are represented as black dots, indicating major power stations, petrochemical plants and pyrometallurgical smelter related industries	59
Figure 5.2:	Rain event trajectories for (a) 7 and (b) 9-10 January 2015. The difference in CBH trajectories in relation to point sources is evident	60
Figure 5.3:	The difference in major point source contributions and the CBH trajectories can be seen in the events of (a) 6 and (b) 18 April 2015	62
Figure 5.4:	An example of a relatively clean rain event with regional below cloud air mass movement and CBH trajectories bypassing the major pollution point sources	64
Figure 5.5:	The trajectories for the events of (a) 4 and (b) 5 September 2015 that indicates notable scavenging	66
Figure 5.6:	The pollutant build-up and effective scavenging during the winter rainfall events on (a) 13 June and (b) 25 July 2015	69
Figure 5.7:	The influence of biomass burning (veld fires) on rainwater chemistry of (a) 20 and (b) 22 September 2015, in the peak fire season	71
Figure 5.8:	Mid-summer rainfall events influenced by biomass burning activities for rain events occurring on (a) 16 March, (b) 19 November and (c) 2-3 December 2015	74

List of Tables

Chapter 4

Table 4.1:	The Welgegund wet deposition sample collection and efficiency summary for the period of December 2014 to July 2016 (*From the WMO GAW-PCP in Allan (2004))	40
Table 4.2:	The VWM ionic concentrations (in $\mu\text{eq.L}^{-1}$) and wet deposition fluxes (in $\text{kg.ha}^{-1}\text{.yr}^{-1}$) for: Welgegund precipitation events for the two defined 10 month periods, as well as for the entire sampling period from December 2014 to July 2016 and for two South African DEBITS sites, viz. Amersfoort and Vaal Triangle are presented for contextualisation (Section 4.6). *(Conradie et al., 2016)	42
Table 4.3:	The potential acidity and the actual measured acidity are presented as VWM ionic concentrations and as a percentage.	47
Table 4.4:	The neutralisation factors (NF) for NH_4^+ , Mg^{2+} and Ca^{2+}	48
Table 4.5:	The ratios of Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and K^+ to Na^+ in seawater as presented by Keene et al. (1986), ratios of each of these ions to Na^+ in the Welgegund rainwater, and the respective enrichment factors (EFs).	51
Table 4.6:	The estimated source contributions to SO_4^{2-} (in $\mu\text{eq.L}^{-1}$). The values were calculated with the first method described in Section 3.2.7.2. as an excess concentration to the SO_4^{2-} supplied by gypsum. The values in brackets are the results from the second method based on the global estimated background SO_4^{2-} concentration of $7 \mu\text{eq.L}^{-1}$	53
Table 4.7:	A contextualisation of Welgegund with two South African DEBITS sites. The order of VWM concentrations are listed from highest to lowest from left to right	56

Chapter 5

Table 5.1:	The precipitation chemistry presented as normalised values ($\mu\text{eq.L}^{-1}$) for 7 and 9-10 January 2015	61
Table 5.2:	The normalised rainwater ionic concentrations for the events of 6 and 18 April 2015	63
Table 5.3:	The relatively diluted chemical content of the rain event occurring on 4 April 2015	65
Table 5.4:	The ionic concentration difference between rain events on two consecutive days (4 and 5 September 2015) showing the scavenging (washout) effect	67
Table 5.5:	Ionic concentrations of rainwater events indicating the build-up of atmospheric pollutant loads taking place during winter	70
Table 5.6:	The chemical content of typical fire season rain events	73
Table 5.7:	Ionic concentrations for rainfall events influenced by summer fires	76

1. Introduction and Objectives

Total deposition is the sum of the major removal processes of gaseous and aerosol species from the lower troposphere onto the Earth's surface, which is controlled by both wet- and dry- deposition (Galy-Lacaux et al., 2009). Precipitation chemistry is the quantification of important chemical species in atmospheric moisture that is returned to the Earth's surface during precipitation events such as rain. Precipitation chemistry plays an instrumental role in understanding atmospheric processes, as well as changes that occur in the atmosphere due to anthropogenic activities and natural processes (Galy-Lacaux et al., 2009; Laouali et al., 2012). Rainwater is considered to be in equilibrium with the atmospheric composition and is therefore a good indicator of the ambient air quality (Mphepya et al., 2004; Laouali et al., 2012; Li et al., 2012). Determining the chemical composition of rainwater is crucial in understanding the temporal and spatial evolution of air masses and their composition (Mphepya et al., 2006). As an important sink of chemical compounds in the atmosphere, precipitation introduces these species into the surface environment (Pauliquevis et al., 2012). This deposition can, depending on the current state of the system, either be detrimental or beneficial to the environment. Essential nutrients and pollutants deposited onto the surface affect the nutrient levels, quality and fertility of soil and water, as well as the general health of the ecosystem and humans. The fertility and productivity of the soil is affected when the nutrient levels of soil are unfavourably altered (Mphepya et al., 2006). Furthermore, rainwater chemistry is ecosystem specific as the source origins of chemical species will be different for each environment (Christner et al., 2008).

The factors affecting the chemical composition of rainwater are complex. Atmospheric moisture is subject to numerous physical mechanisms such as cloud mechanics and microphysical droplet properties, as well as chemical reactions occurring throughout the processes of cloud formation up to the precipitation event (Al-Khashman, 2009; Laouali et al., 2012; Zhang et al., 2012). Mass transfer of soluble species in the atmosphere into cloud or rain droplets can occur during nucleation (condensation of moisture onto a particle), or during the precipitation event itself. The intensity or rainfall rate also plays an influential role in the amount of the ambient chemical species that are taken up into the rainwater. Smaller droplets have prolonged contact time with the air due to its lower terminal velocity and will therefore be more effective in scavenging chemical species from the air compared to larger drops (Hall, 2003). Other factors, for example the type of ecosystem and proximity to the ocean, have an effect on the dust and sea salt content of rainwater, as well as the droplet- and/or cloud nucleation capacity of the atmosphere (Christner et al., 2008; Galy-Lacaux et al., 2009). Several natural and anthropogenic aerosol pollutants can undergo long-range

transportation, which can act as condensation nuclei in regions other than their original emission areas (Garstang et al., 1996; McGranahan and Murray, 2003). Certain pollutants, including sulfur- and nitrogen oxides (SO_x and NO_x) have the ability to acidify rainwater. Acid rain lowers the pH of soil and natural surface water bodies, thereby leading to the leaching of essential nutrients, mobilising heavy metals and harming aquatic life. Infrastructure such as limestone buildings, carbonate containing cement, bricks and roads dissolve when it comes in contact with acid rain (McGranahan and Murray, 2003). From the afore-mentioned it is evident that numerous and complex factors affects rainwater composition and consequently wet deposition.

South Africa, as a developing country with growing industries, is prone to the negative effects of relatively higher sulfur (S) and nitrogen (N) deposition (Allan, 2004; Collett et al., 2010; Josipovic et al., 2011; Conradie et al., 2016). Most of the large industries in South Africa also do not yet remove SO_x and NO_x from the off-gas (de- SO_x or de- NO_x) (Pretorius et al., 2015). Additionally, stricter legislation on pollution and the implementation of mitigation strategies are still emerging. Some precipitation chemistry measurements conducted in South Africa that have been published in the peer reviewed public domain, include long-term precipitation chemistry studies conducted at Louis Trichardt, Amersfoort, Skukuza and the Vaal Triangle within the Deposition of Biogeochemical Important Trace Species (DEBITS) programme (Mphepya et al., 2004; Mphepya et al., 2006; Conradie et al., 2016). However, since deposition studies are limited for this region, more studies are required at different sites in southern Africa in order to increase the spatial representation and to assess the possible extent of the environmental impacts of anthropogenic related activities on wet deposition over South Africa. Additionally, all of these previous studies were conducted at sampling sites where limited atmospheric measurement instrumentation was deployed, making it impossible to relate more complex processes (e.g. air mass histories, rainfall rate) to precipitation chemistry.

In this study precipitation chemistry was assessed at the Welgegund atmospheric research station that is situated on a privately owned farm approximately 25 km north-west from the city of Potchefstroom and 100 km west of the Johannesburg metropolitan. The Welgegund research station is considered representative of a regional background site, since there are no large point sources in close proximity. However, it is frequently impacted by pollution plumes from the Vaal Triangle Airshed, the Mpumalanga Highveld and Waterberg Priority Areas, and the Johannesburg-Pretoria conurbation (Beukes et al., 2013; Jaars et al., 2014; Tiitta et al., 2014; Venter et al., 2016). The current extent of the influence of these pollution source areas on rainwater quality at this site is unknown.

The Welgegund station is likely the most comprehensively equipped long-term continuously operating atmospheric measurement station in the South African interior. Measurements conducted at this site include among others aerosol- and ion size distributions, aerosol optical properties, trace gas concentrations, carbon dioxide (CO_2), NO_2 - and SO_2 - fluxes, radiation, soil moisture and -temperature, rain intensity, vertical atmospheric profiles (cloud base height) and several other meteorological measurements (Beukes et al., 2013). Since the chemical composition of precipitation can be interpreted and contextualised using various on-site measurements, this site is ideal to relate more complex processes to precipitation chemistry.

The aim of this study was to determine the chemical content of rainwater collected at the Welgegund station and to establish initial techniques that can be used to relate the composition of precipitation with processes that affect it.

The specific objectives were to:

- i. conduct wet-only precipitation sampling at the Welgegund atmospheric research station over at least one full seasonal cycle;
- ii. analyse the collected rainwater to determine the chemical content, which entails ion-chromatography (IC) analyses of water soluble species, i.e. nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-) formic acid (HCOO^-), propionic acid ($\text{C}_3\text{H}_5\text{O}_2^-$), acetic acid (CH_3COO^-), oxalic acid ($\text{C}_2\text{O}_4^{2-}$), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+})). as well as determining pH and electrical conductivity (EC);
- iii. determine the potential acidic contributors and to identify possible neutralising species through the calculation of neutralisation factors;
- iv. identify, calculate and categorise specific source contributions (e.g. fossil fuel combustion, marine) through empirical and statistical methods;
- v. contextualise precipitation measured at Welgegund with regard to other South African sites;
- vi. develop a method to identify rain event specific parameters that could affect the chemical composition, which involves cloud base height (ceilometer) and rain

intensity (tipping-bucket intensity instruments) measurements in conjunction with air mass history analysis (HYSPLIT_4.8 model back-trajectories);

- vii. make recommendations with regard to future wet deposition measurements at Welgegund and the further development of the above-mentioned pilot method to link rain chemistry with processes that influence it.

2. Literature Review

2.1 Precipitation and Cloud Processes

2.1.1 An introduction to atmospheric moisture

Water is fundamental to life. In the atmosphere, moisture is mainly present in the troposphere and tropopause – the atmospheric layers that are closest to the earth's surface (Critchfield, 1983). Atmospheric moisture undergoes many physical and chemical processes and transformations. Water is present in the atmosphere in its three physical states, viz. liquid, gas and solid states. Most of the moisture in the atmosphere is, however, contained in water vapour. Water vapour is considered a naturally occurring greenhouse gas, which exhibits positive (warming) radiative forcing (RF) by absorbing infrared radiation emitted from the earth. Radiative forcing (in W.m^2) is the measure to what extent the Earth-atmosphere energy balance is influenced and therefore indicates the climate forcing ability. A positive RF value, as is the case with water vapour, indicates a warming effect on the climate (IPCC, 2013). More evaporation occurs as a result of global warming, which in turn increases the radiative forcing effect. In contrast to the positive radiative forcing of water vapour, clouds reflect incoming solar radiation and therefore have a cooling effect. Both of these atmospheric water related processes play important roles in climate change (Jain and Hayhoe, 2003; IPCC, 2013).

The amount of water vapour in the atmosphere cannot be expressed using a single standard measure and therefore different measures exist for specific uses. One such measure, vapour pressure, is defined as the partial pressure exerted by the water in the gas phase. There is a continual change in the physical states of water through the processes of crystallisation, evaporation, sublimation and condensation. Any change from one state to another involves the exchange of latent heat energy (Critchfield, 1983). The change in physical states that water undergoes is dependent on the temperature and vapour pressure (Preston-Whyte and Tyson, 1988).

When considering the chemical composition of precipitation, the various processes and reactions that influence and determine the chemistry have to be recognised and evaluated. Three major environments can roughly be identified in the progression of precipitation chemistry, i.e. the condensation and droplet evolution, the in-cloud environment and the precipitation event itself. The processes and conditions for cloud formation and precipitation are complex and will be discussed subsequently in this chapter.

2.1.2 Clouds and cloud formation

Approximately 4% of the total available atmospheric water is contained in clouds at any given moment (Brimblecombe, 2003). Spontaneous nucleation of water droplets from ambient moisture without the presence of condensation nuclei (CN) can only occur when the air mass rapidly expands, which leads to an increase in relative humidity with several hundred percent. This can only occur in simulated situations as the atmosphere naturally contains CN and the relative humidity rarely rises above 100%. The formation of water droplets or clouds in the atmosphere requires CN or cloud condensation nuclei (CCN), which are small particles (aerosols) on which the atmospheric moisture condenses whilst releasing latent heat. CN are classified according to their size which can range from 1×10^{-4} to 1×10^1 μm . When these CN exhibit hygroscopic properties condensation can occur above dew point temperatures. This is called the solute effect (Critchfield, 1983; Preston-Whyte and Tyson, 1988; Brimblecombe, 2003). Dew point temperature is the temperature at a constant pressure and vapour content where the air becomes saturated and dew or small droplets can condensate (Preston-Whyte and Tyson, 1988; Roberts, 2003).

CN can be organic, inorganic or biological. Electrolytic salts are more effective as CN and lower the vapour pressure over the droplet making smaller droplets more resistant to evaporation (Brimblecombe, 2003). Atmospheric aerosols require activation to act as CN (McFiggans et al., 2005). Common CN include sea salt, sulfuric acid (H_2SO_4), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and certain organic species (Brimblecombe, 2003). Dust and other particles, though less hygroscopic, can also act as CN in more saturated air. Some of these nuclei are also water soluble, which increases the growth rate of the formed droplets in a saturated environment (Critchfield, 1983; Brimblecombe, 2003). The type and amount of nucleators found in the ambient air are dependent on the local ecosystem, emission sources, topography, climate, season and existing cloud water chemistry (Christner et al., 2008). During nucleation, i.e. the process of condensation on CN, the chemical composition of the droplet is inherently affected.

Once formed, the droplet growth is dependent on the solute concentration and droplet surface curvature. The droplet can only grow to an equilibrium size when the vapour pressure over the droplet is smaller or equal to that of the ambient air. Once the droplet grows larger than the equilibrium size, evaporation will take place to restore the droplet to its equilibrium size. If evaporation reduces the size below equilibrium size (and in effect the vapour pressure over the droplet), condensation will occur to restore the droplet to the equilibrium size. However, a rise in relative humidity will increase the equilibrium size and the droplets will be able to grow further. The surface tension of the water droplet associated

with the curvature of its form has to be overcome by a sufficient vapour pressure in order for the droplet to grow. This pressure will thus be greater than the saturation vapour pressure for a plane surface. This is known as the curvature effect (Abraham, 1974; Preston-Whyte and Tyson, 1988). The concentration of aerosols that served as CN in the droplet changes as the droplet grows. Firstly, as the droplet is formed and grows in size up to a radius of 10 μm , the concentration of the CN in the droplet becomes diluted. Then, at the stage where the droplet grows to 50 μm radius, the surrounding additional CN (aerosols) can diffuse into the droplet. The aerosol species (or CN) concentration in the droplet can thereby be increased. When the droplet reaches this size, coalescence with other smaller droplets can take place more easily. This can again lead to dilution of the CN concentration. The droplet grows through further accumulation to a few hundred micrometers with thorough mixing between various droplets creating a constant concentration throughout all the cloud droplets (Brimblecombe, 2003). The term rainout is used to describe the removal or scavenging of particles or gases from the atmosphere during the formation of the droplet (Hall, 2003; Pauliquevis et al., 2012).

The droplets can further absorb soluble species and catalyse aqueous reactions in the cloud. Soluble gasses present in the interstitial air inside of a cloud are rapidly transferred into the cloud droplets through mass transfer. This scavenging process or process of inclusion of other soluble species into the droplets is an effective equilibrium process. Interstitial aerosols (aerosols between droplets) are also scavenged by the droplets. However this process of mass transfer is considered to be relatively slow and not an effective aerosol removal mechanism (Brimblecombe, 2003; Hall, 2003).

Although interstitial aerosols are not easily taken up into the cloud droplets, aerosols do have direct (as mentioned above) and indirect impacts on the cloud and droplet properties. Indirect effects include the Twomey and the cloud lifetime effects. These effects occur when there is a change in the cloud droplet number and thereby affecting the cloud albedo (reflection of the incoming solar radiation), as well as the persistence of the cloud. Aerosols of anthropogenic origin that serve as CN tend to increase the cloud droplet number by reducing the size of the cloud droplets. An increase in cloud droplet number with constant water content reduces the precipitation capability and increases the evaporation, which thereby affects the cloud lifetime. This is also the case for light-absorbing aerosols, such as black carbon present beneath the cloud layer, which increase the ambient air temperature thereby stabilizing the below-cloud air layer, as well as assisting in cloud burn-off. This is a semi-direct effect of aerosols on cloud properties (McFiggans et al., 2005; Koch and Del Genio, 2010; Ekman et al., 2011; Konwar et al., 2012). These absorbing aerosols present in the boundary layer decrease the ambient relative humidity, thereby reducing the cloud

coverage by up to 40% (Koch and Del Genio, 2010). Considering all of the afore-mentioned, it is evident that aerosol perturbations affect cloud systems.

Physical processes assist cloud formation when the air is supersaturated with moisture. This can occur when unsaturated air ascends, adiabatically expands and cools to the point of saturation. There are various ways this ascension can take place, but is not of relevance to this study. Cloud formation can also occur without ascension through diabatic cooling (Preston-Whyte and Tyson, 1988; Graedel and Crutzen, 1993).

Clouds can be classified as warm or cold clouds, with warm clouds considered having temperatures above 0°C. In cold clouds, droplets can exist alongside ice crystals. The droplets in these clouds are supercooled at temperatures ranging from 0 to -40°C (Preston-Whyte and Tyson, 1988; Rauber and Tokay, 1991).

Eventually equilibrium is reached in the cloud droplets and they will at some stage return to the earth in the form of precipitation (Brimblecombe, 2003). The chemical composition and properties of the droplets are determining factors for not only cloud formation and lifetime, but also the eventual initiation of the precipitation event.

2.1.3 Precipitation process

Precipitation is regarded as the form in which atmospheric moisture returns to the surface of the earth in a liquid or solid state, after condensation and/or sublimation. However, fog, dew and frost are generally not included in this category. Precipitation is mainly classified according to the physical state of the falling moisture (e.g. rain, hail or snow), or according to the formation processes (e.g. orographic or convective precipitation) (Preston-Whyte and Tyson, 1988).

The terminal velocity of falling raindrops is dependent on the droplet size and density. Precipitation from warm clouds (>0°C) commences when the updraught velocity that keeps the cloud in suspension is less than the terminal velocity of the raindrops. Droplets from cold clouds (0°C to -40°C) can only fall or precipitate once ice crystals have formed or aggregation into snowflakes occurred. Ice formation therefore triggers these precipitation events. This phenomenon is presented by the Bergeron-Findeison theory. The crystals or snowflakes will remain in a solid state or melt into raindrops when falling through ambient air with a temperature of 0°C or colder (Preston-Whyte and Tyson, 1988; Rauber et al., 2000). In order for this crystallisation to take place, particles are needed to act as ice nuclei (IN). Aerosols such as black carbon can act as IN through deposition, contact and immersion

freezing of water vapour or droplets (Christner et al., 2008; Koch and Del Genio, 2010). Anthropogenic aerosols can affect the crystallisation process either directly or indirectly by inducing heterogeneous freezing, or by changing the temperature required for freezing, respectively (Christner et al., 2008; Ekman et al., 2011). The local ecosystem largely influences the type of IN in the air, since bacteria, fungi, algae and pollen can act as IN. Biological IN can catalyse freezing processes in clouds at much higher temperatures (-2°C) than inorganic aerosols. These biological nucleating particles, for example different bacteria related to plants (*Pseudomonas*), are pH sensitive and are indicative of the acidic and chemical content of the precipitation (Christner et al., 2008). Christner et al. (2008) determined a directly proportionate relationship between the bicarbonate (HCO_3^-) concentration and the amount of biological IN. A positive correlation was also observed between terrigenous total organic carbon (TOC), NH_4^+ and Ca^{2+} aerosol concentrations with the amount of biological nuclei (Christner et al., 2008). IN can therefore also contribute to the ultimate precipitation chemistry. However, there are significant uncertainties associated with the specifics of aerosol particles acting as IN (McFiggans et al., 2005; DeMott et al., 2011).

During the precipitation process, the size and composition of the droplets are subject to further change. Larger raindrops coalesce more effectively with smaller droplets (Lutgens and Tarbuck, 1982). As the raindrops fall through the air, collide and coalesce with each other, they also scavenge other particles and gases through the same processes. Scavenging processes include rainout, washout, collision-coalescence, sweepout and wake capture.

Rainout and washout are in-cloud scavenging processes. As mentioned previously, rainout involves the collecting of species into the droplets during the initial droplet formation, while washout refers to the removal of species in the interstitial air inside the cloud (Hall, 2003; Pauliquevis et al., 2012). Collision-coalescence is the process whereby a larger drop falls more rapidly than smaller droplets and in collision with other droplets, coalesce and increase in size (Lutgens and Tarbuck, 1982). During the precipitation event, the earthbound raindrops also collide with ambient aerosols and gases, which further evolve the rainwater chemistry. Falling raindrops create streamlines of perturbed airflow and Brownian motion around the droplets, sweeping surrounding particles downward. The motion of the particles is also subjected to the Bernoulli Effect at this stage (Preston-Whyte and Tyson, 1988; Urone, 2001; Hall, 2003). Removal of particles by this means is called sweepout (Hall, 2003). Occasionally atmospheric particles (other droplets, gases or aerosols) will be collected into the raindrop along these streamlines, which is determined among others by the droplet- and aerosol diameters. Particles with a larger diameter will most likely be

collected into the drop, whereas smaller particles will more likely continue to follow the streamline motion and not be collected into the droplet. This scavenging process, called wake capture is relatively efficient (Preston-Whyte and Tyson, 1988).

Hall (2003) describes scavenging processes as a function of space, time, precipitation characteristics, aerosol distribution and solubility of the species being scavenged. The degree of scavenging that can take place during precipitation largely depends on the droplet size, since mass transfer will be easier to occur for larger drops. Scavenging is furthermore proportional to the rainfall rate or intensity, which consequently is proportional to droplet size and droplet size distribution. Smaller drops will scavenge more effectively as their terminal velocity is slower. The chemical driving force of scavenging processes is related to the difference between the atmospheric concentration and the gas-phase concentration near the surface of the droplet that is in equilibrium with the droplet concentration. Scavenging in the cloud itself occurs rapidly as mass transfer in the equilibrium process is aided by the small size of the droplets (Hall, 2003). The aqueous solubility of the gas being scavenged affects the effectiveness of the rainout and washout processes. Highly soluble gases beneath the cloud are easily removed through the washout process, while aerosols are predominantly scavenged during the nucleation process. Scavenging of aerosols are affected by Brownian and turbulent shear diffusion, inertial impaction, diffusiophoresis, thermophoresis and electrical charge effects (Chate and Pranisha, 2004).

Considering the discussion above, below-cloud scavenging is therefore a major removal process in the boundary layer, with the efficiency thereof being dependent on factors such as the terminal velocity, collision efficiency, raindrop and particle size distributions, and rain intensity (Bae et al., 2006).

2.1.4 Cloud base heights and long-range transportation

Sun et al. (2010) found that the chemistry of liquid water in clouds differed from the rainwater chemistry of the related event. It was suggested that different air mass origins were the major factor influencing this observation. An air mass refers to a body of air with relative homogenous composition, temperature and moisture characteristics. In order to have these homogenous characteristics, an air body should be relatively stable over the source region for a sufficient time to achieve equilibrium. As the air mass moves onward, it will tend to keep those characteristics determined by the source region (Critchfield, 1983). Other studies have associated varying air mass origins at different altitudes with the chemical composition of rainwater. Li et al. (2011), for instance, determined differences in trace

element concentrations of rainwater sampled on a mountaintop compared to rainwater samples taken at the base of the same mountain, which were ascribed to varying air mass origins. The pH also differed for these rainwater samples. These authors found that the major ionic concentrations were much higher at the base than at the summit (Li et al., 2011). Air masses can carry primary and secondary pollutants over long distances. Therefore distant emission sources can affect the air quality, nucleation capability, precipitation chemistry and deposition at a remote site. Moody and Samson (1989) attributed a variability of up to 40% for certain ionic concentrations measured in rainwater samples to differences in the long-range transportation of air masses. These studies point to the relevance of air mass origin and movements at different altitudes to the scavenging processes that determine the rainwater chemistry. The cloud and boundary layer air mass origins therefore play a significant role in establishing the rainwater composition.

Various previous studies (Sun et al., 2010; Shen et al., 2012; Liu et al., 2013; Aikawa et al., 2014) used back trajectory analysis to determine air mass history and identify pollution source regions by using different arrival heights of the lower atmosphere. Some of these studies used statistical methods such as Ward's method to compute Euclidean distances and K-means clusters. Although the importance of determining air mass trajectories when studying cloud and precipitation chemistry has been highlighted by these and other studies, none of these studies determined the actual cloud base heights in order to calculate the associated air mass histories.

Back trajectories for the air mass associated with the cloud can be calculated by considering the cloud base height (CBH) before the commencement of a precipitation event as the estimated arrival height. CBHs are most commonly measured with ceilometers (Nguyen and Kleissl, 2014). Ceilometers were originally designed as commercial lidars (LIght Detection and Ranging) for use at airports in order to determine CBHs for aircraft safety purposes (Emeis et al., 2012). Ceilometers have been used for other atmospheric measurements, such as determining possible pollution sources, mixing layer heights, atmospheric boundary layer heights and vertical profiles of the atmosphere (Emeis et al., 2012; Shen et al., 2012).

2.1.5 Meteorology of the South African interior

Precipitation is not only influenced by the microphysical properties of clouds and the path of the droplet towards the surface of the earth, but also by the regional meteorology. The meteorology of South Africa is influenced by circulations of tropical and temperate origin, as well as by the prevailing high pressure cells of the Southern Hemisphere. A mean anticyclonic circulation pattern prevails over the interior of southern Africa, which intensifies and moves northward during winter (Preston-Whyte and Tyson, 1988). Anticyclonic circulation patterns are dominant over the subcontinent with easterly disturbances prominent in the summer and westerly disturbances prominent throughout the year (Garstang et al., 1996). During the winter months, a continental high pressure system dominates the central plateau (Freiman and Tyson, 2000).

The South African plateau is dominated by fair-weather conditions, which promotes the formation of stable layers that inhibits vertical mixing of the troposphere (Harrison, 1984; Freiman and Tyson, 2000). These stable layers, or inversion layers, over the South African plateau occur at approximately 850, 700 and 500 hPa. The layer at 700 hPa (or ~3000 m in altitude), which occurs most frequently over continental South Africa during the winter, has the largest influence on the moisture transport over South Africa. Easterly disturbances have been shown to disrupt these stable layers through low pressure waves. In the austral summer months, these types of disturbances, along with deep convection, disrupt the stable layers over the interior of South Africa (Newell et al., 1972; Garstang et al., 1996; Freiman and Tyson, 2000). Air masses trapped underneath the stable inversion layers recirculates and leads to the atmospheric build-up of pollutants during winter. This recirculation of air masses can last for up to 20 days (Garstang et al., 1996; Tiitta et al., 2014). According to Held et al. (1996), orographic features drive night-time surface winds over the South African plateau, which stabilise the boundary layer. However, during daytime the gradient winds create a convective boundary layer. Therefore strong diurnal and seasonal variations are observed.

South Africa is characterised by distinct wet and dry seasons. The annual average rainfall over subtropical southern Africa is approximately 500 mm (Harrison, 1986). The Central South African wet season ranges from mid-October to April, through mostly convective precipitation systems (Harrison, 1986; Mphepya et al., 2004). Autumn rainfall over western southern Africa can most often be attributed to moisture-rich air coming from the tropical north, while summer precipitation is mostly of the convective type (Harrison, 1986; Preston-Whyte and Tyson, 1988). Diurnal patterns are observed in these convective precipitation events as there is diurnal heating and cooling of the land surface. This is partly due to South

African soils, which have low heat capacities and therefore contribute to the night-time formation of inversions (Garstang et al., 1996; Laakso et al., 2012). Surface inversion forms during the night, while sunrise induces convective mixing (Garstang et al., 1996; Collett et al., 2010). Convective rain events predominantly occur during the afternoon or early evenings. These convective rain events are associated with relatively high rainfall intensities, as well as hailstorms over the interior with the hailstones classified as hard hail. Hailstorms are common during late spring to early summer. More severe storms occur early in the wet season. Cloud-bands also move over South Africa in a north-western to south-eastern direction and are frequently associated with precipitation events. Rainfall over the central plateau is mostly correlated with tropical-temperate pressure troughs and associated cloud-bands (Harrison, 1986; Preston-Whyte and Tyson, 1988). Tropically-induced rain events have an annual cycle that peaks in summer and temperate rain events peak biannually in spring and autumn respectively (Preston-Whyte and Tyson, 1988).

2.2 Precipitation Chemistry

2.2.1 Fundamental reactions of analysed species

By 1983 more than 1 600 chemical compounds had been identified in the atmosphere. This number reached over 3000 species by 1992 (Critchfield, 1983; Graedel and Crutzen, 1993). The chemical composition of cloud- or rain droplets are inherently determined by the CN onto which the droplet originally condensates. The chemical and physical characteristics of the CN therefore influence the properties of the droplets. This composition changes during the lifetime of the droplet through chemical reactions, as well as the physical changes the droplet is subjected to.

Many pollutants are hygroscopic and therefore act as CN, while also having a stabilisation effect on the droplet. When pollutants or CN particles have an oily nature, they can further stabilise the droplet by deferring dispersion and evaporation (Critchfield, 1983). Salts in the initial droplet decrease the water vapour pressure and thereby increase the droplet stability by preventing evaporation (Brimblecombe, 2003). Atmospheric moisture in the form of cloud- or rain droplets creates the environment wherein numerous aqueous chemical reactions occur (Brimblecombe, 2003; Sun et al., 2010). Gases and other particulate matter, from various natural and anthropogenic sources, are also taken up into the droplets during numerous scavenging processes as discussed in Section 2.1 (Sun et al., 2010; Liu et al., 2013). The chemical characteristics of the eventual precipitation are the net result of complex processes and interactions of cloud mechanics, microphysical properties of the

droplets and chemical reactions occurring during the scavenging processes (Al-Khashman, 2009; Zhang et al., 2012). Although there are numerous chemical species in different forms and phases present in the atmosphere, the intrinsic properties of the species will also determine to what extent it could be deposited through wet deposition. For example, the aqueous solubility of a gaseous species contributes to their susceptibility for uptake into the clouds and raindrops, which can be described by Henry's law (Finlayson-Pitts and Pitts, 2000; Connell, 2005).

The emission sources of various chemical species found in the troposphere are of natural and anthropogenic origin. Soil and dust particles lifted into suspension by, e.g. tilling, agricultural activities and vehicles, can affect the atmospheric concentrations of water insoluble species, such as aluminium silicates, as well as water soluble species, such as carbonates, K^+ , Ca^{2+} and Mg^{2+} . Ions of these origins are classified as terrigenous or crustal elements. Crustal contributions to the chemical composition are related to the geological properties of the region. Crustal ionic species that are associated with alkali feldspars, lime rich dolomite, diabase and silicate rich minerals, such as those found in granites, micas and chert, are dominant over southern Africa (McCarthy and Rubidge, 2005; Conradie et al., 2016). Although not considered in this study, trace metals such as antimony (As), lead (Pb) and cadmium (Cd), as well as biological species such as algae, pollen, bacteria and fungi can also be present in rainwater (Christner et al., 2008; Li et al., 2011). Ultimately, the chemical composition of rainwater can give information on the regional and local tropospheric composition and pollution levels (Mphepya et al., 2004; Vet et al., 2014).

In the following subsections some of the characteristics of the species analysed in this study will be discussed. These species are water soluble inorganic and organic ions namely nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), acetic acid (CH_3COO^-), formic acid ($HCOO^-$), oxalic acid ($C_2O_4^{2-}$), propionic acid ($C_3H_5O_2^-$), ammonium (NH_4^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) and sodium (Na^+).

i. NO_3^-

Nitrogen oxides (NO_x) are present in the atmosphere mainly as nitric oxide (NO) and nitrogen dioxide (NO_2) together with dinitrogen pentoxide (N_2O_5) and nitrous acid ($HONO$) (Finlayson-Pitts and Pitts, 2000; Shallcross et al., 2003).

These chemical states of NO_x show strong diurnal and seasonal concentration tendencies (Shallcross et al., 2003; Collett et al., 2010; Lourens et al., 2012). NO_x do not have long atmospheric residence times, which are in the order of a few hours. NO_x levels are usually

more elevated over continental and polluted areas in comparison with marine environments. Natural and anthropogenic emissions contribute to continental NO_x levels (Shallcross et al., 2003; Collett et al., 2010; Lourens et al., 2012). Soil, wildfires (e.g. lightning induced), tilling of fertilised soil, and lightning are examples of natural emission sources. Lightning approximately contributes 10-33 Tg.y⁻¹ to the global atmospheric NO_x budget. In addition, stratospheric influx also contribute to tropospheric NO_x (Finlayson-Pitts and Pitts, 2000; Jackson, 2003; Rakov and Uman, 2003). There is a global increase in anthropogenic emission of NO_x compounds (Shallcross et al., 2003). The main anthropogenic sources of NO_x are vehicular emissions, biomass burning (man-made savannah and grassland fires, as well as household combustion for space heating and cooking, and fossil fuel combustion (Graedel and Crutzen, 1993; Finlayson-Pitts and Pitts, 2000; Jackson, 2003; Shallcross et al., 2003).

The South African Highveld and the Johannesburg-Pretoria megacity is well-known for exhibiting a satellite observable NO₂ hotspot, which has a tropospheric column density similar to some of the most polluted areas of the world (Lourens et al., 2012). Atmospheric NO_x are furthermore notable pollutant species since tropospheric O₃ can only be formed in the atmosphere through the photolysis of NO₂. NO and NO₂ reacts with ozone (O₃) in a photochemical reaction to interchange between these two chemical forms (Reactions 2.1 and 2.2).



The concentration of NO₂ can be enhanced by the presence of other precursor species such as volatile organic compounds (VOCs) and carbon monoxide (CO) (Finlayson-Pitts and Pitts, 2000; Shallcross et al., 2003). NO and NO₂ are not significantly absorbed into cloud or rainwater, since they are not highly soluble and kinetically the reactions are too slow. However, reactions at the droplet surface exist where NO₂ reacts with water vapour to form HONO through a mechanism that is not yet well understood (Reaction 2.5) (Finlayson-Pitts and Pitts, 2000).

Nitric acid (HNO₃), which contributes to the acidic content of precipitation, is formed through the hydrolysis of N₂O₅. The reaction of NO_x with hydroxyl radicals to form HNO₃ is part of the removal mechanisms of NO_x (Reactions 2.3, 2.4 and 2.5).





Elevated NO_3^- concentrations in rainwater can increase the NO_3^- levels in drinking water which can be toxic and can cause among others a blood disorder called methemoglobinemia (Kanayo et al., 2010). Additional negative aspects associated with excessive nitrogen (N) deposition will be discussed in the next subsection, together with ammonium (NH_4^+).

ii. NH_4^+

In addition to NO_3^- , further nitrogenous contribution to rainwater chemistry include ammonia (NH_3) emissions that is present as ammonium (NH_4^+) in rainwater (Galy-Lacaux et al., 2009). NH_3 is a short-lived gas in the atmosphere with a residence time of approximately 10 days. NH_3 levels in the atmosphere are highly variable as its sources are both natural (e.g. decomposition and hydrolysis of urea and excreta, agricultural activities and emission from the soil and ocean) and anthropogenic (primarily from the agricultural and fertilisation industry). NH_3 is an important basic gas in the atmosphere and therefore plays an important role in neutralising acids such as H_2SO_4 by forming $(NH_4)_2SO_4$ (Shallcross et al., 2003; Galy-Lacaux et al., 2009; Laouali et al., 2012; Conradie et al., 2016).

Although N is an essential nutrient, an elevated N influx into sensitive ecosystems ultimately has a detrimental effect. At first plants would experience an increase in growth rate, which would then generate an imbalance in the carbohydrate-protein levels. Other essential minerals such as Mg^{2+} , K^+ and phosphate (PO_4^{2-}) are used to restore this balance. The excess N then reacts to form toxic substances such as amides and amines, as well as ammonium derivatives. This can lead to increased parasitic activity, dehydration and excess stress on the plants (Halsall, 2003). Ammonium sulfate ($(NH_4)_2SO_4$) has an acidifying effect on soil, which can inhibit plant growth (Shallcross et al., 2003). N cycling and concentrations in soil are directly dependent on the nitrogenous concentration in the precipitation (Sanger et al., 1996). Excess N deposition can cause eutrophication of ecosystems. The detrimental effects of eutrophication have been highlighted in various publications including those referenced in Halsall (2003).

iii. SO_4^{2-}

Sulfate (SO_4^{2-}) aerosols are some of the most abundant particulates in the atmosphere. Sulfur (S) is emitted into the atmosphere in different chemical forms, which include sulfur dioxide (SO_2), hydrogen sulfide (H_2S) and dimethyl sulfide (DMS). SO_2 is predominantly generated through the combustion of S-containing fossil fuels such as coal and oil, as well as smelting of S containing ores. Anthropogenic emissions of SO_2 through mainly fossil fuel combustion contribute approximately 75% to the total global S emission budget. In addition, SO_2 is emitted naturally through erupting volcanoes and other geochemical sources (Aiuppa et al., 2004; Kanayo et al., 2010). Volcanic eruptions can largely affect the S budget in the atmosphere by a sudden release of a large amount of SO_2 . Marine environments contribute as a natural source of SO_2 as sea salt is released into the atmosphere as ocean spray. This salt is, however, mostly deposited soon after its release back to the ocean (Shallcross et al., 2003). In South Africa, SO_2 concentrations are relatively high in semi- and informal settlements, as well as in industrialised regions (Lourens et al., 2011; Venter et al., 2012; Pretorius et al., 2015). However, SO_2 levels are expected to be relatively low in background air (Vet et al., 2014). Biogeochemical S emissions include species such as H_2S , DMS and other reduced forms of S (Finlayson-Pitts and Pitts, 2000; González and Aristizábal, 2012).

In a dry atmosphere, SO_2 and SO_4^{2-} will persist for a couple of days and are therefore subject to long-range transportation. SO_4^{2-} is formed when gaseous SO_2 reacts with moisture to form an acidic solution whereafter H^+ is abstracted from reactive metals to form H_2SO_4 (McGranahan and Murray, 2003; Adon et al., 2010; Kanayo et al., 2010; Aikawa et al., 2014). Hydroxyl radicals ($OH^\bullet$) also play a significant role in the production of H_2SO_4 (Reactions 2.7-2.9) (Shallcross et al., 2003). Additionally, there are many redox reactions through which S containing species such as H_2S , DMS, methyl mercaptan (CH_3SH), carbon disulfide (CS_2) and carbonyl sulfide (COS) are oxidised with $OH^\bullet$, nitrate radical ($NO_3^\bullet$), O_3 and halogens (Finlayson-Pitts and Pitts, 2000).



In general, SO_4^{2-} comprises the largest fraction of water soluble ions in particulate matter and has the largest concentration in rainwater, even at background sites (Vet et al., 2014; Aurela et al., 2016; Conradie et al., 2016). SO_4^{2-} extends cloud lifetimes through increasing the cloud droplet number concentration and decreasing the precipitation efficiency (Lohmann

and Feichter, 1997). SO_4^{2-} acts as CN in the form of $(\text{NH}_4)_2\text{SO}_4$ and ammonium bisulfate (NH_4HSO_4) (Kanayo et al., 2010; Aikawa et al., 2014). SO_4^{2-} exhibits a negative RF value (Banerjee, 2008), which indicates a cooling effect on the climate (IPCC, 2013). SO_4^{2-} is not considered by the World Health Organization (WHO) to be very toxic, although elevated levels can irritate the skin and mucous membranes, as well as potentially aggravating heart and respiratory diseases (EPA, 1999; EPA, 2008). Elevated atmospheric SO_2 levels can also lead to respiratory illness in humans and animals (Shallcross et al., 2003). SO_4^{2-} and NO_3^- are mobile in soils and can be taken up by plant systems (Menz and Seip, 2004). SO_4^{2-} deposition can stimulate microbes to methylate mercury (Hg); a process that introduces Hg into the food chain and contributes to bioaccumulation of Hg (Greaver et al., 2012).

iv. Other inorganic ions considered

Most of the Ca^{2+} and K^+ contributions to the cationic content of precipitation are usually attributed to mineral dust or crustal contributions and is, especially, associated with environments where soil minerals such as K-feldspar are abundant (Yang et al., 2012). Ca^{2+} can also originate from sea salt spray. The alkalinity of water is influenced by the concentration of Ca- and Mg- bicarbonates. These ions therefore act as buffering agents against acidification (Kanayo et al., 2010; González and Aristizábal, 2012). The aforementioned elements, i.e. Ca, K and Mg, together with all dissolved metals also contribute to the hardness of the rainwater. Hardness is classified according to the equivalent calcium carbonate (CaCO_3) concentration in the water with hard water considered to have a concentration greater than 150 mg.L^{-1} (Kanayo et al., 2010). Soft water is corrosive and causes the dissolution of metals, such as Pb and Cd, which when introduced into potable water systems can have detrimental effects on human health (Nishijo et al., 1995; Kanayo et al., 2010).

Na^+ and Cl^- are usually correlated with each other, since these ions are indicative of sea salt spray and are considered to be tracers for marine salt influence (Keene et al., 1986; Sun et al., 2010; Yang et al., 2012; Zhang et al., 2012; Conradie et al., 2016). Cl^- can also be associated with K^+ , which is emitted through biomass burning (Cheng et al., 2013; Park et al., 2013; Aurela et al., 2016).

v. Organic acids (HCOO^- , $\text{C}_3\text{H}_5\text{O}_2^-$, CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$)

Oxalic acid ($\text{C}_2\text{O}_4^{2-}$) is the most abundant dicarboxylic acid in the atmosphere (Kawamura et al., 1996; Pauliquevis et al., 2012). Oxalic acid can be formed when natural vegetation emits isoprene, a volatile organic compound (VOC), which is then oxidised to pyruvic acid and methylglyoxal. These two compounds then react further to form oxalic acid in the cloud environment. Furthermore, oxalic acid is prominent in the atmosphere as it is stable, accumulates and is a product of photochemical oxidation reactions involving the hydroxyl radical. Since nitric acid forms through similar reactions, the rate of formation of oxalic acid is expected to correspond to that of nitric acid formation and a possible concentration relationship is expected. Precipitation is considered to be the major removal process of oxalic acid. The oxalic acid concentration in rainwater is expected to be higher than the sum of formic (HCOO^-) and acetic (CH_3COO^-) acids when pollution levels are elevated (Pauliquevis et al., 2012).

Acetic- and formic acid, which constitutes a large fraction of the organic gaseous acidity, have high vapour pressures and are therefore mostly present in the gas phase in the atmosphere. They are also considered to be major acids, which can even exceed HNO_3 concentrations in certain conditions. These organic acids are formed when O_3 reacts with alkenes in an aqueous environment. Acetic- and formic acid are also emitted by anthropogenic and natural sources, which include fossil fuel combustion and biomass burning. There are, however, significant uncertainties with regard to the individual source contributions to these acids. These acids are easily removed through both wet- and dry deposition processes as they have high Henry's law constant values (Finlayson-Pitts and Pitts, 2000; Connell, 2005). Concentrations of oxalic-, acetic-, formic- and propionic acids can be combined to give a total value for the water soluble organic acid (OA) fraction of the precipitation chemistry. A strong correlation between K^+ and OAs have been related to biomass burning, while the OA fraction is regularly used as an estimate for biomass burning contribution to the precipitation chemistry (Helas and Pienaar, 1996; Galy-Lacaux et al., 2009). Conradie et al. (2016) attributed the OA fraction to natural wildfires and household combustion.

2.2.2 pH and acid rain

The natural pH of unpolluted rain in equilibrium with CO₂ is approximately 5.7. The reason for the naturally low pH is that rainwater reacts with CO₂ to form a weak acid, viz. carbonic acid (H₂CO₃) (Reaction 2.10). Rainwater acidity is sometimes expressed as the amount of CaCO₃ that can be neutralised. An annual rainfall with a pH of 5.6 of 1 meter depth over a surface of one hectare can dissolve about 400-500 kg CaCO₃.ha⁻¹.y⁻¹ (Krug and Frink, 1983; Connell, 2005).



Other naturally occurring acidifying compounds such as SO₂ and NO_x, as well as organic acids can also make a contribution (Krug and Frink, 1983; Schindler, 1988; Eby, 2004; Menz and Seip, 2004; Banerjee, 2008). Alkaline species such as NH₃, carbonates, and Ca⁺- and Mg²⁺-containing dust can increase the pH by neutralising the acidic species and can even lead to alkaline rain (Laouali et al., 2012).

The term acid rain was originally used by Angus Smith in 1852 with reference to the anthropogenic influence of industrial emissions on rain quality (Schindler, 1988). Acid rain gained more public interest later when it was identified as the cause of the acidification of surface water bodies and subsequent decline in fish population in Scandinavia and the northern United Kingdom in the 1970s, which contributed to the now popular term (Krug and Frink, 1983). Acid rain is mainly caused by SO₂ and NO_x, which oxidises to form H₂SO₄ and HNO₃ as shown in Reactions 2.3-2.5 and 2.7-2.9 (Halsall, 2003; McGranahan and Murray, 2003; Connell, 2005). According to references in Halsall (2003) between 48 and 84% of all the SO₂ conversion to H₂SO₄ in the troposphere occurs within clouds. Acid rain has been considered an environmental threat, as it acidifies natural water bodies and mobilises heavy metals such as iron (Fe) and aluminium (Al), which contribute to leaching of nutrients from the soil (Krug and Frink, 1983). Acid rain has been known to have detrimental effects not only on water bodies and aquatic life, but also on soil composition and the related biosphere. Acidic rainwater influences the pH of the uppermost horizon of the soil. This layer of soil contains most root growth and facilitates healthy plant life (Krug and Frink, 1983). Humic acids found in topsoil are especially sensitive to acid rain, as its solubility is pH dependent. When the rain pH is too low, the humic acid becomes less soluble and can no longer regulate the acidity and anionic fluxes in the soil. The result is an increase in the SO₄²⁻ concentration and a decrease in organic acid flux through the soil. Al complexation is inhibited in an acidic soil environment (pH <4.5) and lead to elevated Al concentrations in leached water (Krug and Frink, 1983; Likens et al., 1996). Acid rain also precedes an

equivalent net loss of cations in the soil. Soils that have high acidity and low nutrient content are generally more susceptible to further acidification due to acid rain. Other soils that are prone to acidification through precipitation are soils with a pH >5 and soils where basic cations are easily exchanged. These are typically coarse, siliceous soils with a low cation exchange capacity (CEC). The type and composition of the soil will therefore determine whether it will act as an acid sink or source, as well as the extent of the detrimental influence from acidic precipitation (Krug and Frink, 1983). Alkaline rain can also be detrimental as it can cause nitrification and subsequent acidification of soils. In more basic soil environments Ca^{2+} and Mg^{2+} can also be leached out.

Gaseous NH_3 can partially neutralise H_2SO_4 and HNO_3 by producing ammonium nitrate (NH_4NO_3) and $(\text{NH}_4)_2\text{SO}_4$ (Finlayson-Pitts and Pitts, 2000). Some studies have found a link between the droplet size and pH. These studies suggest that larger drops contain larger particles such as dust and salts, while smaller droplets contains species such as SO_4^{2-} and NH_4^+ (Finlayson-Pitts and Pitts, 2000). Acid rain is not only harmful to ecosystems and the biosphere, but also impacts infrastructure. The negative impacts associated with acid rain have been widely noted as in Banerjee (2008) and other publications.

2.2.3 Wet deposition

The removal of biogeochemical compounds from the atmosphere during precipitation, together with dry deposition of gaseous species and aerosols, balances the biogeochemical budget in the atmosphere (Laouali et al., 2012). Total deposition is determined by the sum of deposition occurring through dry and wet processes (Hall, 2003; Laouali et al., 2012). The terms wet- or dry deposition refers to the moistness of the transport mechanism whereby chemical species are returned to the surface of the earth (Finlayson-Pitts and Pitts, 2000). Dry deposition therefore is the dry removal of gaseous compounds and aerosols, while wet deposition indicate the scavenging of species from the atmosphere through moisture either during droplet and cloud nucleation or during the precipitation event as discussed in Section 2.1.3 (Hall, 2003; Allan, 2004). The removal of chemical species through deposition is directly related to the ambient concentration of those species and therefore deposition can give an indication of the current chemical state of the atmosphere and anthropogenic influence. Wet deposition can play a more crucial role in flux than dry deposition (GESAMP, 1985; Özsoy et al., 2008; Yang et al., 2012). Considering wet deposition, the rate of change in gaseous concentration due to scavenging in a homogenous air mass can be defined in the following equation (2.11) where C is the concentration in moles.m^{-3} , t is time in s and Λ is the scavenging coefficient in s^{-1} (Hall, 2003):

$$\frac{dC}{dt} = -AC \quad (2.11)$$

The scavenging coefficient is dependent on the solubility of the gaseous species. Mass transfer can occur from the air to the droplet or vice versa, depending on the equilibrium concentration in the ambient air mass and in the droplet. This can especially occur in the cloud environment through in-cloud scavenging, as there is sufficient time for this transfer to take place. As indicated earlier (Section 2.1.3), below-cloud scavenging mass transfer coefficients factor in a few more parameters (diffusivity, droplet diameter, the terminal velocity of the droplet, rainfall rate). The droplet size distribution also has a large effect on the total scavenging coefficient. Smaller droplets scavenge more effectively as they have slower terminal velocities and larger mass transfer coefficients. For example, a droplet with a diameter of 0.01 mm has a scavenging coefficient 10^8 times larger than that of a 10 mm droplet (Hall, 2003).

The washout ratio (W_r) is a function of the precipitation concentration (C_p) and the ambient concentration. Using the precipitation concentration together with the precipitation rate or intensity (p_0 in mm.h^{-1}), the specific flux (F) of the species being deposited can be calculated. (Equations 2.12-2.13) (Hall, 2003)

$$W_r = \frac{C_p}{C_{air}} \quad (2.12)$$

$$F = p_0 C_p \quad (2.13)$$

Scavenging processes as described in Section 2.1 are functions of the concentration and solubility of the gas being scavenged. For example, HNO_3 and hydrogen peroxide (H_2O_2) are efficiently scavenged under equilibrium conditions. Since the concentration difference is the chemical driving force of these processes, a droplet containing a concentration of a species, that is deficient in the ambient atmosphere, will undergo mass transfer diffusion out of the droplet into the atmosphere. The amount of scavenging that can take place mostly depends on the size of the raindrops and the distance travelled to the ground (Hall, 2003).

2.2.4 South African perspective

Long-term precipitation studies were conducted at four sites in South Africa within the framework of the Deposition of Biogeochemical Important Trace Species (DEBITS) project. Two of the DEBITS sites, i.e. Vaal Triangle and Amersfoort are in close proximity to anthropogenic activities, while the two other sites, i.e. Skukuza and Louis Trichardt are considered to be regionally background sites. Mphepya et al. (2004) and Mphepya et al. (2006) reported precipitation chemistry for 1986 to 1999 for Amersfoort and Louis Trichardt, and for 1999 to 2002 for Skukuza. In these studies, it was indicated that SO_4^{2-} and NO_3^- concentrations at Amersfoort, Louis Trichardt and Skukuza, were similar to regions around the globe that are affected by acid rain. It was also concluded that the acid formation was subdued by neutralising species such as Ca^{2+} , Mg^{2+} and NH_4^+ . However, the average pH was still determined to be acidic with values of 4.35 and 4.91 at Amersfoort and Louis Trichardt, respectively. Conradie et al. (2016) also indicated higher SO_4^{2-} and NO_3^- concentrations at all four South African DEBITS sites for rain samples collected from 2009 to 2014. In addition, it was also indicated that more rain events were associated with lower pH at Amersfoort, Louis Trichardt and Skukuza, compared to the earlier study period reported by Mphepya et al. (2004) and Mphepya et al. (2006) for these sites. These studies indicated that elevated total ionic concentrations are related to the distance from the source regions (Mphepya et al., 2004; Mphepya et al., 2006; Conradie et al., 2016). However, it was shown through air mass history analysis that recirculation and subsequent aging of air masses influence the chemical content (Conradie et al., 2016).

Coal-fired power plants are a major contributor to anthropogenic SO_4^{2-} concentrations in South Africa (Mphepya et al., 2004; Pretorius et al., 2015). These power plants also contribute to fly ash that is associated with Ca^{2+} . The industrial SO_2 and NO_2 emissions contribute to increased ambient concentrations. This has led to ambient SO_2 and NO_2 levels exceeding South African ambient air quality (AQ) standards in certain areas (Laakso et al., 2012).

In South Africa, seasonal variations exist for species such as NO_3^- , SO_4^{2-} and NH_4^+ , with elevated atmospheric concentrations of these species usually occurring over the winter months (Mphepya et al., 2004; Collett et al., 2010). During these months, an increase in biomass burning is observed through more frequent household combustion and grassland fires (Venter et al., 2012; Vakkari et al., 2013). The stability of the troposphere and the prevalence of stable layers over the interior of South Africa, also trap pollutants by inhibiting dispersion and vertical mixing of the layers (Freiman and Tyson, 2000; Collett et al., 2010). However, pollutants can be transported through advection in the atmospheric layer in which

these species are trapped in, thereby being transported and deposited in distant locations (Freiman and Tyson, 2000; Collett et al., 2010). The anthropogenic emissions and their effect on precipitation from the South African DEBITS sites have increased over the past two decades (Conradie et al., 2016). Conradie et al. (2016) also highlights the regional differences in precipitation chemistry from the four different sites in South Africa and therefore the necessity of expanding spatial information of throughout South Africa.

2.3 Literature Conclusion

Numerous chemical reactions and physical mechanisms influence the precipitation chemistry and hence wet deposition. The precipitation composition is subjected to the influence of the temporal and spatial evolution of the troposphere, local and regional pollution point sources, atmospheric dispersion and long range transportation. High density monitoring networks are established in developed countries in north America and Europe, but relatively few wet deposition studies have been carried out in South Africa (Vet et al., 2014). Determining wet deposition at Welgegund will contribute to the spatial and temporal precipitation chemistry information (in addition to sites for which data have been published) for southern Africa. Furthermore, the complex relationship between the precipitation formation- and event processes to the rainwater chemistry is largely unascertained. Therefore, this study will contribute to the understanding of this linkage by relating appropriate high resolution measurements conducted at Welgegund with the precipitation chemistry. The literature presented and the gaps identified supports the objectives set in Section 1.

3. Experimental

3.1 Site Description

The sampling site for this project is the Welgegund atmospheric measurement station operated by the North-West University (NWU), in collaboration with the University of Helsinki (UH) and the Finnish Meteorological Institute (FMI). The Welgegund research station was established in 2010 (Welgegund, 2015). It is situated on a privately owned farm approximately 100 km west of the Johannesburg metropolitan area and 25 km north-west of Potchefstroom, in the Republic of South Africa. The farm is mainly used for cattle grazing and maize cultivation. Figure 3.1 depicts the geographical location of the measurement site ($26^{\circ}34'10''\text{S}$, $26^{\circ}56'21''\text{E}$) within a regional context, while Figure 3.2 shows a photo of the measurement station. The site is considered to be a regional background station, since it is removed from major pollution point sources. However, it experiences occasional pollution plumes from the Johannesburg-Pretoria (JHB-PTA) megacity, the Mpumalanga Highveld, the Bushveld Igneous Complex and the Vaal Triangle (Collett et al., 2010; Lourens et al., 2011; Lourens et al., 2012; Venter et al., 2012). Apart from pollution plumes from these source regions, the site is also affected by the dominant anticyclonic air mass movement over the South African interior. As a result, air masses analysed at Welgegund have passed over or around the source regions and have substantially aged over the course of movement to the site (Zunckel et al., 2000). In addition, the site is also impacted by relatively clean regional air masses arriving from the west. According to the guidelines of the Global Atmospheric Watch - Precipitation Chemistry Programme (GAW-PCP) of the World Meteorological Organization (WMO), the Welgegund station is considered a regional station since it is less remote than a global station, experiences medium pollutant levels and is located in a rural area with few to no local pollution point sources (Allan, 2004). The terrain surrounding the station is relatively flat and covered with savannah grasslands. A recent vegetation survey within a 60 km radius from the site was presented by Jaars et al. (2016).

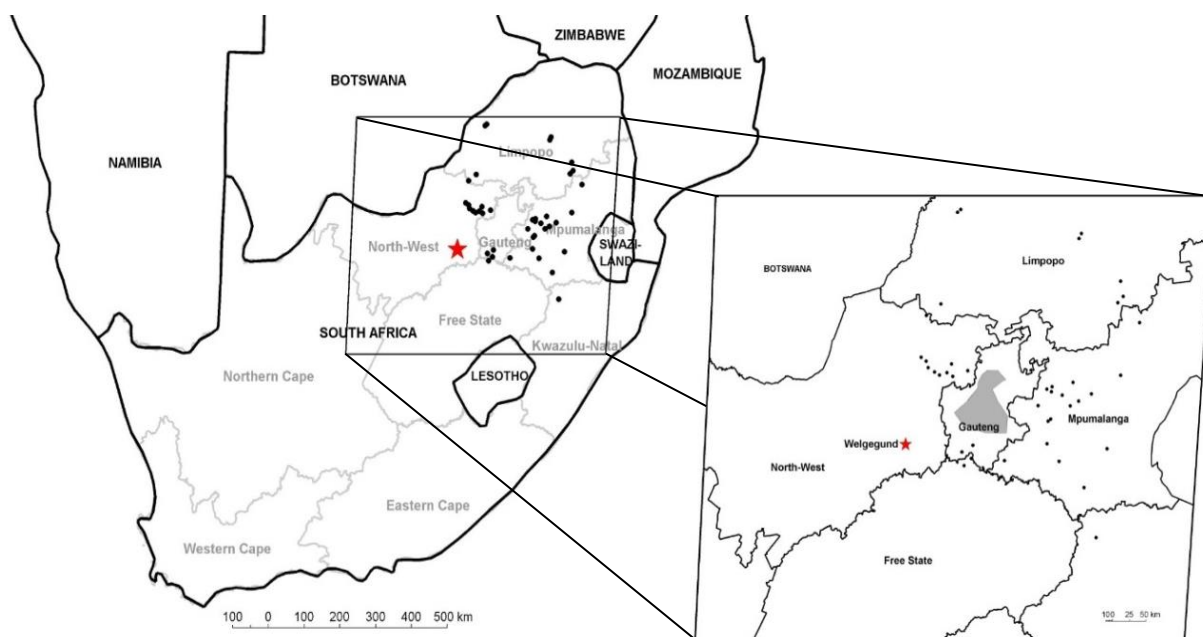


Figure 3.1: Map of southern Africa with a zoomed insert showing the Welgegund atmospheric research station with a red star, relative to major pollution sources indicated with black dots, and the grey shaded area representing the JHB-PTA metropolitan

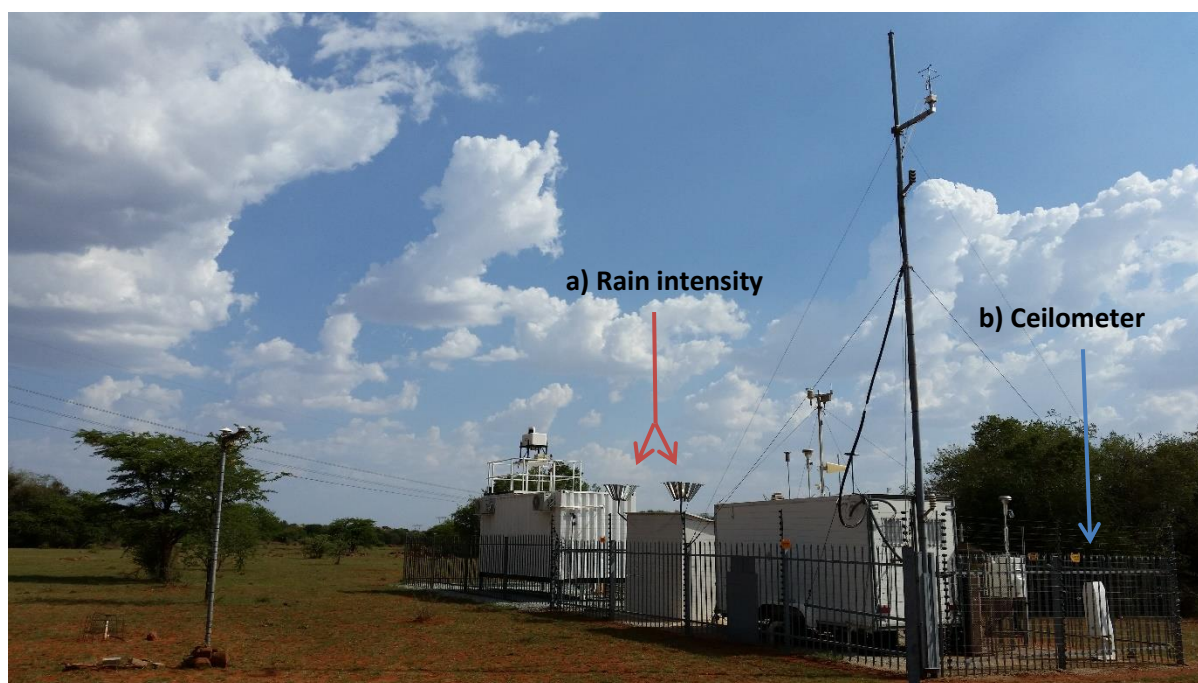


Figure 3.2: The Welgegund atmospheric measurement station with the *Vaisala* and *Casella* (a) rain intensity instruments indicated along with the (b) *Vaisala* CT25K ceilometer (Photo credit: Paul Beukes)

Welgegund is located in the Highveld region and the regional meteorology is therefore similar to the description given in Section 2.1.5. The six year measurement record indicates that temperatures range from -5°C to 36°C with an annual average of 18°C (Welgegund, 2015; Jaars et al., 2016). The wet season ranges from mid-October to April with precipitation being mainly of the convective type (Harrison, 1986; Welgegund, 2015). The assumption is therefore that the boundary layer air is relatively well mixed just before a rain event starts. Gierens et al. (2016) recently presented the evolution of the planetary boundary layer (PBL) at Welgegund. Their results indicated that a stable layer at a depth of 200 m, or lower, traps pollutants during the night and is especially well developed during the colder winter months. After sunrise a mixed layer rapidly grows with the growth rate being more pronounced in the summer months when the most rain events occur. This mixed layer grows to a depth of approximately 1.75 to 2.25 km, with relatively large standard deviations of around 500 m. These depths stabilise and a residual layer remains after sunset, and shrinks as the night passes.

The measurement site has been described in more detail by several authors (Beukes et al., 2013; Jaars et al., 2014; Jaars et al., 2016). The station is comprehensively equipped with measurements including, but not limited to, rain intensity- and other meteorological measurements, ceilometer lidar, aerosol and ion size distributions, aerosol optical properties, trace gas measurements, carbon dioxide- (CO_2), nitrogen dioxide- (NO_2) and sulfur dioxide- (SO_2) fluxes, radiation and soil moisture and -temperature measurements (Beukes et al., 2013; Welgegund, 2015).

3.2 Materials and Methods

Various measurement and analytical techniques were used in this study. The methods and their application are briefly discussed in the following sections. These include in-situ measurements (e.g. wet-only sampling, and rain intensity- and ceilometer lidar measurements), as well as laboratory techniques (including pH and electrical conductivity (EC) measurements, as well as ion chromatography analysis), statistical analysis and modelling of air mass movement.

3.2.1 Rainwater sampling

An automated wet-only sampler, manufactured by the instrument makers of the NWU and derived from the design of the *AeroChemetric* wet-only sampler (Mphepya et al., 2004), was used to collect rainwater samples (see photo in Figure 3.3). The instrument was installed in accordance to the WMO GAW-PCP regulations and to the guidelines regarding the placement relative to obstructive objects (Allan, 2004). The sampler operates using a light-refracting sensor switch. This enables the instrument to open the lid of the collection vessel when precipitation starts and to close the lid a few minutes after the rain event has stopped, therefore preventing contamination and further collection of dry deposition. Sampling was carried out from December 2014 to July 2016. Sample collection (removal from the wet-only sampler) was performed on a daily basis by a site operator, and thereafter directly frozen at approximately -10°C in high-density polyethylene bottles. The precipitation amount was measured as rain depth using a graduated, funnel-shaped rain gauge that limits evaporation. These rain depths were recorded to the nearest millimetre with depths below 0.25 mm regarded as trace amounts. The samples were transported in a frozen state in insulated containers to the laboratory where it was kept in a freezer until chemical analysis commenced.



Figure 3.3: The wet-only sampler (*NWU Instrument Makers*). The light-refracting sensor is visible at the foremost corner of the instrument. The instrument is in the “open” position (Photo credit: Micky Josipovic)

3.2.2 Chemical analyses of rainwater

Analyses was based on the methods recently presented by Conradie et al. (2016). The samples were defrosted overnight, before filtering aliquots using a 0.2 μm filter for ion chromatographic (IC) analysis. The aliquots were then analysed with a *Dionex* ICS 3000 suppressed IC system (Figure 3.4.1) to determine the dissolved inorganic and organic content. For the analyses of the anionic content an *IonPac* AS15 (4 mm) analytical column was preceded by an *IonPac* AG15 (4 mm) guard column with an AERS-500 suppressor (4 mm). The potassium hydroxide (KOH) eluent was prepared in-situ with an eluent generator. For the cationic analyses, an *IonPac* CS16 (3 mm) analytical column preceded by an *IonPac* CG16 (3 mm) guard column along with a self-regulating CERS-500 suppressor (4 mm) was used. The methane sulfonic acid (MSA) eluent was generated in-situ.

The species measured included the inorganic cations and anions, i.e. nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), ammonium (NH_4^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) and sodium (Na^+) as well as the water-soluble organic acids (OAs) viz. acetic- (CH_3COO^-), formic- (HCOO^-), oxalic- ($\text{C}_2\text{O}_4^{2-}$) and propionic acid ($\text{C}_3\text{H}_5\text{O}_2^-$). Standard stock solutions for each ion were obtained from *Industrial Analytical*. A five-point calibration was performed for each ion within the concentration range expected for rainwater in South Africa (Mphepya et al., 2004; Mphepya et al., 2006; Conradie et al., 2016). The detection limits of the IC for the species analysed were 28 ppb for NO_3^- , 31 ppb for SO_4^{2-} , 11 ppb for Cl^- , 4 ppb for NH_4^+ , 2 ppb for Ca^{2+} , 1 ppb for, K^+ , Mg^{2+} and Na^+ . The remaining sample volume not used in the IC analysis was used to measure the EC and pH using a *Hanna Instruments* HI 255 combined meter (Figure 3.4.2). The instrument includes in-situ temperature compensation. The electrodes were calibrated using standard buffer solutions with respective pH values of 4.01, 7.01 and 10.01, as well as a potassium chloride (KCl) EC buffer solution all supplied by *Hanna Instruments*.



Figure 3.4.1: The *Dionex ICS-3000* ion chromatographic system utilised for the ionic content analysis

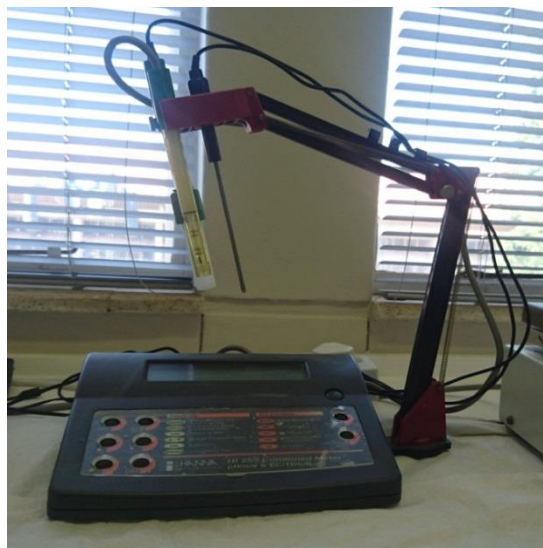


Figure 3.4.2: The *Hanna Instruments* combined EC and pH meter

3.2.3 Rain intensity measurements

The rainfall intensity was measured in this study using *Vaisala QMR102* and *Casella 0.1 mm* tipping bucket instruments (Figure 3.1 and 3.5). These instruments have fixed volume buckets that fill with rainwater and are then tipped by a cantilever action. A time stamp is created for every time the bucket is tipped out. The volume rainwater accumulated over the time period between bucket tips is then calculated. The intensity is reported in mm.h^{-1} (Michaelides et al., 2009). There exists some variability for different instruments, as well as

for the varying effects of wind speed and precipitation intensity on the instruments (Sevruk, 1996). Wind induced loss of precipitation volume accumulating in the tipping buckets exceed the influence of loss due to instrument surface wetting and evaporation. The wind field is furthermore disturbed by the instrument itself being elevated above the ground. Loss of precipitation volume, as measured with the intensity instrument, notably increases with a precipitation rate smaller than 2 mm.h^{-1} . Wind induced losses will thus be more pronounced on the smaller non-convective type droplets. The accuracy of the measured precipitation intensity is reduced by higher wind speeds, lower precipitation intensity and non-convective type rainfall (Chvìla et al., 2005). However, the data from both instruments correlated well in this study and the average of both instruments were used in all calculations. The time stamps created by the instruments were used to find the rain event commencement time, as described in the following section.



Figure 3.5: The *Vaisala* QMR102 and *Casella* 0.1 mm tipping bucket rain intensity instruments as installed at the Welgegund measurement station (Photo credit: Micky Josipovic)

3.2.4 Cloud base height measurements

The cloud base height (CBH) was measured with a *Vaisala* ceilometer CT25K (Figure 3.6). Ceilometer observations were utilised rather than satellite observations or modelled data due to the low time resolution obtained from satellites and lower CBH estimated by models (Vaisala, 1999; Costa-Surós et al., 2013). Ceilometers are mainly used to obtain a vertical profile of the atmospheric visibility at airports. The ceilometer is based on lidar (light detection and ranging) principles. A high intensity near-infrared green laser beam is pulsed vertically from a fixed height above the ground into the air as a collimated beam, i.e. a beam that minimally diverges as it propagates. Backscattering of the light is caused by atmospheric moisture such as haze, fog, rain, mist and clouds. This is a stereographic measurement method whereby the ceilometer software calculates the vertical profile and CBH using the speed of light, the time delay between the laser pulse emissions, and the backscatter signal detection. A vertical profile of the atmospheric backscattering is obtained and visualised as a quantitative signal image. The CBH is automatically obtained where the backscattering value reaches a maximum. However, precipitation obscures this maximum value. Three respective CBH layers can be obtained from the backscattering values. Clouds can occur in more than three distinct layers, or even in indistinct, merged layers. It is also possible for the layers to obscure each other, in which case only the lowest CBH will be detected (Costa-Surós et al., 2013). The Class 1 laser transmitter source in this instrument is an indium gallium arsenide (InGaAs) diode laser with a centre wavelength of 905 ± 5 nm (25°C). The ceilometer has a silicon Avalanche Photodiode (APD) photoelectric element detector (Vaisala, 1999).



Figure 3.6: The *Vaisala* CT25K ceilometer (Photo credit: Micky Josipovic)

Certain assumptions concerning CBHs were made for this study. Firstly, the lowest CBH as detected with the ceilometer was used in all calculations, since very few second and third CBHs were detected. Also, if second and third CBHs were detected, their heights were very similar to the lowest CBH. This can possibly be explained by the different cloud layers that have merged, or due to the lowest layer obscuring the higher layers, as previously suggested (Costa-Surós et al., 2013). The second important assumption was that the CBH was calculated from the median height over a period of 2 hours before the commencement of the rain event (as logged by the rain intensity instruments). This was done mainly to enable the calculation of 3 individual hourly arriving trajectories (i.e. one at the beginning, one in the middle and one at the end of the 2 hours) per rain event. Since individually calculated trajectories could have errors of up to 15 to 30% (Stohl, 1998; Stohl and Koffi, 1998), the use of three instead of only one trajectory significantly mitigated such possible errors.

3.2.5 Air mass histories

Back trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory's (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4.8). This is a computer model that is globally used for atmospheric research, to calculate and simulate air mass trajectories, dispersion, transformation and temporal history of air masses (Fleming et al., 2012; Stein et al., 2015). The model is called a hybrid model because it integrates the numerical Lagrangian approach and the Eulerian method. These methods differ in their approach to the reference frame or grid, as well as methodology in measuring advection and diffusion components. Version 4 of the HYSPLIT model has been extensively used since 2000 (Stein et al., 2015).

Meteorological data, obtained from the Global Data Assimilation System (GDAS) archive of the US National Weather Service's National Centre for Environmental Prediction (NCEP), was used in the HYSPLIT model. Trajectories were calculated for each rain event sampled, by taking the arrival height as the median CBH (as measured by the ceilometer) of the 2 hours before the precipitation events commenced. It was also assumed that the boundary layer is well mixed in the austral summer months (which correlate with the wet season). As mentioned in Section 3.1, this is supported by the results presented by Gierens et al. (2016), who indicated that the mixed layer at Welgegund evolve rapidly after sunrise. For this reason, event-based back trajectories were also calculated for the below-cloud air mass, with the arrival height set at 100m (AGL). This arrival height minimises error margins by avoiding diminished orographic details of the model (Draxler and Hess, 2004; Stein et al., 2015). All calculated trajectories were visualised along with the point source coordinates, population density and fire distributions using MATLAB (www.mathworks.com). Daily fire distribution data was retrieved from the National Aeronautics and Space Administration's (NASA) Distributed Active Archive Centers (DAAC). The data is derived from the Moderate Resolution Imaging Spectrometer (MODIS) on board the polar-orbiting Earth Observation System's (EOS) Terra satellite. The burn scar distribution data for 4 days prior to the rain event was plotted on back trajectory maps (Kaufman et al., 2003).

The population density of South Africa for the 2010 estimate was mapped using data from (CIESIN, 2010). The map displays a population density with a colour index over a 0.25° by 0.25° resolution (Laakso et al., 2012).

3.2.8 Data quality of the chemical rainwater analyses

The WMO Data Quality Objectives procedures were followed to determine the ion balance for each sample. An ion difference (ID) percentage was calculated using the anionic and cationic micro-equivalents (AE and CE respectively in $\mu\text{eq.L}^{-1}$). Samples with an ID outside of the WMO acceptable ranges were flagged and removed from the data set (Equation 3.1-3.2) (Allan, 2004; Laouali et al., 2012).

$$\text{Ion Difference (\%)} = \frac{CE-AE}{CE+AE} \times 100 \quad (3.1)$$

with

$$AE (\mu\text{eq.L}^{-1}) = \left[\sum \frac{C_{Ai}}{(EqWt)_{Ai}} \right] + \left[\frac{5.1}{10^{6-pH}} \right] \times 1000 \quad (3.2)$$

where C_{Ai} is the concentration of the i^{th} anion in mg.L^{-1} , $(EqWt)_{Ai}$ is the equivalent weight of anion i and the second term represents the bicarbonate concentration at 25°C and at a pH above 5.0;

and

$$CE (\mu\text{eq.L}^{-1}) = \left[\sum \frac{C_{Ci}}{(EqWt)_{Ci}} \right] + 10^{(6-pH)} \times 1000 \quad (3.3)$$

where C_{Ci} is the concentration of the i^{th} cation in mg.L^{-1} , $(EqWt)_{Ci}$ is the equivalent weight of cation i and the second term represents the H^+ concentration in $\mu\text{eq.L}^{-1}$.

In addition to the above-mentioned, accuracy (how close the concentration is to the correct value), precision (how large the standard deviation is), as well as general quality control of IC chemical rainwater analyses were established by the Atmospheric Chemistry Research Group's (ACRG) laboratory of the NWU through participation in the bi-annual inter-laboratory comparison study (LIS) of the World Meteorological Organization (WMO). The results of LIS study 54 in 2016 are presented in Figure 3.7.

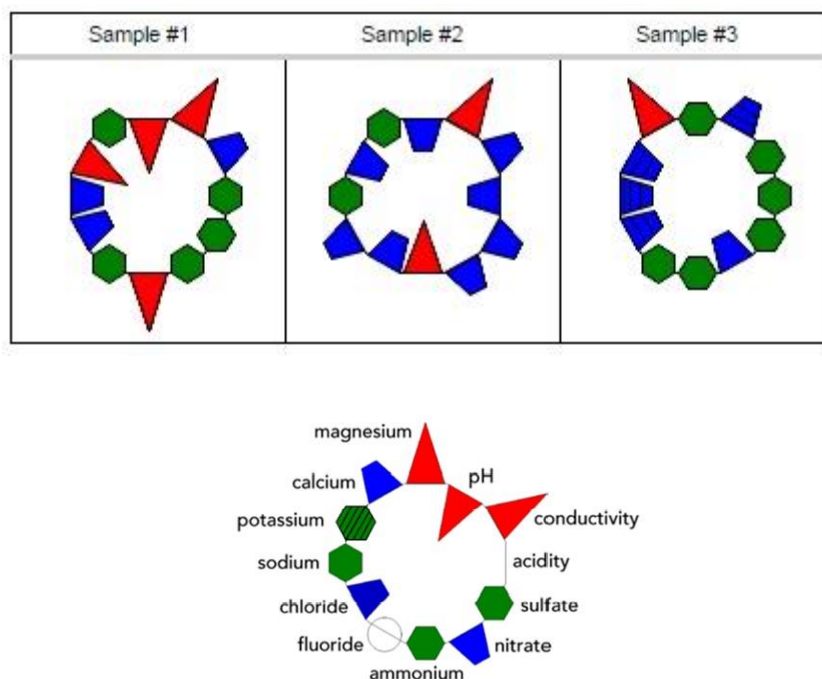


Figure 3.7: The ring diagram results from the LIS 54 study conducted in 2016. The ion legend is shown below the three sample results. The following explanation of the legend is applicable. A green hexagon represents a good result (within the interquartile range (IQR)); a blue trapezoid indicates a satisfactory result (within the range of the median $\pm$ IQR/1.349, also known as the pseudo-standard deviation); unsatisfactory results (outside of the satisfactory range) are represented by a red triangle (QA/SAC-Americas, 2016)

3.2.9 Statistical calculations and evaluation

3.2.9.1 Volume weighted mean and wet deposition flux calculations

Ionic concentrations of rainwater samples were determined in ppb with the IC, which were then converted to micro-equivalents per liter ($\mu\text{eq.L}^{-1}$) by dividing the concentration with the equivalent weight of each of the ionic species. These values were then multiplied with the rainfall event depth ($C_i \times P_i$) and related the event-based chemistry with the back trajectory analysis of air mass movement. The volume weighted mean (VWM) concentration was calculated for the entire sampling period, which was also used to calculate wet deposition fluxes (Equation 3.4 - 3.6).

$$C_{vwm}(\mu\text{eq.L}^{-1}) = \sum_{i=1}^m \frac{C_i \times P_i}{P_{tot}} \quad (3.4)$$

$$\text{Deposition flux (kg.ha}^{-1}\text{.year}^{-1}) = C_{vwm} \times P_{tot} \quad (3.5)$$

with

$$P_{tot}(mm) = \sum_{i=1}^n P_i \quad (3.6)$$

C_{vwm} is the volume weighted mean concentration in $\mu\text{eq.L}^{-1}$ and C_i is the analyte concentration in the i^{th} to the m^{th} sample with invalid samples excluded. P_i is the standard gauge precipitation depth for the sample and n is the total number of all rain events that occurred during the entire sampling period (including rain events for which the ionic analysis was excluded) (Allan, 2004). The VWM is calculated to normalise ionic concentrations measured for different rain depths for a sampling period (González and Aristizábal, 2012).

3.2.9.2 Source contributions and enrichment factor calculations

Certain general sources can be assumed to be emitters of specific ions present in the atmosphere. In this dissertation, source groups were classified as marine-, terrigenous-, agricultural-, biomass burning-, or fossil fuel combustion- sources. A similar approach has been followed in several previous studies where source apportionment of rain chemistry was conducted (Galy-Lacaux et al., 2009; Li et al., 2011; Conradie et al., 2016).

In order to determine the marine contribution to the rainwater chemistry, it is assumed that all Na^+ is of seawater origin. Sea salt fractions (SSFs) are then determined by comparing the ratio of a certain ion X (where $X = \text{K}^+; \text{Ca}^{2+}; \text{Mg}^{2+}; \text{Cl}^-; \text{SO}_4^{2-}$) to Na^+ , to the reference ratios for each ionic species in seawater, as presented by Keene et al., (1986). The excess ionic concentrations ($\mu\text{eq.L}^{-1}$) in the rainwater in comparison to that found in seawater is then determined. Equation 3.7 is used to determine the SSF of the ion X (Keene et al., 1986; Laouali et al., 2012; Shen et al., 2012).

$$\text{SSF}_X = [\text{Na}^+]_{rain} \times \left[\frac{X}{\text{Na}^+} \right]_{seawater} \quad (3.7)$$

Thereafter, the non-sea salt fraction (nSSF) of the ion X can be calculated by subtracting the SSF from the concentration of ion X as measured in the rainwater (Equation 3.8) (Laouali et al., 2012; Shen et al., 2012).

$$\text{nSSF}_X = [X]_{rain} - \text{SSF}_X \quad (3.8)$$

An enrichment factor (EF) can then be calculated to determine the contribution of non-marine sources to the relevant ion concentration in precipitation. The EF is a representation of the relationship between the ratios of the ion X to Na^+ in the rain to the same reference

ratios in seawater (Keene et al., 1986). This EF can thus be calculated with Equation 3.9 (Shen et al., 2012; Conradie et al., 2016).

$$EF_x = [X/Na^+]_{rainwater}/[X/Na^+]_{seawater} \quad (3.9)$$

When evaluating the EF, a value close to 1 is indicative of marine sources dominating the contribution to that ionic concentration. An indication of the terrigenous source contributions is obtained by considering the EF together with the nSSFs (Keene et al., 1986).

Fossil fuel combustion is related to the anthropogenic SO_4^{2-} and NO_3^- concentrations. In order to estimate the anthropogenic SO_4^{2-} contribution, the marine SO_4^{2-} contribution is subtracted from the total SO_4^{2-} measured in the rain. This nSSF- SO_4^{2-} can then further be distinguished as terrigenous or anthropogenic by two methods. The first method uses Ca^{2+} as a reference ion for gypsum ($CaSO_4 \cdot H_2O$). Gypsum is considered to be the reference mineral for continental crust contribution and therefore by determining the excess SO_4^{2-} with regard to gypsum, the anthropogenic contribution can be estimated (Equation 3.10) (Delmas, 1981; Conradie et al., 2016).

$$[SO_4^{2-}]_{anthro} = [SO_4^{2-}]_{nss} - 0.47[Ca^{2+}]_{nss} \quad (3.10)$$

The second method to estimate the anthropogenic contribution to SO_4^{2-} , regards a global modelled annual average background SO_4^{2-} concentration of $7 \mu eq.L^{-1}$. This value is then subtracted from the rainwater SO_4^{2-} VWM. This method was used as an additional measure (Galy-Lacaux et al., 2009; Vet et al., 2014).

The terrigenous contribution can be related to the correlations between Ca^{2+} , Mg^{2+} , K^+ and SO_4^{2-} , because southern African soils are characterised by minerals such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum and clay minerals (e.g. K-rich illite and smectite micas) (Piketh and Pranglely, 1999; Laouali et al., 2012; Conradie et al., 2016). The agricultural source contribution is characterised by the NH_4^+ concentration. Fertilisation, wood fires and bacterial decomposition of biological substances such as urea release ammonia (NH_3) into the atmosphere, which forms NH_4^+ in aqueous solution. Agricultural activities are expected to be an important source contributor due to the rural location of Welgegund. Biomass burning is characterised by the emission of water-soluble organic substances. Therefore the total dissociated organic acid (OA*) correlation with the nSSF of K^+ is taken as an indicator of the biomass burning contribution (Helas and Pienaar, 1996).

3.2.9.3 Acidity

The acidity (H^+ concentration) is determined from the pH measurement with Equation 3.11.

$$pH = \log[H^+] \quad (3.11)$$

The neutralisation of rainwater is indicated when the actual measured acidity (mA) is less than the acidic potential (pA) of the acidic contributors, i.e. SO_4^{2-} , NO_3^- and OA. A neutralisation factor (NF) can be calculated to describe the cation-anion interaction. In Equation 3.12, the relation of a neutralisation cation Y ($Y = Ca^{2+}$, NH_4^+ or Mg^{2+}) to the sum of the potential mineral acids, i.e. H_2SO_4 and HNO_3 is evaluated to calculate the NF with regard to ion Y (NF_Y) (Laouali et al., 2012; Yang et al., 2012; Conradie et al., 2016).

$$NF_Y = \frac{Y}{NO_3^- + SO_4^{2-} + anthro} \quad (3.12)$$

4. Results and discussion:

Precipitation chemistry and wet deposition fluxes

4.1 Ionic composition of wet deposition

Ideally it would have been preferable to collect rain water samples over a period of at least two complete calendar years, which would have allowed assessment of time-related aspects of precipitation chemistry such as inter-annual variations that can be quite significant in South Africa (e.g. Conradie et al. (2016)). However, within the time framework of the current MSc study, the sampling period ranged over a total of 20 months from December 2014 to July 2016. Therefore, in order to obtain some insight into inter-annual variability, two 10 month periods covering approximately two separate rain seasons are compared. These periods are defined from December 2014 to September 2015 and October 2015 to July 2016. As mentioned in Chapter 2, this part of South Africa is characterised by distinct wet and dry seasons, with the wet season occurring from mid-October to April. In Table 4.1, the total amount of events sampled and analysed is presented. The number of samples discarded due to an ion difference (ID) not in the acceptable range, the rain depth (mm) of all the rain events and the collected samples that pass the criteria, as well as the collection efficiencies are also shown (Section 3.2.6, Chapter 3).

Table 4.1: The Welgegund wet deposition sample collection and efficiency summary for the period of December 2014 to July 2016 (*From the WMO GAW-PCP in Allan (2004))

	Dec 2014 - Sept 2015	Oct 2015 - Jul 2016	Dec 2014- July 2016
Events collected	37	19	56
Events contaminated during field and analytical procedures	0	0	0
Events failing ID% criteria (WMO*)	3	0	3
Collected events depth (mm)	431	368	799
Total events depth (mm)	466	368	834
Collection efficiency (%)	92.49	100	95.80

As is evident from these results, only 3 out of the 56 events collected did not pass the ID criteria. It is also clear that the October 2015 to July 2016 wet season was significantly drier than the December 2014 to September 2015 rain season. The percentage of the samples that passed the World Meteorological Organization (WMO) ID% criteria represents wet

deposition samples that were in the WMO percentage total precipitation (%TP) acceptance range, i.e. the %TP for each of the sampling periods were $\geq 70\%$, which is considered to be good (Allan, 2004). The %TP is the percentage of the total measured rainfall depth that was related to valid precipitation chemistry data.

The volume weighted mean (VWM) ionic concentrations ($\mu\text{eq.L}^{-1}$) and wet deposition flux values ($\text{kg.ha}^{-1}.\text{yr}^{-1}$) together with the average pH and electrical conductivity (EC) measured for the entire sampling period (December 2014 to July 2016) and for the two defined periods are listed in Table 4.2. In this table, summed values of the concentrations and wet deposition fluxes for total organic acids (OA) and total dissociated organic acids (OA*) is given, which is the combined values for acetic- (CH_3COO^-), formic- (HCOO^-), oxalic- ($\text{C}_2\text{O}_4^{2-}$) and propionic acid ($\text{C}_3\text{H}_5\text{O}_2^-$), as well as their respective dissociated forms (CH_3COO^* , HCOO^* , C_2O_4^* , $\text{C}_3\text{H}_5\text{O}_2^*$.)

Table 4.2: The VWM ionic concentrations (in $\mu\text{eq.L}^{-1}$) and wet deposition fluxes (in $\text{kg.ha}^{-1}.\text{yr}^{-1}$) for: Welgegund precipitation events for the two defined 10 month periods, as well as for the entire sampling period from December 2014 to July 2016, and for two South African DEBITS sites, viz. Amersfoort and Vaal Triangle are presented for contextualisation (Section 4.6). *(Conradie et al., 2016)

	Welgegund				Amersfoort*		Vaal Triangle*			
	Dec 2014 - Sept 2015		Oct 2015 - Jul 2016		Dec 2014 - Jul 2016		2009 - 2014		2009 - 2014	
	VWM	Flux	VWM	Flux	VWM	Flux	VWM	Flux	VWM	Flux
pH	4.40		5.11		4.62		4.32		4.51	
EC	43.76		57.03		51.93		42.6		33.6	
H⁺	54.78	0.26	23.03	0.09	40.16	0.34	61.18	0.45	44.64	0.43
Na⁺	31.93	3.42	29.90	2.53	30.99	5.94	17.79	2.98	3.50	0.77
NH₄⁺	34.63	2.91	33.34	2.21	34.03	5.12	28.50	3.75	29.06	5.01
N in NH₄⁺		2.26		1.72		3.97		2.91		3.89
NO₃⁻	36.21	10.46	37.22	8.49	36.68	18.97	33.40	15.11	22.97	13.62
N in NO₃⁻		2.36		1.92		4.29		3.41		3.08
K⁺	12.23	2.23	10.11	1.45	11.25	3.67	7.35	2.10	1.41	0.53
Mg²⁺	5.96	0.34	28.65	1.28	16.41	1.66	5.54	0.49	4.55	0.53
Ca²⁺	22.91	2.14	48.60	3.58	34.74	5.81	16.39	2.40	16.18	3.10
Cl⁻	32.33	5.34	29.14	3.80	30.86	9.12	17.96	4.65	4.52	1.53
SO₄²⁻	64.28	14.39	58.74	10.38	61.72	24.73	67.21	23.56	55.00	25.27
S in SO₄²⁻		4.81		3.47		8.26		7.87		8.44
F⁻	0.79	0.07	0.47	0.03	0.65	0.10				
OA	13.86	3.22	31.14	5.80	21.82	9.16	14.64	5.57	12.51	6.10
OA*	9.61		23.91		16.20		13.24		11.49	

It is evident from the results presented in Table 4.2 that the highest ionic VWM concentration and wet deposition contribution over the entire sampling period, as well as during the separately defined rain seasons, was SO_4^{2-} . Conradie et al. (2016) who recently reported wet deposition chemistry measured at the Vaal Triangle, Amersfoort, Skukuza and Louis Trichardt, also reported that SO_4^{2-} had the highest VWM concentration at all four of these sites. Sulfur (S) emissions in the South African interior are mainly associated with anthropogenic activities, hence it is evident from Conradie et al. (2016) that anthropogenic activities strongly influence rain chemistry within industrialised areas (e.g. the Vaal Triangle and Amersfoort), as well as at regional background sites (e.g. Welgegund, Skukuza and Louis Trichardt) (Section 2.2.1 and 2.2.4, Chapter 2).

Of particular interest in this study at Welgegund is that the VWM concentration for SO_4^{2-} over the entire sampling period, i.e. $61.72 \mu\text{eq.L}^{-1}$, was almost as high as that reported for Amersfoort (i.e. $67.21 \mu\text{eq.L}^{-1}$ by Conradie et al. (2016)) that is located within the industrialised Highveld where relatively high SO_2 precursor gas concentrations have been observed (Lourens et al., 2011). The SO_4^{2-} value reported for Welgegund is also higher than that reported for the Vaal Triangle (i.e. $55 \mu\text{eq.L}^{-1}$ by Conradie et al. (2016)), which is also an area with relatively high pollutant levels. Furthermore, the VWM SO_4^{2-} concentration measured at Welgegund is also higher than what has been reported for other African sites and most other regions in the world except for eastern North America, Eastern Europe and East Asia (Galy-Lacaux et al., 2009; Vet et al., 2014).

Although Welgegund is a regional background site, with no nearby pollution point sources (Section 3.1, Chapter 3), it mostly samples air masses that have circulated over or around the major anthropogenic source regions of the South African interior (Beukes et al., 2013; Jaars et al., 2014; Tiitta et al., 2014; Venter et al., 2016). Figure 4.1 presents individual hourly arriving back trajectories (calculated for 96 hours backwards and arriving at 100 m (AGL)) overlaid for the entire sampling period of this study, with colour indicating the percentage frequency of trajectories passing over 0.2×0.2 grid cells. This overlay back trajectory map clearly indicates that the dominant flow of air masses that are sampled at Welgegund, follow a typical anticyclonic recirculation pattern (Garstang et al., 1996; Tyson et al., 1996) over the Bushveld Complex, with several large pyrometallurgical smelters (Hirsikko et al., 2012; Venter et al., 2012), the Waterberg, where two large coal-fired power stations are located (Pretorius et al., 2015), as well as around the relatively polluted Johannesburg-Pretoria megacity (Lourens et al., 2012; Lourens et al., 2016), the Vaal Triangle and the Mpumalanga Highveld (Collett et al., 2010; Lourens et al., 2011; Lourens et al., 2012). This recirculating flow pattern results in relatively aged pollution plumes being analysed at Welgegund, which was proven by Tiitta et al. (2014). The aging process gives

primary pollutants such as SO_2 enough time to oxidise to secondary pollutants, e.g. SO_4^{2-} , which can serve as condensation nuclei (CN) or be scavenged during the rain process (see Section 2.1.2 and Section 2.2.1, Chapter 2) (McGranahan and Murray, 2003; Kanayo et al., 2010; Aikawa et al., 2014). Therefore, although Welgegund is a regional background site, it is clear that the rainwater chemistry is strongly influenced by relatively distant anthropogenic activities.

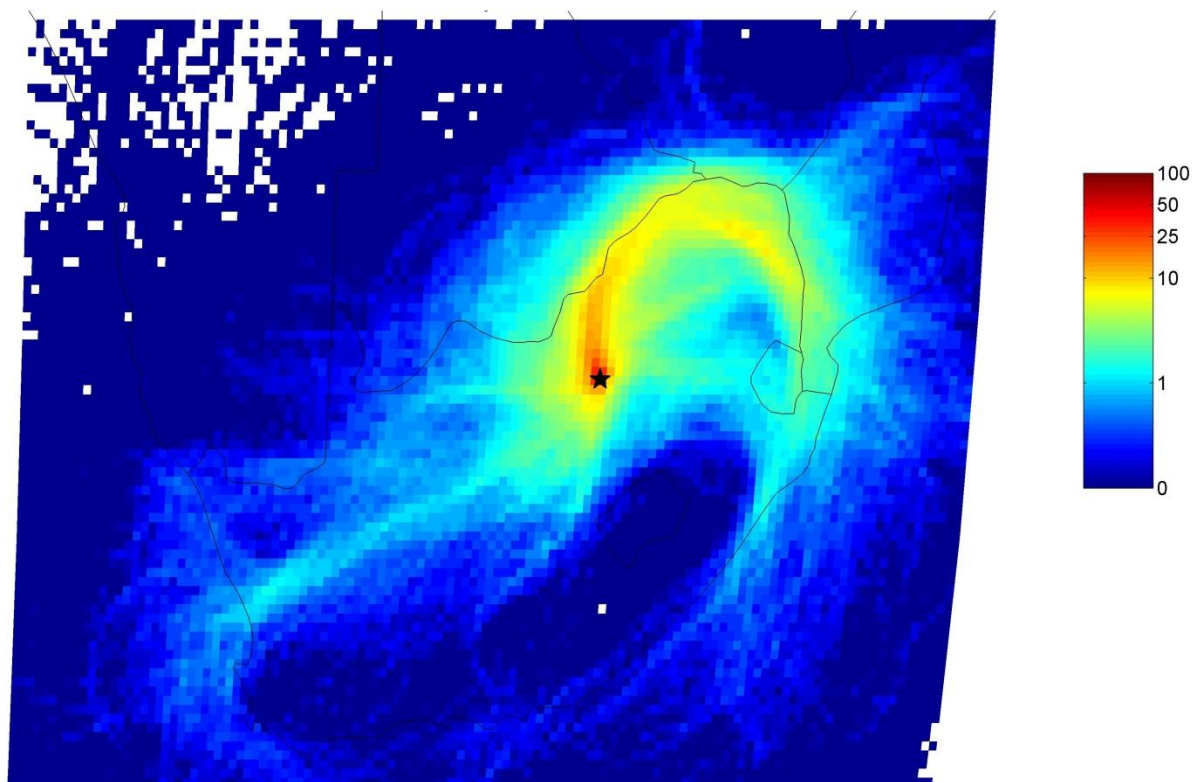


Figure 4.1: The typical anticyclonic recirculation pattern is evident in the hourly arriving back trajectories calculated for 96 hours backwards and arriving at 100 m (AGL), which were overlaid for the entire sampling period (Dec 2014 – Jul 2016). The frequency of trajectories passing over 0.2×0.2 grid cells are shown as percentage indicated with a colour index

Following SO_4^{2-} in VWM concentration order was NO_3^- , Ca^{2+} and NH_4^+ . The NO_3^- and NH_4^+ ionic VWM concentrations reported here were higher than all the values at the sites reported by Conradie et al. (2016). For NO_3^- , this is again likely to be attributed to the oxidation of NO_x emitted in source regions that are strongly influenced by anthropogenic activities, and thereafter having sufficient time for oxidation. NO_3^- can then also act as CN and be scavenged by precipitation events (Section 2.1.2, Chapter 2) (Collett et al., 2010; Pretorius et al., 2015). The relatively high NH_4^+ ionic concentrations at Welgegund could at least partially be attributed to the agricultural activities in the region. Jaars et al. (2016) presented

a vegetation survey of the area within a 60 km radius from Welgegund, and indicated that a significant fraction of the total surface area is being cultivated (mainly maize, but also other crop species), which require substantial fertiliser input. Tiitta et al. (2014) also proved that PM_{10} NH_4^+ at Welgegund is mostly paired with SO_4^{2-} , NO_3^- and Cl^- that serve as CN when water soluble compounds are formed and scavenged (Section 2.1.2, Chapter 2). Ca^{2+} is most-likely associated with wind-blown dust, which is expected to be related to air masses measured at a regional background station. Conradie et al. (2016) also indicated relatively higher VWM concentrations for Ca^{2+} .

The next most concentrated ions namely Na^+ and Cl^- are closely related and considered to be mainly of marine origin (Section 2.2.1.iv, Chapter 2) (Keene et al., 1986; Sun et al., 2010; Yang et al., 2012; Conradie et al., 2016). Mg^{2+} , K^+ and F^- are the three inorganic ions with the lowest VWMs. The organic acid fractions (indicated as OA and as OA* in Table 4.2), along with the K^+ content can be indicative of biomass burning (veld fires) (Section 2.2.1.iv, Chapter 2) (Cheng et al., 2013; Park et al., 2013; Aurela et al., 2016). Biomass burning plumes are often observed at Welgegund (Vakkari et al., 2014). However, from the data presented in Table 4.2, it is evident that the influence of biomass burning on the precipitation chemistry, as indicated by the VWM of OAs, is less pronounced than the effects of anthropogenic-, crustal- and marine- related ions. This limited contribution of biomass burning can be ascribed to the wet season not coinciding with the main fire season. Figure 4.2 depicts the fire pixels detected monthly within 100, 250 and 500 km radius from Welgegund during 2015, as well as the number of rain events sampled per month (data was obtained from the remote sensing observations of fires from the MODIS collection 5 burned area product (Section 3.2.6, Chapter 3)) (Roy et al., 2008). As is evident from this figure, the fire season and wet season do not overlap significantly. Possible source contributors and fire event related effects on precipitation chemistry are explored further in Section 4.3 and Chapter 5.

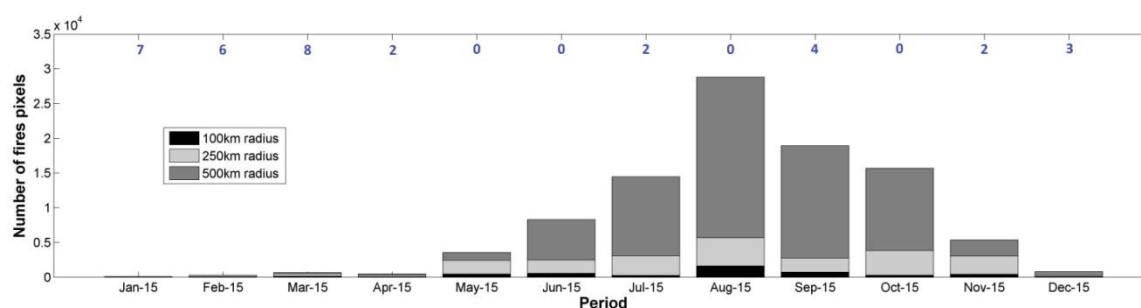


Figure 4.2: The monthly number of fire pixels within a 100, 250 and 500 km radius from Welgegund. The number of rain events sampled monthly is also indicated in blue text, just below the top edge of the figure

4.2 Acidity

The pH measured for the rainwater collected at Welgegund range from 3.55 to 8.06. However, the mean pH for the two periods was 4.40 and 5.11, respectively. These values are relatively low and are considered to be acidic in relation to the natural pH of 5.7 for rainwater in equilibrium with carbon dioxide (CO₂) (Section 2.2.2, Chapter 2) (Seinfeld, 1986; Schindler, 1988). The second 10 month period had a higher mean pH compared to the first period, which can mainly be attributed to significantly higher concentrations of the alkaline ions Ca²⁺ and Mg²⁺ (Table 4.2).

A pH frequency distribution chart for the entire sampling period is presented in Figure 4.3. Considering these frequencies, it is evident that there is a relatively significant variability in pH, however, precipitation events are mostly acidic with approximately 88% of the samples having pH values below 5.6. 7.8% of the samples had a pH <4. The average pH for the two seasons, as well as for the entire sampling period indicated in Table 4.2, are comparable to those of other South African sites such as Amersfoort, Vaal Triangle, Louis Trichardt and Skukuza, as presented in Conradie et al. (2016), Mphepya et al. (2004) and Mphepya et al. (2006). The [SO₄²⁻]/[NO₃⁻] ratio of 1.68 demonstrates that SO₄²⁻ is the main mineral acidic contributor at Welgegund, with almost double the contribution to that of NO₃⁻. Tiitta et al. (2014) indicated that PM₁ SO₄²⁻ at Welgegund, which can serve as CN and be scavenged during rain events, is not fully neutralised by cationic species. Therefore, there seems to be at least some correlation between the rain and aerosol chemistry at Welgegund.

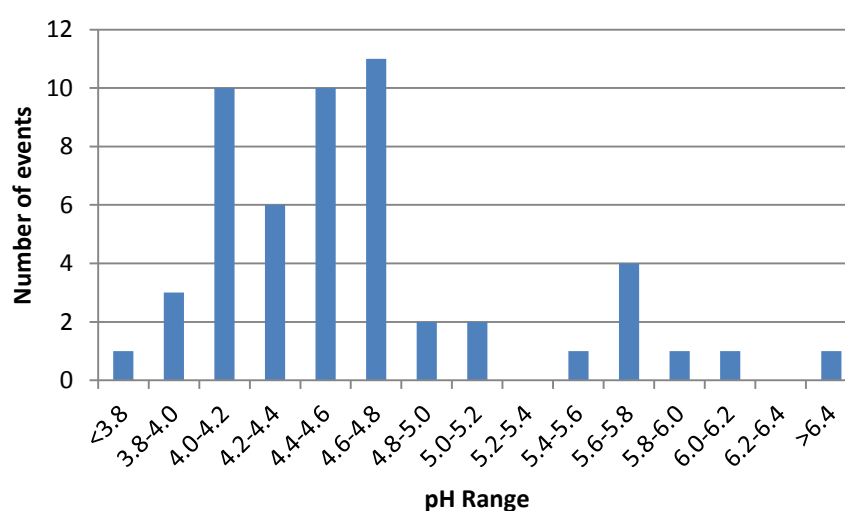


Figure 4.3: The pH frequency distribution measured for precipitation collected at Welgegund from December 2014 to July 2016

The acidity potential (pA) (defined as the sum of the potential acidic compounds, i.e. sulfuric acid (H_2SO_4), nitric acid (HNO_3) and organic acids (OAs)) presented in Table 4.3 indicate that the measured acidity (H^+ , mA) of the rain samples is significantly less than the total H^+ concentration estimated, which can be attributed to neutralisation (Section 3.2.9, Chapter 3) (Mphepya et al., 2004; Laouali et al., 2012; Conradie et al., 2016).

Table 4.3: The potential acidity and the actual measured acidity is presented as VWM ionic concentrations and as a percentage

	$\mu\text{eq.L}^{-1}$	%
Sulfuric acid	42.3	44
Nitric acid	36.7	39
Organic acids	16.2	17
Total estimated H^+ (pA)	95.2	100
Measured H^+ (mA)	40.2	42

Neutralisation factors (NFs) can be calculated to evaluate the neutralisation of H_2SO_4 and HNO_3 by bases consisting of cations (e.g. Ca^{2+} , NH_4^+ and Mg^{2+}) associated with the relevant anions. Table 4.4 presents the respective NFs of NH_4^+ , Ca^{2+} and Mg^{2+} as calculated by Equation 3.12 (Section 3.2.9, Chapter 3). At most South African sites where rain chemistry have been reported (Mphepya et al., 2004; Mphepya et al., 2006; Conradie et al., 2016), it was found that NH_4^+ had the largest neutralising effect. However, from the results presented here it is evident that Ca^{2+} was the main neutralising factor over the entire period and, especially, during the second collection period (Oct 2015 – Jul 2016). The large neutralising contribution of Ca^{2+} can most-likely be attributed to a larger dust contribution to the precipitation chemistry. Welgegund is located closer to the dry and dusty areas of the Kalahari and the Karoo that lie to the west, than any other South African site for which rain chemistry have previously been reported. This notion is also supported by the neutralising contribution of Ca^{2+} being much higher in the second, drier defined rain season than during the first, wetter defined rain season (Table 4.1). Jaars et al. (2016) gave an overview of the location of Welgegund within the context of biomes, which substantiate the afore-mentioned deduction. As expected NH_4^+ also had a notable contribution to the neutralisation with Mg^{2+} having the least influence. The NH_4^+ NF stayed relatively constant throughout the entire sampling period, indicating a relative independence from the rain depth over a season, which is in contrast to the rain depth influence on the Ca^{2+} and Mg^{2+} neutralisation contribution. The rain depth influences the soil moisture and subsequently the atmospheric dust load.

Table 4.4: The neutralisation factors (NF) for NH_4^+ , Mg^{2+} and Ca^{2+}

Sampling period	NF _{NH4+}	NF _{Mg2+}	NF _{Ca2+}
Dec 2014 - Sept 2015	0.400	0.069	0.265
Oct 2015 - Jul 2016	0.475	0.409	0.693
Dec 2014 – Jul 2016	0.431	0.208	0.440

4.3 Source contribution evaluation

Linkages between concentrations of different ionic species detected in rainwater and similar sources most-likely to contribute to the presence of these atmospheric species can be explored statistically by various methods. For instance performing principal component analysis (PCA) can give insight into the possible sources that contribute to the rainwater composition (Conradie et al., 2016). However, the dataset considered for this study is too limited to yield statistically significant results with such an advanced statistical method. It is, however, the intention of the candidate to continue this work in order to gather a larger dataset, which can then be statistically evaluated through methods such as PCA or positive matrix factorisation (PMF) in the future. Notwithstanding the limitations of the relatively small dataset considered in this study, Spearman correlations between the different species analysed were calculated and are presented in Figure 4.4. In this figure the correlation coefficient is displayed with a colour index where red corresponds to a correlation coefficient of 1, which decreases towards blue.

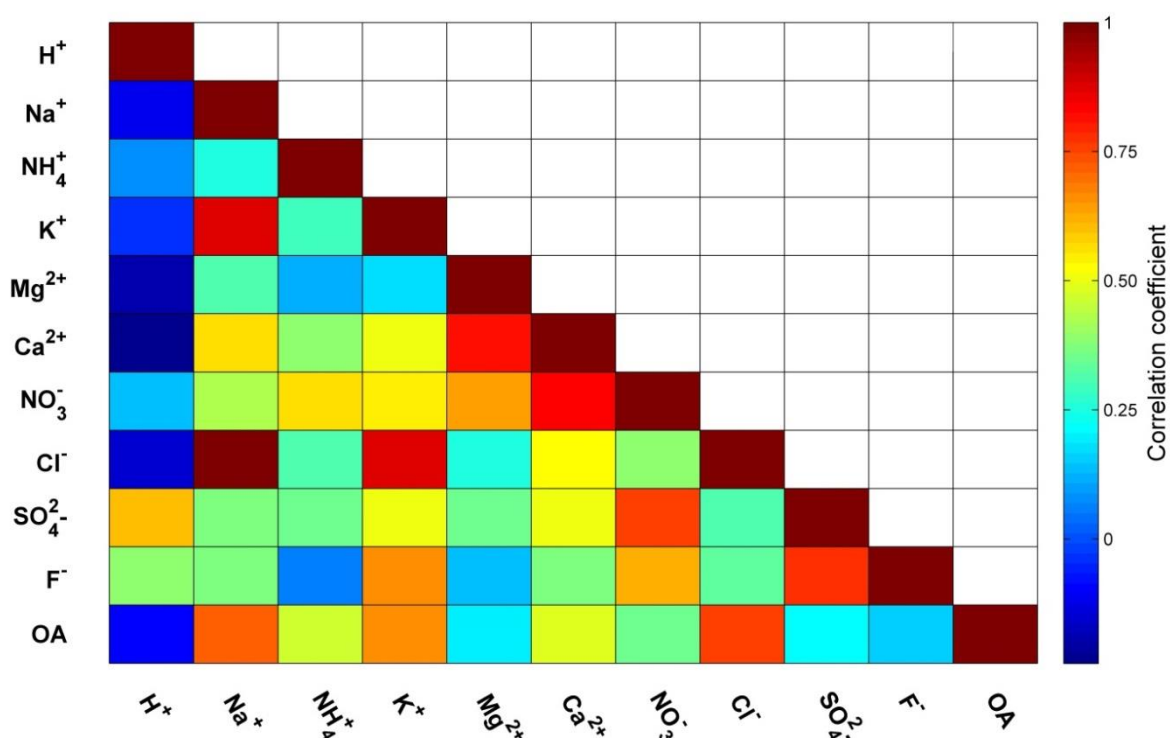


Figure 4.4: Spearman correlations between the ionic species in rain water. Red indicates a good correlation with a correlation coefficient close to 1 and blue indicates a weaker or negative correlation

As is evident from Figure 4.4, Ca²⁺ correlates strongly (0.84) with NO₃⁻ and relatively well with SO₄²⁻ (0.52) confirming a neutralisation relationship, as was indicated earlier in Section 4.2. A prevalent terrigenous CaCO₃ influence (e.g. wind-blown dust) can explain the high neutralisation through Ca²⁺, which can take place for example during the reaction of CaCO₃ with HNO₃ to form calcium nitrate (Ca(NO₃)₂). Likewise, Mg²⁺ as a neutralising agent correlates well with NO₃⁻ (0.64), while also correlating with Ca²⁺ (0.83) as derived from terrigenous sources (Laouali et al., 2012). A high dust influence could therefore explain the neutralisation and confirms that terrigenous sources (e.g. wind-blown dust) are a significant contributing source to the chemistry observed in the rain water at Welgegund. A good correlation between SO₄²⁻ and NO₃⁻ (0.76) confirms that anthropogenic activities (e.g. fossil fuel combustion), emitting both S- and N-containing species, are also important sources. High correlations between K⁺ and Cl⁻ (0.87), as well as between Na⁺ and Cl⁻ (0.99), confirm the origin of KCl and NaCl from biomass burning and marine sources, respectively. The Spearman correlations indicated that the major sources of ionic species in rainwater collected at Welgegund were marine-, terrigenous-, fossil fuel combustion- and biomass burning sources.

The ionic composition of the rainwater was categorised into sources associated with the presence of ionic species in precipitation as described in Section 3.2.9 (Chapter 3), as well as indicated in the above-mentioned paragraph. The sources were classified as marine, terrigenous or crustal, agricultural, fossil fuel combustion and biomass burning. The marine contribution was determined by empirically calculating the sea salt fractions (SSF) of Na^+ , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} and K^+ (Section 3.2.9.2, Chapter 3). The terrigenous or crustal contribution was derived by calculating the non-sea salt fractions (nSSF) of the above mentioned ions (Section 3.2.9.2, Chapter 3). Non-marine SO_4^{2-} was divided into terrigenous and anthropogenic source contributions with the two methods described in Section 3.2.9.2 (Chapter 3). Conradie et al. (2016) assumed that anthropogenic sources of SO_4^{2-} in this part of South Africa are predominantly fossil fuel combustion, which was also assumed in this study. In addition, although NO_3^- and NH_4^+ can be associated with different anthropogenic and natural sources, in this study it was also assumed that NO_3^- is predominantly associated with fossil fuel combustion, while NH_4^+ is mainly related to agriculture, similar to Conradie et al. (2016). Agricultural activities are related to the formation and emission of NH_4^+ through the decomposition of animal excreta. Gaseous NH_3 released from fertilisers and decomposing biomass is subsequently reduced to NH_4^+ . The biomass burning contribution is related to the OA content, which dissociates in atmospheric moisture (OA^*) (Section 2.2, Chapter 2) (Sun et al., 2010; Cheng et al., 2013; Conradie et al., 2016). In Figure 4.5, the estimated percentage contribution of each of the sources identified, are presented. From Figure 4.5, it is evident that fossil fuel combustion is the largest source contributor to the precipitation chemistry, while marine and terrigenous source groups had slightly lower contributions than fossil fuel. Much lower contributions were calculated for agricultural- and biomass burning sources in relation to the other sources.

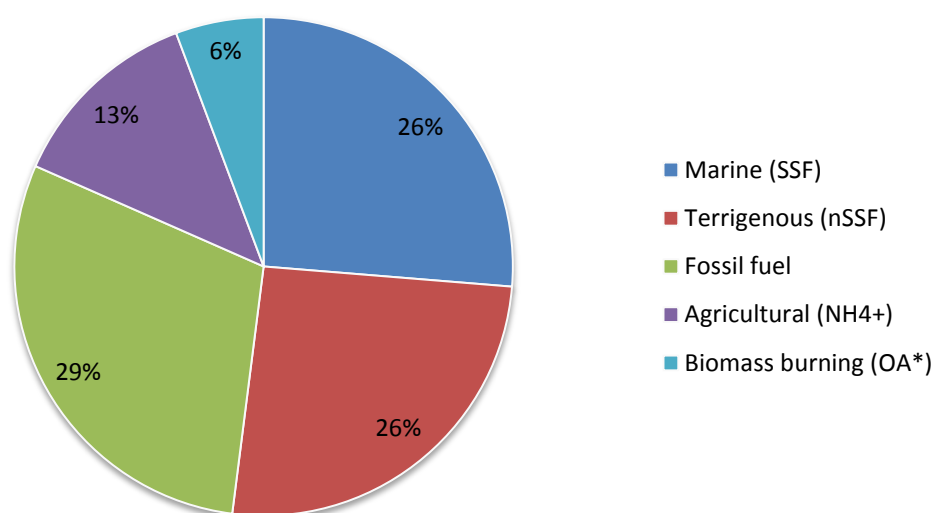


Figure 4.5: Apportioned estimated source contributions to the ionic composition of rainwater collected at Welgegund as calculated through the methods described in Section 3.2.9.2.

As mentioned in Section 3.2.9 (Chapter 3), the marine contribution or SSF to the rainwater is estimated for Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} and K^+ based on the calculated ratios of each of these ions to Na^+ as presented by Keene et al. (1986). In Table 4.5 these theoretical ion to Na^+ ratios for Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} and K^+ in rainwater are presented together with ion to Na^+ ratios calculated for rainwater collected at Welgegund. From these ratios, enrichment factors (EFs) were also calculated and presented in Table 4.5 (Equation 3.9, Chapter 3).

Table 4.5: The ratios of Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and K^+ to Na^+ in seawater as presented by Keene et al. (1986), ratios of each of these ions to Na^+ in the Welgegund rainwater, and the respective enrichment factors (EFs)

Ion	Ion ratio to Na^+ in seawater*	Ion ratio to Na^+ in rain (2014- 2016)	Enrichment Factor (EF)
Cl^-	1.160	0.996	0.86
SO_4^{2-}	0.121	1.992	16.46
Mg^{2+}	0.227	0.529	2.33
Ca^{2+}	0.044	1.121	25.54
K^+	0.022	0.363	16.50

By examining the Spearman correlation coefficients, source group estimations and EFs, the following deductions can be made. Comparison with the seawater ratios indicate that only the Na^+/Cl^- rain ratio is equivalent to the seawater ratio. The enrichment factor of Na^+/Cl^- is

also close to 1, which indicates that there is little influence on concentrations of these species from sources other than marine sources. The ratios of all the other ions are all more than double in rainwater collected at Welgegund compared to seawater ratios, which consequently exhibit high EFs. Na^+ and Cl^- also correlate strongly with each other (0.99) as indicated in Figure 4.4. K^+ also shows a strong correlation with Na^+ (0.88) indicating a marine K^+ contribution. Mg^{2+} shows a relatively weak correlation to Na^+ (0.32) and Cl^- (0.26), which also has a ratio to Na^+ that is two times higher compared to the seawater ratio. This indicates that sea spray is not a major contributor to Mg^{2+} levels. This conclusion is supported by the strong correlation of Ca^{2+} and Mg^{2+} (0.83) that indicates a terrigenous contribution, which is related to the alkaline nature of the regional geology surrounding Welgegund (Section 2.2.1, Chapter 2) (McCarthy and Rubidge, 2005; Conradie et al., 2016).

The correlation coefficient of 0.87 between K^+ and Cl^- , as well as their respected correlations with OAs, i.e. 0.66 and 0.76, respectively, indicate biomass burning as a likely source origin of KCl. As mentioned previously, a strong correlation (0.76) between NO_3^- and SO_4^{2-} is indicative that these species originate from similar source regions influenced by anthropogenic activities. These are typically fossil fuel combustion sources associated with populated and industrial regions. NH_4^+ is relatively correlated to NO_3^- (0.56), which indicates a possible common nitrogenous source such as ammonium nitrate (NH_4NO_3) fertilisers typically used in agriculture.

Anthropogenic activities have been known to contribute largely to the total SO_4^{2-} concentration in wet deposition throughout South Africa (Mphepya et al., 2004; Mphepya et al., 2006; Conradie et al., 2016). SO_4^{2-} has been identified as an important pollutant species, which contributes to acid rain formation. It is therefore important to determine the anthropogenic contribution to the SO_4^{2-} in wet deposition. The anthropogenic contributions to SO_4^{2-} concentrations in wet deposition are related to fossil fuel combustion activities, such as coal-fired power stations and petrochemical plants. These combustion activities emit SO_2 and H_2S , which are gaseous precursors to SO_4^{2-} as described in Section 2.2.1.iii (Chapter 2). An estimation of the different source contributions to the SO_4^{2-} concentrations in the Welgegund rainwater, calculated with Equations 3.7, 3.8 and the two methods described for determining the anthropogenic contribution (Equation 3.10, Chapter 3), is given in Table 4.6.

Table 4.6: The estimated source contributions to SO_4^{2-} (in $\mu\text{eq.L}^{-1}$). The values were calculated with the first method described in Section 3.2.9.2. as an excess concentration to the SO_4^{2-} supplied by gypsum. The values in brackets are the results from the second method based on the global estimated background SO_4^{2-} concentration of $7 \mu\text{eq.L}^{-1}$

Total ($\mu\text{eq.L}^{-1}$)	SSF ($\mu\text{eq.L}^{-1}$)		nSSF ($\mu\text{eq.L}^{-1}$)	Anthropogenic contribution to total [SO_4^{2-}] (%)	
	Marine	Terrigenous		Method 1	Method 2
61.7	3.8	15.7 (3.3)	42.3 (54.7)	69	89

It is evident that the anthropogenic contribution to the total SO_4^{2-} concentration in the rainwater is much higher than the marine and terrigenous contributions. The contribution percentage calculated with the first method is comparable to values determined by Conradie et al. (2016) for Louis Trichardt (72%). The anthropogenic contributions calculated with the second method are similar to anthropogenic contributions estimated for Amersfoort (90%) and Vaal Triangle (87%). The difference between the two methods can be ascribed to an underestimation of the gypsum contribution in the second method. It is clear that the anthropogenic influence on the SO_4^{2-} concentration is significant even at the regional background site of this study.

4.4 Temporal trends

Seasonal changes in meteorology (e.g. rainfall depth and frequency) and in the environment (e.g. land cover), contributes to seasonal variations in the chemical composition of the rainwater. In Figure 4.6, the variability in monthly ionic concentrations is presented. Monthly averaged pH values are represented by Figure 4.7.

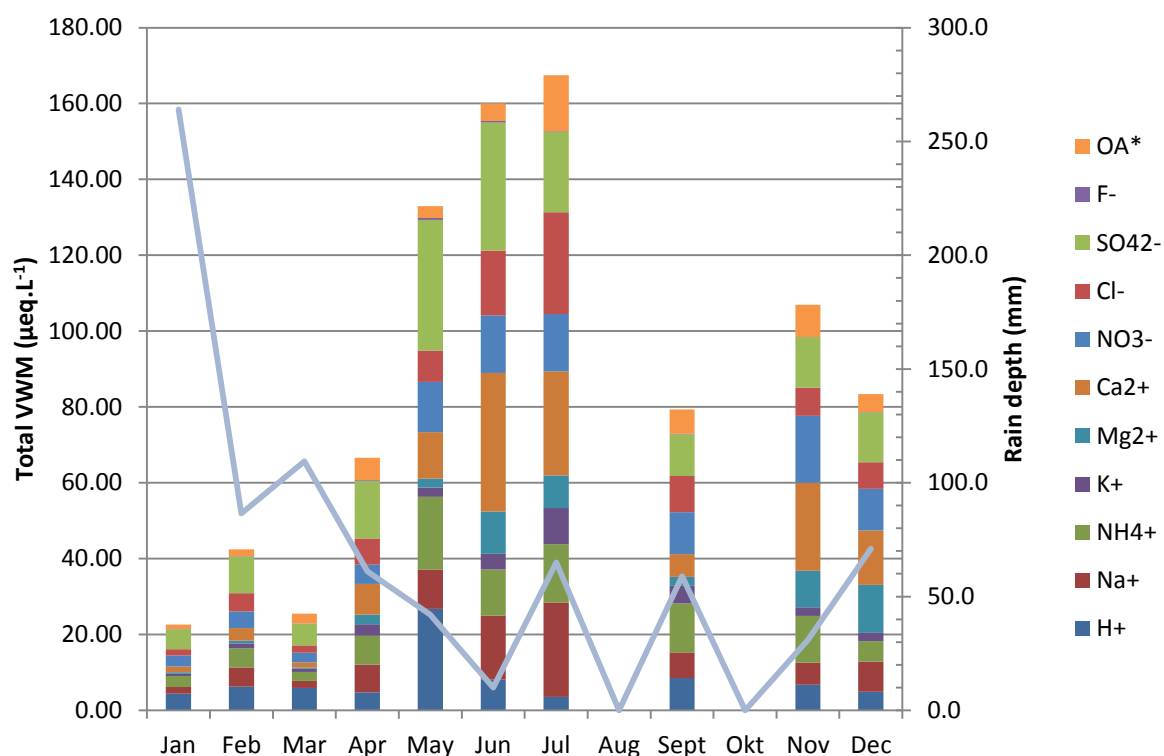


Figure 4.6: The monthly total VWM ionic content (in $\mu\text{eq.L}^{-1}$) of the Welgegend precipitation for the entire sampling period. The mean monthly rainfall depth (in mm) is indicated by a blue line

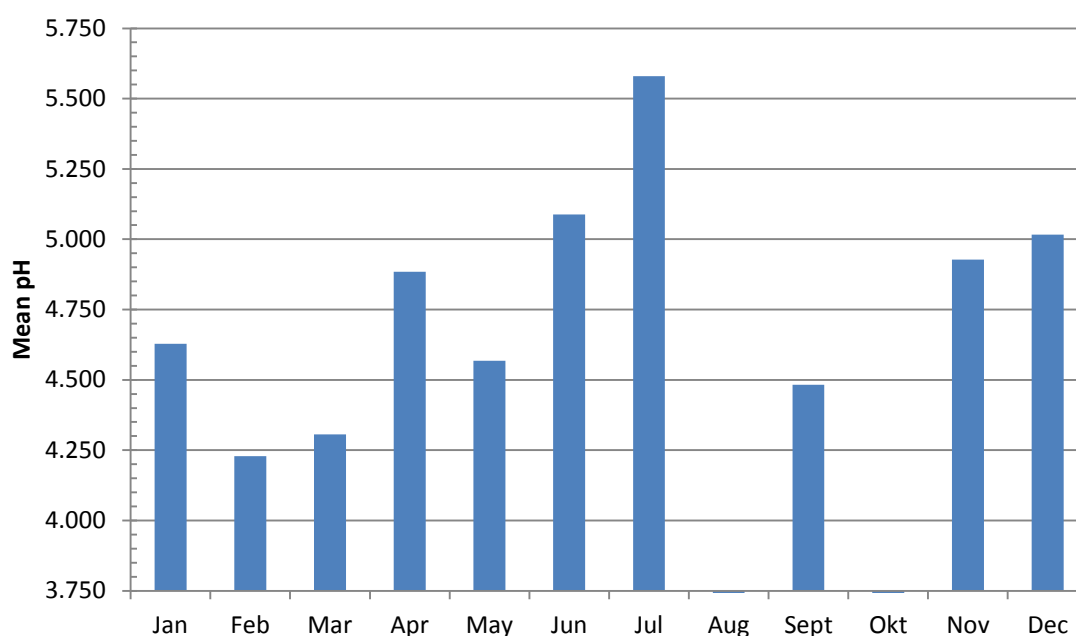


Figure 4.7: The monthly averaged pH values for Welgegend over the entire sampling period

From Figure 4.6 it is evident that in the months associated with the dry season, i.e. the austral fall and winter months, April to July, the VWM ionic concentrations are elevated. It is expected that the atmospheric concentrations of the species will increase during the dry season because less frequent rainfall events decrease the wet removal of species from the atmosphere and dry deposition together with chemical transformation becomes the main removal mechanisms. The first rain events of the wet season, starting in September, also have higher levels than in the rest of the wet season.

The levels of pollutant species, such as SO_4^{2-} and NO_3^- , increase in the austral winter months. This phenomenon can be ascribed to the build-up of pollutants in the atmosphere due to more pronounced low-level inversion layers that trap and concentrate pollutants near the surface of the earth, as well as more distinctive recirculation of air masses (Section 2.1.5 and 2.2.4, Chapter 2) (Freiman and Tyson, 2000; Collett et al., 2010). In addition, NO_3^- and OA concentrations also increase due to an increase in biomass burning, i.e. household combustion for space heating and wildfire events, during these months. January has the lowest VWM loading, which is most-likely due to dilution through the large rainfall depth. The highest average pH was observed in July (5.58) and June (5.09), which can be linked to the neutralisation capacity of the atmosphere through higher atmospheric concentrations of Ca^+ and Mg^+ from terrigenous origin that is more likely to occur during these drier months. These increased VWM concentrations are also correlated to increasing pH values as seen in Figure 4.7.

4.5 Wet deposition fluxes

The wet deposition fluxes are presented in Table 4.2 (in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$). The wet deposition fluxes reflect the VWM ionic concentrations as described in Section 4.1, with the largest flux contributions associated with SO_4^{2-} and NO_3^- . The S and total N wet deposition fluxes were determined to be 8.26 and 8.26 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ respectively. The S flux is similar to S fluxes determined for Amersfoort (7.87 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) and for Vaal Triangle (8.44 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$). The total N flux at Welgegund is much higher than those reported by Conradie et al. (2016) for all the sites e.g. at Amersfoort (6.32 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) and Vaal Triangle (6.97 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$).

4.6 Contextualisation

Although some values reported during this study have been contextualised to some degree, a more comprehensive contextualisation follows. Overall, the Welgegund VWM and wet deposition fluxes are higher than the values for the South African DEBITS sites Amersfoort, Vaal Triangle, Louis Trichardt and Skukuza reported by Conradie et al. (2016). A comparison is given in Table 4.1 (Section 4.1) and Table 4.6 for Welgegund, Amersfoort and Vaal Triangle, as these sites have comparable values. The values of Na^+ , NO_3^- and K^+ are higher yet similar to those measured at Amersfoort. NH_4^+ is slightly higher, but comparable to Vaal Triangle and Amersfoort values. SO_4^{2-} concentrations at Welgegund are lower than at Amersfoort, but higher than SO_4^{2-} levels at Vaal Triangle. Two possible explanations can be given for the generally elevated levels measured at Welgegund. Firstly, as explained earlier, air masses sampled at Welgegund are mainly aged (Figure 4.1; Section 4.1 and 2.1.5). In addition, another possible explanation for the overall elevated levels can be that the sampling period was exceptionally dry. Therefore an increase in atmospheric build-up can occur between rain events.

Table 4.7: A contextualisation of Welgegund with two South African DEBITS sites (Conradie et al., 2016). The order of VWM concentrations are listed from highest to lowest from left to right

	[Highest]							[Lowest]	
Welgegund	SO_4^{2-}	NO_3^-	Ca^{2+}	NH_4^+	Na^+	Cl^-	OA	Mg^{2+}	K^+
Amersfoort	SO_4^{2-}	NO_3^-	NH_4^+	Cl^-	Na^+	Ca^{2+}	OA	K^+	Mg^{2+}
Vaal Triangle	SO_4^{2-}	NH_4^+	NO_3^-	Ca^{2+}	OA	Mg^{2+}	Cl^-	Na^+	K^+

5. Results and discussion:

Air mass origin and rain intensity

One of the objectives of this study was to initialise the development of a method capable of identifying rain event specific parameters that could affect the chemical composition of the rainwater (Objective vi, Chapter 1). In order to fulfil this objective, it was proposed that event-based measurements of cloud base height (CBH) and rain intensity in combination with back trajectory analysis may be a possible method to evaluate the effect of air mass movement over source regions on the ionic composition of rainwater. The basic principles of the proposed method are as follows:

- Event-based rainwater samples were collected at Welgegund, stored and chemical analysis performed (Sections 3.2.1 – 3.2.2, Chapter 3).
- In order to assist in relating the rainwater chemistry of a specific event with possible sources or source region effects, the onset (time) of the rain event is determined with the aid of the rain intensity instruments at Welgegund (Section 3.1 and 3.2.3, Chapter 3). This event-based start-time is then rounded off to the nearest hour.
- The ceilometer at Welgegund (Section 3.2.4, Chapter 3) is used to determine median CBHs for the 2 hours before the onset of the rain event, as determined in the above-mentioned step.
- HYSPLIT 4.8 is then used to calculate 3, hourly arriving back trajectories (calculated for 96 hours backwards), which correspond to the afore-mentioned 2 hours before the onset of the rain event, both at CBH, as well as at 100 m above ground level (AGL). For example, if the rain event started at 16:00 p.m., three 96 hour back trajectories (arriving at 14:00, 15:00 and 16:00 p.m.) will be calculated to arrive at the measured averaged CBH, as well as at 100 m AGL.
- The reasoning behind the above-mentioned step is that the back trajectories calculated at the CHB could possibly give insight into the air mass history of condensation nuclei (CN) particles that formed part of the cloud droplets, as well as aerosol and pollutant gasses that can be scavenged at the CHB by in-situ cloud processing. Additionally, the back trajectories calculated at 100 m AGL will most likely give insight into the air mass history of the air mass below the cloud base height through which additional pollutant scavenging can occur during the actual rain event (see Section 2.1.2 – 2.1.4, Chapter 2 for a detailed description of CN, in-cloud scavenging and rain event scavenging processes). The height of 100 m AGL was chosen, since it can be assumed that most rain events sampled at Welgegund was formed due to convective processes ((Harrison, 1986; Preston-Whyte and Tyson,

1988), Section 2.1.5, Chapter 2), which implies that the planetary boundary layer below the cloud base should be well mixed. This is an apparent assumption and it is expected that this method will be further developed in future to reduce the assumptions made in this pilot study.

- The two above-mentioned rain event specific sets of back trajectories are then plotted on a map and examined against the location of large point sources, source regions (both strongly impacted by anthropogenic activities, as well as more natural source areas), pollution densities across southern Africa, as well as the occurrences of veld fires in order to assess whether air mass histories present any insight into the measured rain chemistry.

In order to assist in determining whether air masses, from which clouds have formed, or through which rain droplets will fall and scavenge pollutants, large point sources and population densities were considered. Figure 5.1 presents a population density map of southern Africa for 2010 obtained from CIESIN (2010). It is evident that a relatively low population density area exists towards the western sector relative to Welgegund, with high population density in Gauteng, the northern parts of Limpopo and on the east coast in the Eastern Cape and KwaZulu-Natal. Another region of high population density is seen in the Western Cape near Cape Town. In Figure 5.1, Welgegund is indicated with a red star and the large pollution point sources are indicated with black dots. These represent major power stations, petrochemical plants and pyrometallurgical smelters.

In the following subsection selected case studies will be presented to introduce the potential significance of the above mentioned method.

On the following maps (Figures 5.2 to 5.8) the blue lines indicate the 96-hour backward trajectories calculated at the median CBH height prior to the rain event. The bold blue lines indicate the movement over the last 12 hours. The yellow/gold or red lines represent the 96-hour backward trajectories calculated to arrive at 100 m AGL (which is associated with the planetary boundary layer (PBL) or below-cloud base air mass). The pollution point sources are depicted with the black dots, the Welgegund atmospheric research station is shown by a black star and the Johannesburg-Pretoria (JHB-PTA) conurbation is indicated by the grey shaded area. Following each map, a table lists the rainwater composition for the event. The ionic concentrations are normalised by multiplying the respective concentrations in the rainwater sample with the event rainfall depth (in $\mu\text{eq.L}^{-1}$). The rainfall depth (mm) and maximum intensity (mm.h^{-1}) for each rain event are also listed.

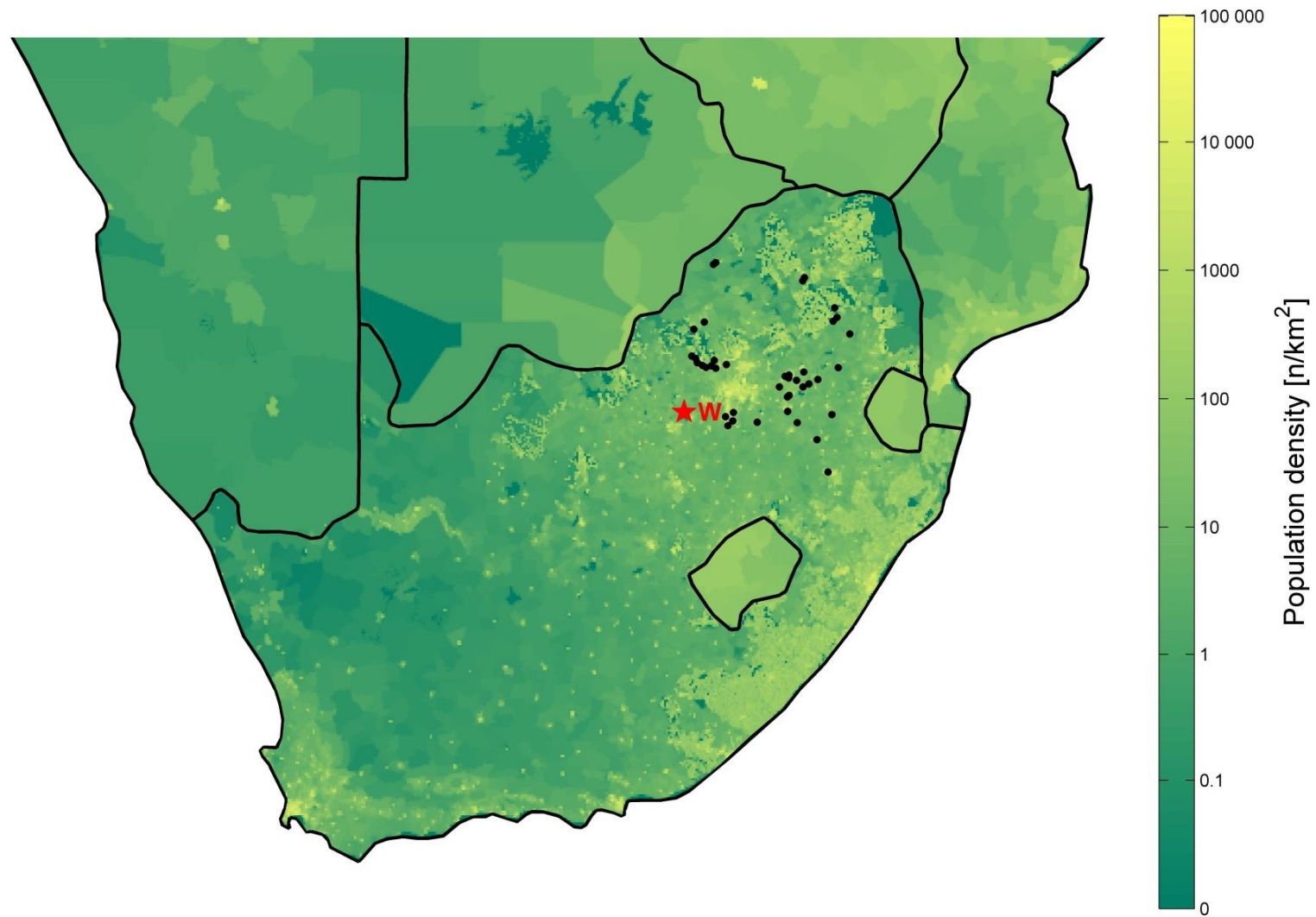


Figure 5.1: A map of southern Africa with the population density obtained from CIESIN (2010) indicated with a colour index, with an increase in population density indicated with an increase from green to yellow. The Welgegend atmospheric research station is indicated with a red star, whereas major pollution point sources in the interior of South Africa are represented as black dots, indicating major power stations, petrochemical plants and pyrometallurgical smelter related industries

5.1 Anthropogenic contribution

Figure 5.2 presents the back trajectories, calculated according to the described method, for the two rain events that occurred on 7 and 9–10 January 2015, respectively. Table 5.1 lists the ionic rainwater concentrations, the rainfall depth and maximum rainfall intensity for these rain events.

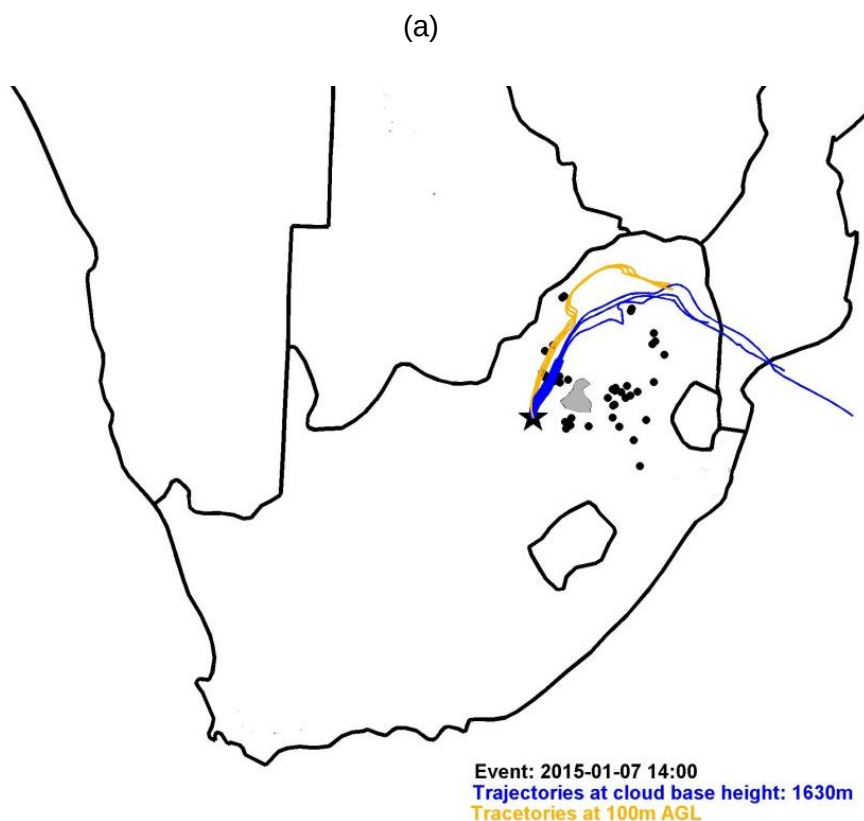


Figure 5.2: Rain event trajectories for (a) 7 and (b) 9-10 January 2015. The difference in CBH trajectories in relation to point sources is evident

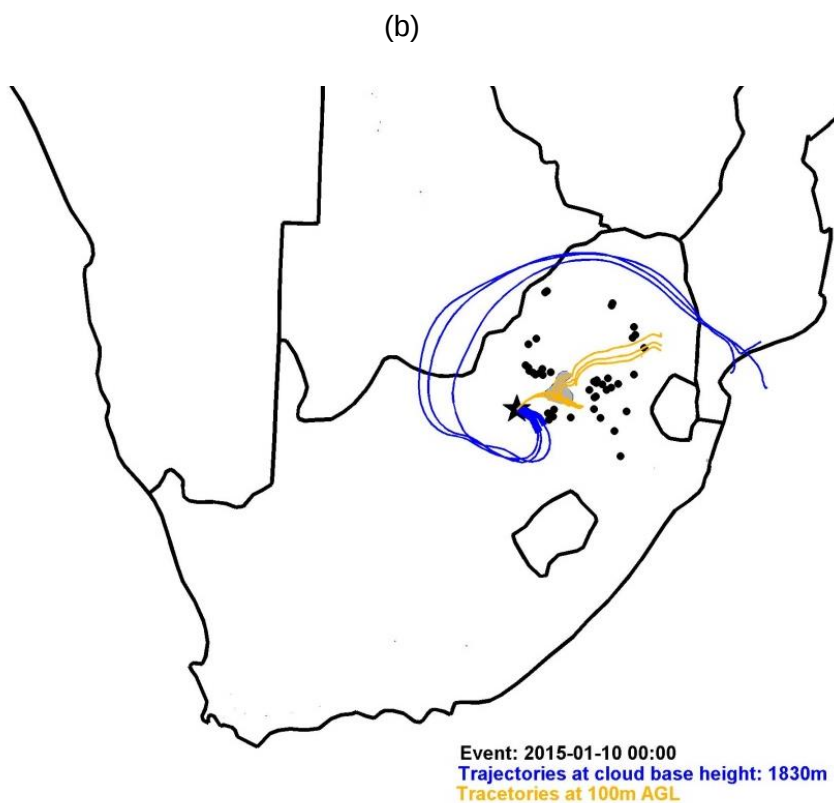


Figure 5.2 (continued): Rain event trajectories for (a) 7 and (b) 9-10 January 2015. The difference in CBH trajectories in relation to point sources is evident

Table 5.1: The precipitation chemistry presented as normalised values ($\mu\text{eq.L}^{-1}$) for 7 and 9-10 January 2015

Event date	7 Jan 2015	9-10 Jan 2015
Rain depth (mm)	70.0	40.0
Intensity (mm.h^{-1})	32.5	11.8
pH	4.20	4.10
SO_4^{2-}	5285	3024
NO_3^-	2453	1444
NH_4^+	2442	1386
Ca^{2+}	1221	514
Mg^{2+}	442	68
Na^+	1670	95
Cl^-	1439	112
OA	28	28
K^+	510	32

As is evident from Figure 5.2, for both the rain events on 7 and 9-10 January 2015, the CBH related air masses and the below-cloud related air masses generally moved from an easterly direction, where the air masses passed over areas that included the western Bushveld Complex, the Waterberg, the JHB-PTA megacity and the Vaal Triangle. The anthropogenic influence on the rain chemistry is evident from Table 5.1, since both of these events had elevated levels of NO_3^- and SO_4^{2-} . However, the CBH air mass histories for the event on the 9-10 January travelled in a typical re-circulation pattern and bypassed most of the large pollution point sources. This is reflected in the rain chemistry as the concentration of all the ions, except the organic acids (OAs) were lower for this event.

Another example of the influence of source regions on rain chemistry is presented by the rain events occurring on 6 and 18 April 2016, which is presented in Figure 5.3. Considering the chemical composition of the events (Table 5.2), a significant difference in concentration is observed. The CBH and below-cloud base air mass histories indicate that air masses travelled over the JHB-PTA megacity, the Vaal Triangle and the Mpumalanga Highveld for the rain event on the 6th and hence had higher concentrations of ionic species in the rainwater. Both trajectory sets for the 18th moved along the typical anticyclonic circulation pattern, essentially bypassing the major pollution point sources, which resulted in much lower concentrations of ions in the rainwater.

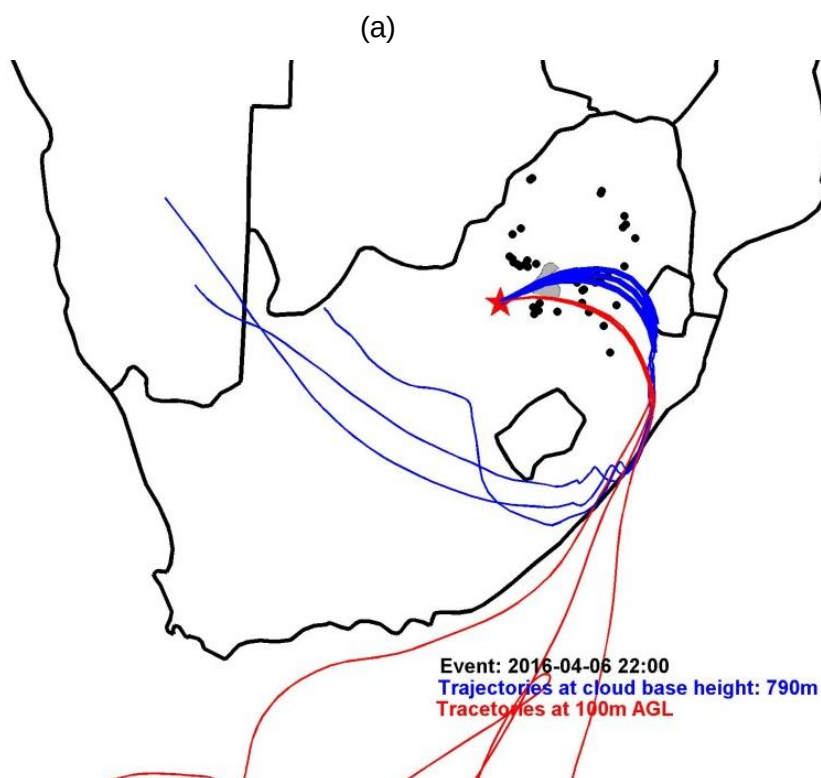


Figure 5.3: The difference in major point source contributions and the CBH trajectories can be seen in the events of (a) 6 and (b) 18 April 2015

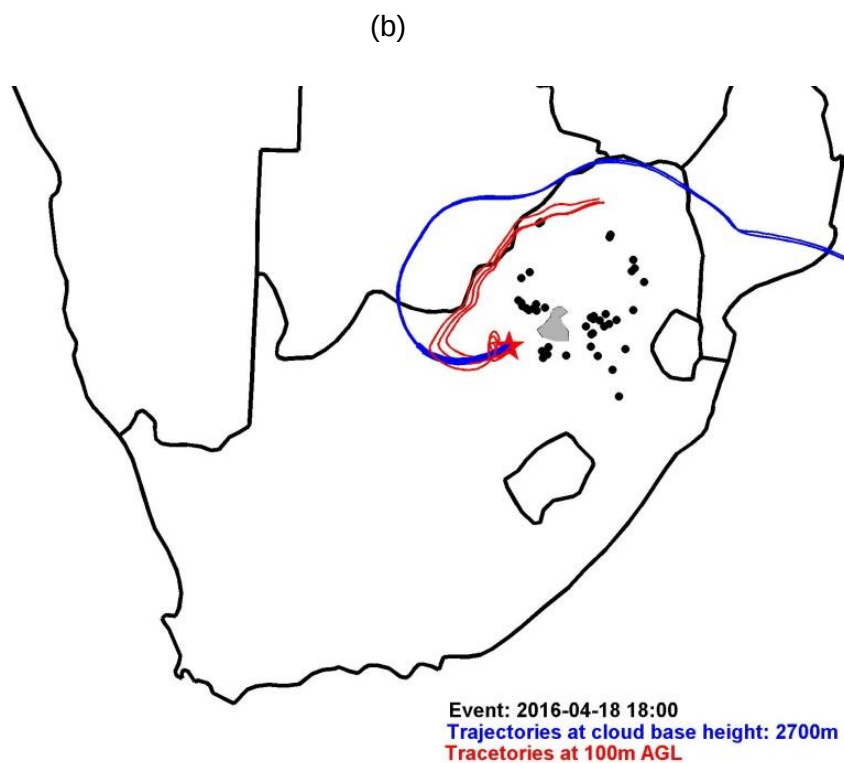


Figure 5.3 (continued): The difference in major point source contributions and the CBH trajectories can be seen in the events of (a) 6 and (b) 18 April 2015

Table 5.2: The normalised rainwater ionic concentrations for the events of 6 and 18 April 2015

Event date	6 Apr 2015	18 Apr 2015
Rain depth (mm)	34.0	2.0
Intensity (mm.h ⁻¹)	2.4	6.8
pH	4.57	5.84
SO ₄ ²⁻	3559	156
NO ₃ ⁻	968	100
NH ₄ ⁺	1474	94
Ca ²⁺	1890	187
Mg ²⁺	635	41
Na ⁺	1888	72
Cl ⁻	1715	69
OA	2052	58
K ⁺	830	22

5.2 A background event

The rain event on the 4th of April 2015 is presented as an example of a relatively clean or diluted rain event as indicated in Figure 5.4 and Table 5.3. The air mass histories of both the CBH and below-cloud air mass moved over neighbouring countries and did not pass directly over more polluted areas, which is reflected in the low ionic concentrations determined for all the species.

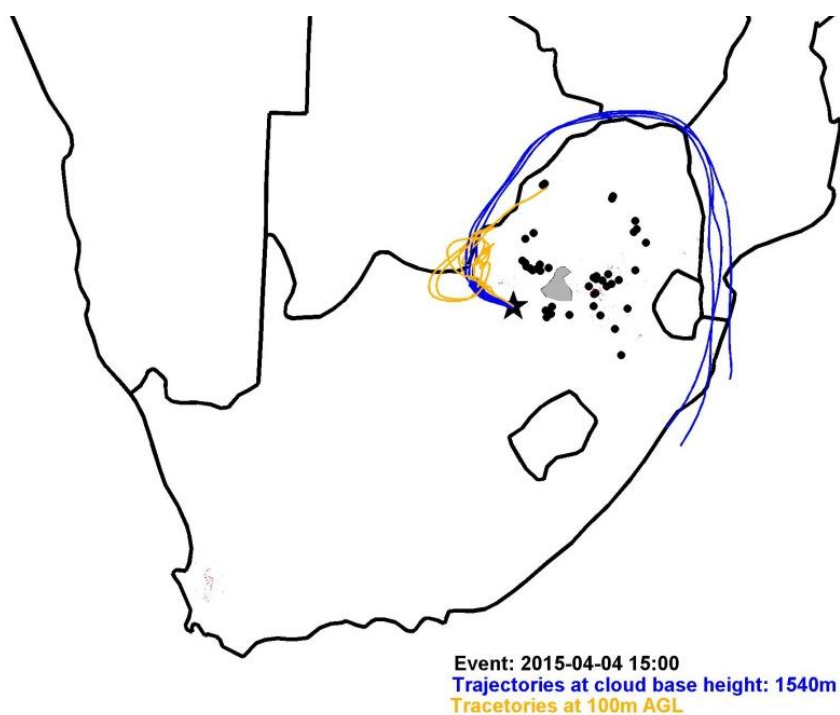


Figure 5.4: An example of a relatively clean rain event with regional below cloud air mass movement and CBH trajectories bypassing the major pollution point sources

Table 5.3: The relatively diluted chemical content of the rain event occurring on 4 April 2015

Event date	4 Apr 2015
Rain depth (mm)	6.0
Intensity (mm.h ⁻¹)	5.0
pH	4.70
SO ₄ ²⁻	149
NO ₃ ⁻	82
NH ₄ ⁺	110
Ca ²⁺	46
Mg ²⁺	9
Na ⁺	11
Cl ⁻	10
OA	4
K ⁺	4

5.3 Scavenging efficiency of two successive events

The rain events that occurred on the 4th and 5th of September 2015 present a good example of the scavenging efficiency and washout of the atmosphere for two successive events (Figure 5.5, Table 5.4). The air mass histories of the CBH and below-cloud air masses for both events are relatively similar, although not identical. However, the overall ionic compositions of the two events differ significantly. The event on the 4th had higher ionic concentrations, while the event that took place on the following day had much lower concentrations. This indicates that the air was cleaned (washout occurred) during the rain event occurring on the 4th, which resulted in a much cleaner air and lower ionic concentrations in the rain collected on the 5th. The rainfall depth is also greater on the 4th, which contributes to the scavenging efficiency.

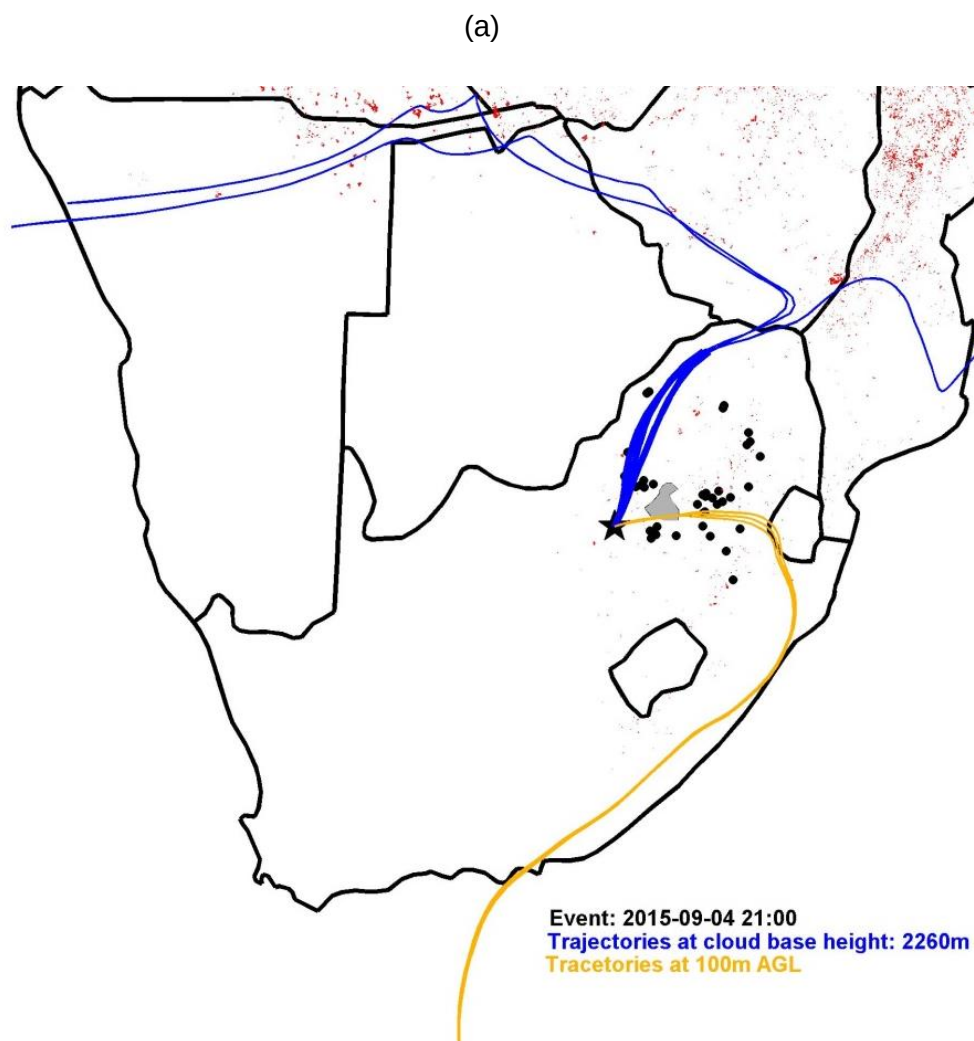


Figure 5.5: The trajectories for the events of (a) 4 and (b) 5 September 2015 that indicates notable scavenging

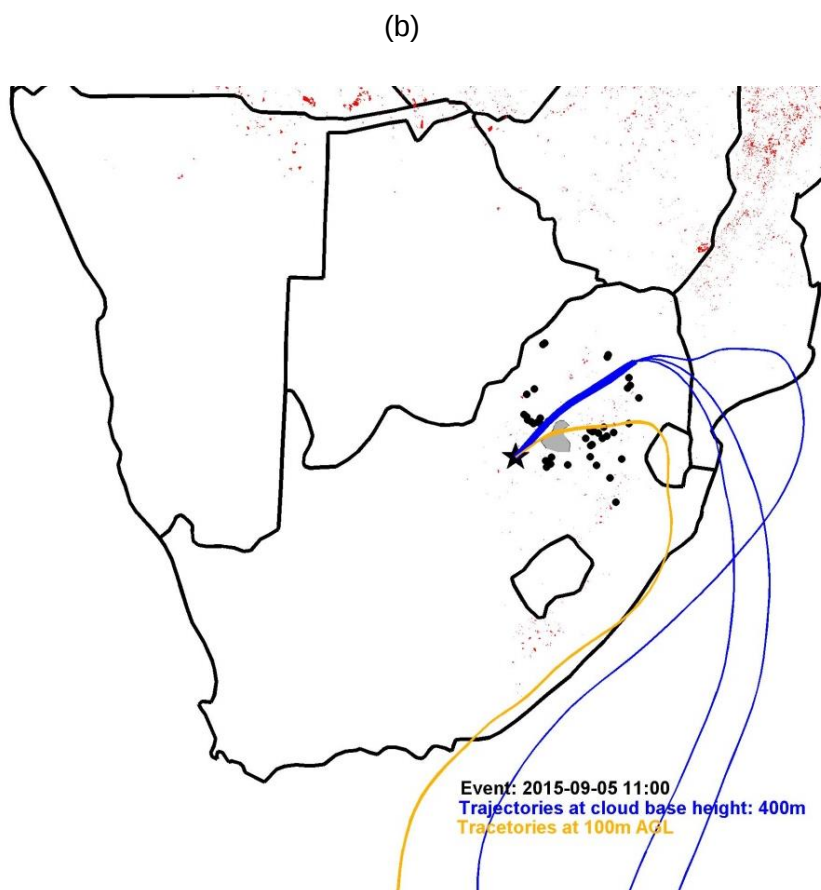


Figure 5.5 (continued): The trajectories for the events of (a) 4 and (b) 5 September 2015 that indicates notable scavenging

Table 5.4: The ionic concentration difference between rain events on two consecutive days (4 and 5 September 2015) showing the scavenging (washout) effect

Event date	4 Sept 2015	5 Sept 2015
Rain depth (mm)	30.0	5.0
Intensity (mm.h ⁻¹)	2.3	0.8
pH	4.43	4.50
SO ₄ ²⁻	1273	211
NO ₃ ⁻	502	147
NH ₄ ⁺	559	97
Ca ²⁺	419	119
Mg ²⁺	138	47
Na ⁺	117	173
Cl ⁻	163	173
OA	456	197
K ⁺	51	89

5.4 Build-up of pollutants in the colder months

An example of the influence of pollutant build-up on rain chemistry can be found in the two winter rainfall events that occurred on 13 June and 25 July 2016 (Figure 5.6 and Table 5.5). Winter rainfall is a rare occurrence. The ionic concentrations of such events are usually much higher than those of the austral summer months (see Section 4.4, Chapter 4). A possible explanation for this phenomenon is that over the winter months, the concentrations of chemical species in the atmosphere increase due to recirculation and vertical trapping of pollutants. Therefore, a precipitation event occurring during this period will scavenge high pollutant loads. By comparing the chemical concentrations of ionic species in rainwater of these two events in Figure 5.6, it is evident that the rainwater of the second rain event in July had much higher ionic concentrations than the event in June. This can most-likely be attributed to no rain events occurring between these two events and the build-up in the pollutant load in the atmosphere, which was scavenged during the second event in July. In addition, although the July rain event also had a greater rain depth (serves to dilute) and intensity (which should reduce scavenging efficiency), it still had higher ionic concentrations in the rain, indicating the strong effect of pollutant build-up in the colder months and the effect thereof on rain chemistry.

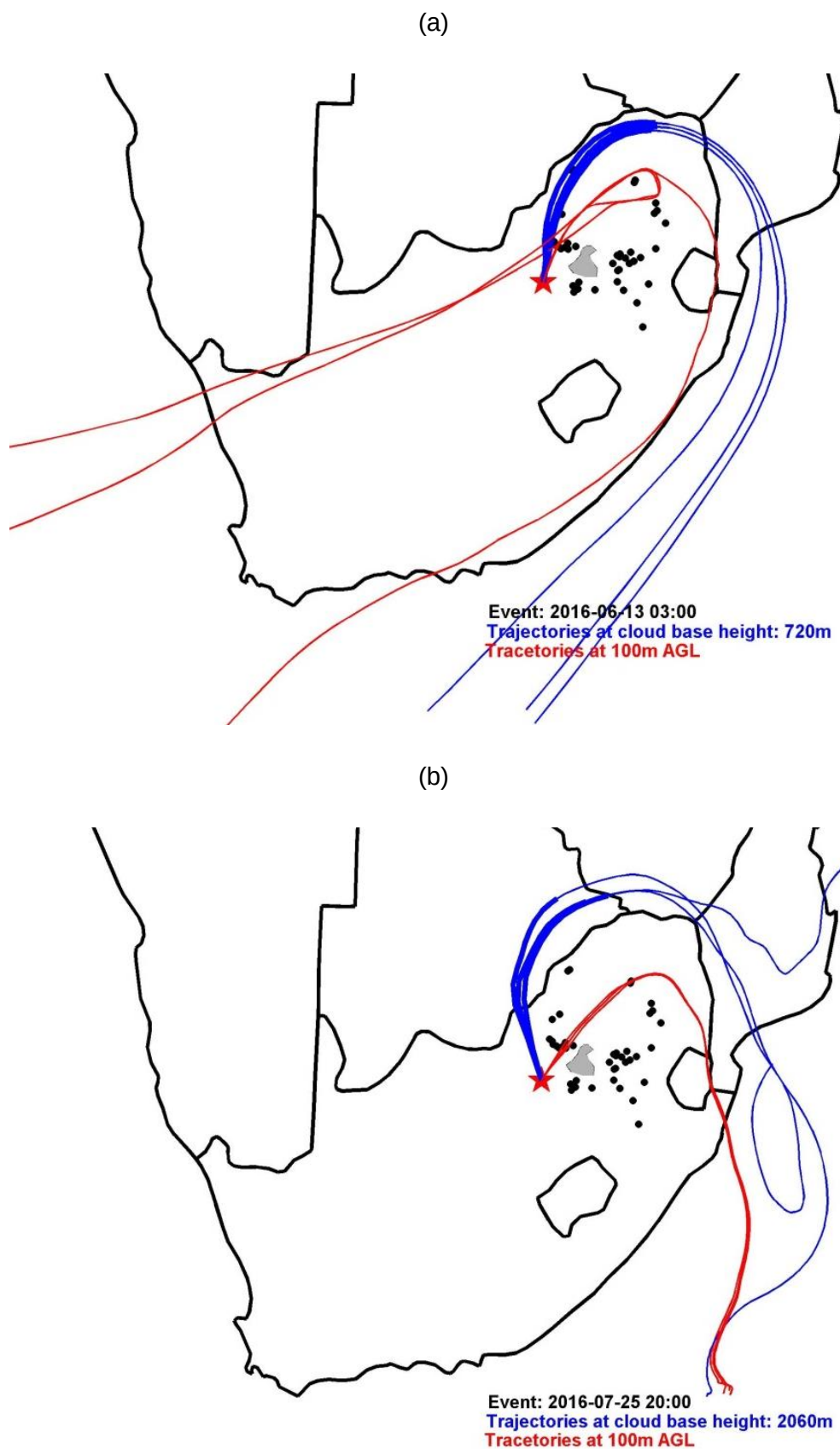


Figure 5.6: The pollutant build-up and effective scavenging during the winter rainfall events on (a) 13 June and (b) 25 July 2015

Table 5.5: Ionic concentrations of rain water events indicating the build-up of atmospheric pollutant loads taking place during winter

Event date	13 Jun 2016	25 Jul 2016
Rain depth (mm)	10.0	55.0
Intensity (mm.h ⁻¹)	1.6	6.0
pH	5.09	4.90
SO ₄ ²⁻	338	2931
NO ₃ ⁻	152	1672
NH ₄ ⁺	121	2168
Ca ²⁺	366	3122
Mg ²⁺	111	1137
Na ⁺	169	1518
Cl ⁻	171	1667
OA	196	2827
K ⁺	42	700

5.5 Long-range biomass burning

It is well known that fires emit OA, which are also correlated to Cl^- and K^+ (Helas and Pienaar, 1996; Galy-Lacaux et al., 2009) (Section 2.2.1, Chapter 2 and Section 4.3, Chapter 4). The air mass histories (CBH and below-cloud air masses) and the rainwater chemical compositions of the events that occurred on 20 and 22 September 2015 presented in Figure 5.7 and Table 5.6, confirmed that air masses that passed over fires contributed to higher OA, Cl^- and K^+ ionic concentrations in the rainwater (Figure 5.7 and Table 5.6). The increased Cl^- concentrations are also reflected by the Cl^- levels being higher than the Na^+ concentrations for these two rain events. In most rain samples collected at Welgegund Na^+ and Cl^- concentrations are usually similar (Section 4.1, Table 4.2, Chapter 4). These events occurred during the peak of the fire season (Section 4.1 and Figure 4.2, Chapter 4). However, it is evident that even distant fires that do not occur during the fire season in South Africa can affect the rain chemistry at Welgegund.

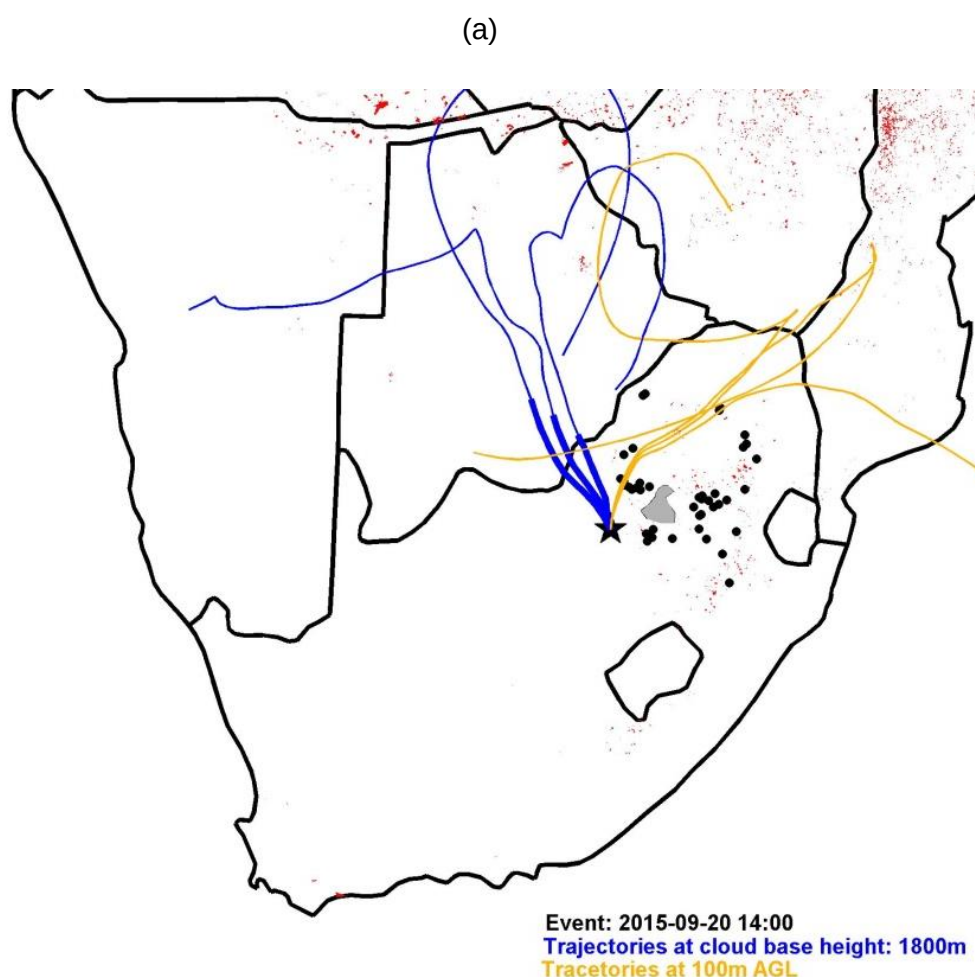


Figure 5.7: The influence of biomass burning (veld fires) on rainwater chemistry of (a) 20 and (b) 22 September 2015, in the peak fire season

(b)

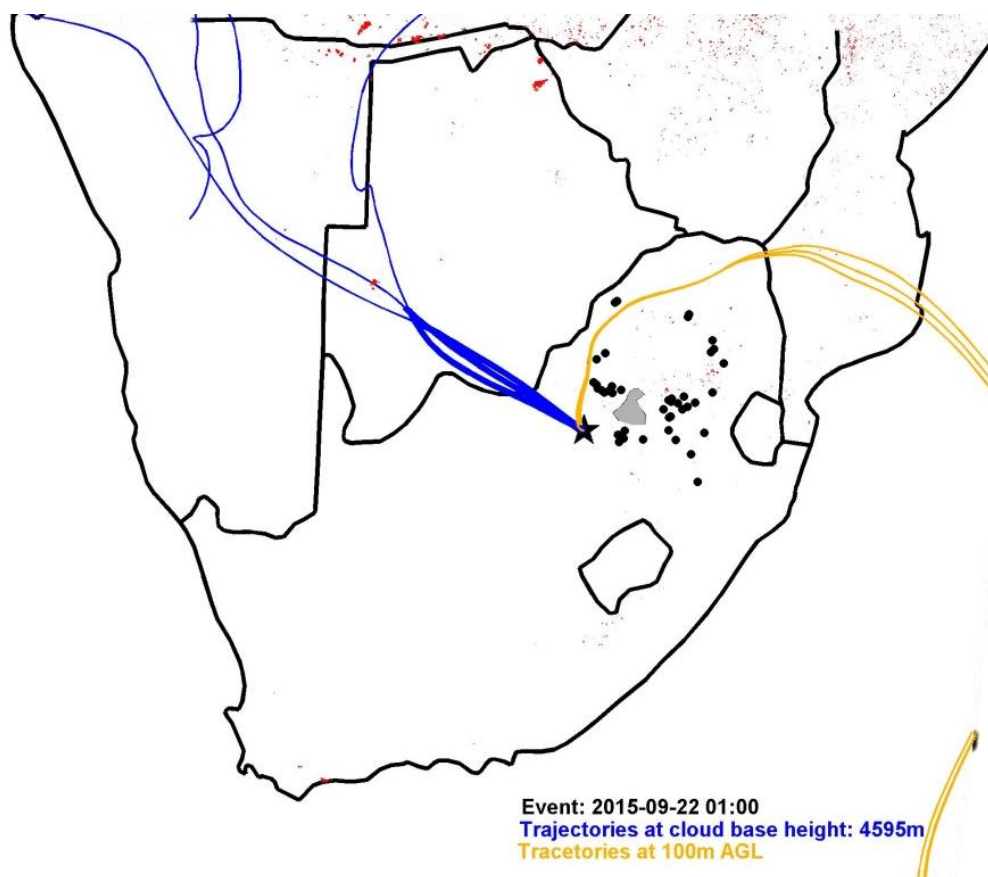


Figure 5.7 (continued): The influence of biomass burning (veld fires) on rainwater chemistry of (a) 20 and (b) 22 September 2015, in the peak fire season

Table 5.6: The chemical content of typical fire season rain events

Event date	20 Sept 2015	22 Sept 2015
Rain depth (mm)	11.0	13.0
Intensity (mm.h ⁻¹)	2.4	4.5
pH	4.49	4.51
SO ₄ ²⁻	513	583
NO ₃ ⁻	904	1049
NH ₄ ⁺	1108	1280
Ca ²⁺	424	453
Mg ²⁺	180	196
Na ⁺	630	680
Cl ⁻	913	1049
OA	800	827
K ⁺	457	501

5.6 Summer fires

A general assumption is that biomass burning will have a major influence on precipitation chemistry during the veld fire season (late winter and early spring) (Section 4.1, Chapter 4). By implementing the technique used in this study, it was noted that for the rain events occurring on 16 March, 19 November and 2-3 December 2015 that the OA content was elevated, which was outside the generally defined fire season (Figure 5.8 and Table 5.7). The nSSF-K⁺ and nSSF-Cl⁻ concentrations relating to biomass burning were also high. Evaluation of the trajectories and MODIS fire data indicated that the air masses passing over Welgegund were influenced by burning in areas just north of the site in the Bushveld Igneous Complex and in the northern part of Botswana.

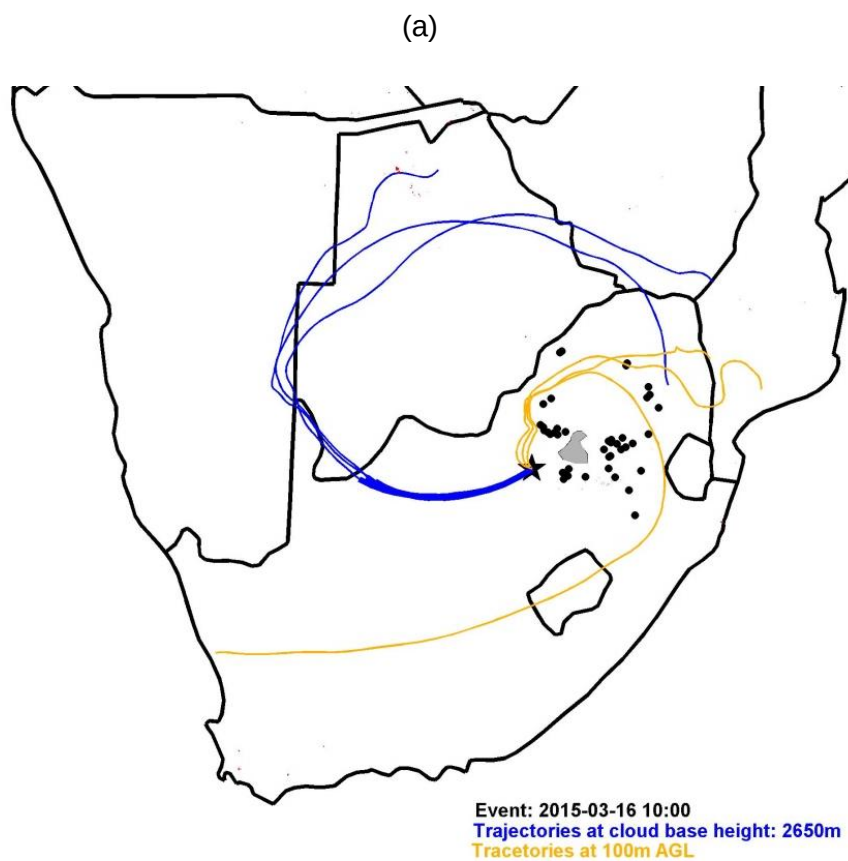


Figure 5.8: Mid-summer rainfall events influenced by biomass burning activities for rain events occurring on (a) 16 March, (b) 19 November and (c) 2-3 December 2015

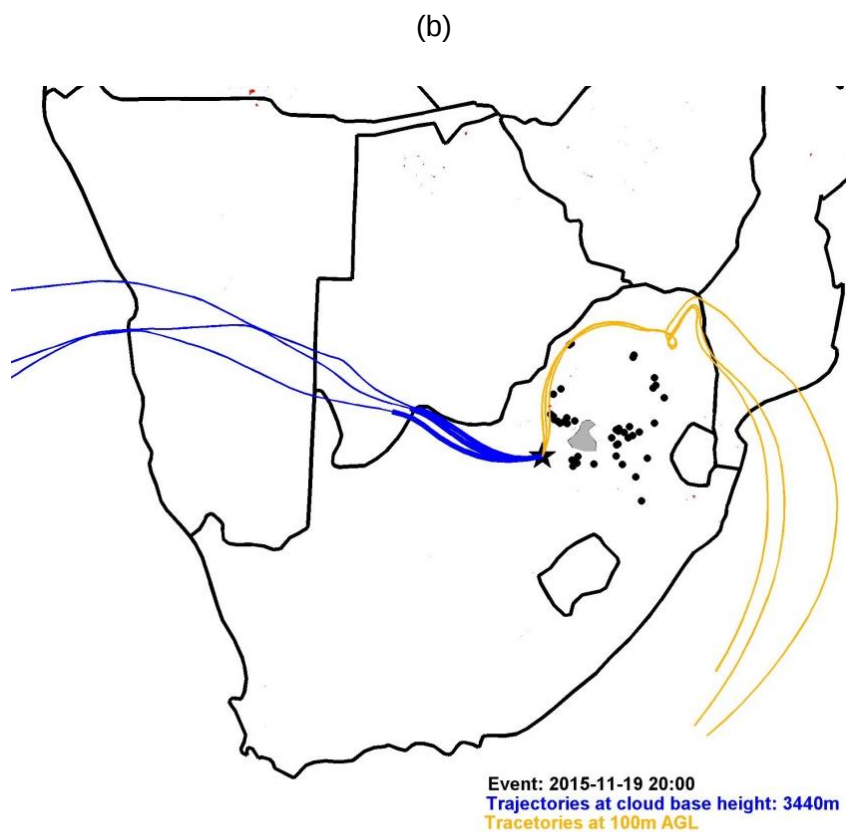


Figure 5.8 (continued): Mid-summer rainfall events influenced by biomass burning activities for rain events occurring on (a) 16 March, (b) 19 November and (c) 2-3 December 2015

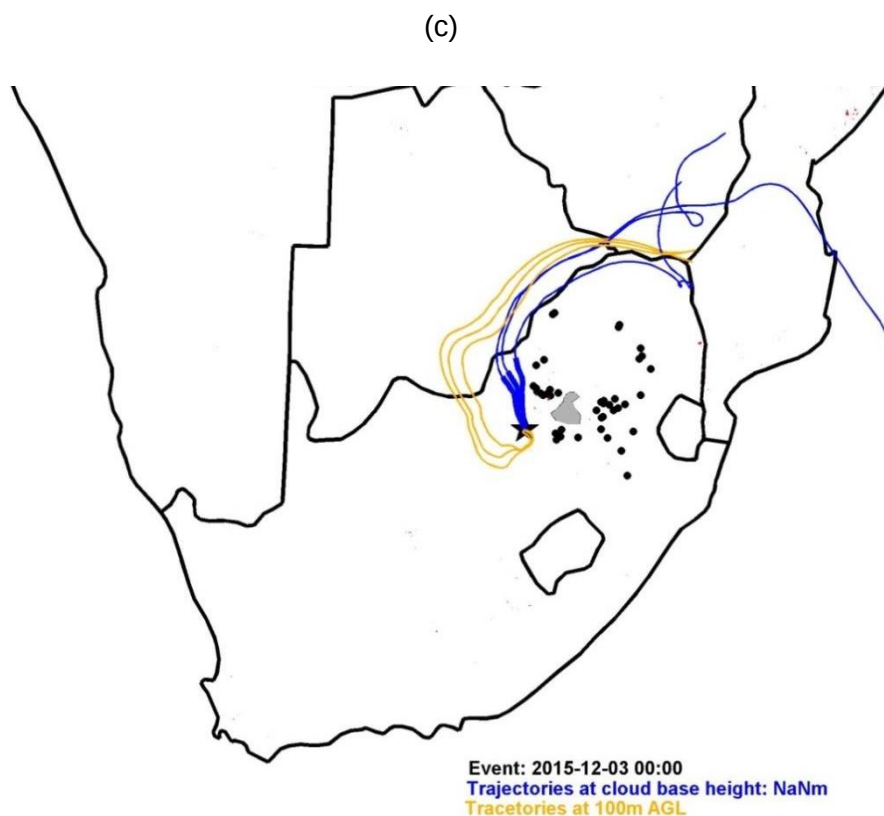


Figure 5.8 (continued): Mid-summer rainfall events influenced by biomass burning activities for rain events occurring on (a) 16 March, (b) 19 November and (c) 2-3 December 2015

Table 5.7: Ionic concentrations for rainfall events influenced by summer fires

Event date	16 Mar 2015	19 Nov 2015	2-3 Dec 2015
Rain depth (mm)	15.0	21.0	8.0
Intensity (mm.h ⁻¹)	2.9	7.1	3.0
pH	4.44	4.79	5.70
SO ₄ ²⁻	366	444	1073
NO ₃ ⁻	318	619	709
NH ₄ ⁺	373	466	554
Ca ²⁺	214	818	1179
Mg ²⁺	30	278	621
Na ⁺	88	208	1128
Cl ⁻	89	273	1414
OA	408	883	736
K ⁺	57	71	544

6. Conclusion

The chemical composition and wet deposition flux of precipitation at a regional background site in South Africa (the Welgegund atmospheric research station) was presented in this study. The acidity, neutralisation factors and possible source contributions to rainwater were evaluated, as well as contextualised with regard to previously published South African precipitation studies. It was determined that SO_4^{2-} followed by NO_3^- had the highest concentrations. In comparison to other South African DEBITS sites, SO_4^{2-} concentrations were comparable and even higher than SO_4^{2-} levels measured at more polluted sites such as Amersfoort and Vaal Triangle (Conradie et al. (2016)). The air masses arriving at Welgegund follows an anticyclonic recirculation pattern that generally moved over the major anthropogenic source regions, i.e. Bushveld Igneous Complex, the Vaal Triangle, the Mpumalanga Highveld and JHB-PTA megacity. This recirculation pattern contributes to the long-range transport of pollutants, and the subsequent aging and oxidation of chemical constituents in the air that is taken up into the rainwater through different scavenging processes. The nitrogenous ionic species, i.e. NO_3^- and NH_4^+ , were also determined to be more concentrated than those reported for other South African sites reported by Conradie et al. (2016). Apart from the long-range transport of anthropogenic emissions, the site is also surrounded by farming activities that contribute to agricultural contributions of NH_4^+ . The influence of biomass burning plumes was evident. However, the wet season does not coincide with the typical fire season and therefore the effect of OAs on the precipitation chemistry was not as pronounced as that of anthropogenic activities. Spearman correlation coefficients were calculated to estimate possible source contributions. SO_4^{2-} and NO_3^- exhibited a strong correlation, which indicated similar source regions emitting both S- and N-containing species. The influence of biomass burning was indicated by a strong correlation between K^+ and Cl^- , as well as strong correlations between these ions to OAs. A definite marine contribution was indicated by a strong correlation between Na^+ and Cl^- . Fossil fuel combustion had the largest source contribution to the precipitation chemistry, while marine and terrigenous source groups had slightly lower contributions than fossil fuel. Agricultural source contributions were notable, with biomass burning contributions having the smallest influence. Seasonal differences were observed with the ionic concentrations and loading increasing during the late autumn and winter months. This was attributed to atmospheric build-up of pollutants trapped by prominent stable inversion layers and less frequent rainfall events.

The pH levels of rainwater samples were generally acidic with approximately 88% of the samples analysed having a pH less than 5.6. SO_4^{2-} was the main mineral acidic component.

The mean pH (4.65) for the entire sampling period was similar to other wet deposition measurements conducted in South Africa. Neutralisation factors were calculated for these species and it was determined that Ca^{2+} and NH_4^+ were the dominant neutralising factors. The high Ca^{2+} neutralisation effect, in contrast to other South African sites, is related to the closer proximity of Welgegund to the dry and dusty Kalahari and Karoo in western South Africa. Ca^{2+} also had a much larger contribution to the neutralisation of the rainwater acidity during the drier second defined wet season.

Another objective of this study was to develop a pilot method to identify rain event specific parameters. In this study, air mass history was related to precipitation chemistry. This method used cloud base height (CBH) and rain intensity measurements to determine event-based air mass movements associated with the precipitating cloud, as well as with the below-cloud air masses. Precipitation chemistry together with air mass history, determined through back trajectory analysis, was then related to the major pollution point sources and/or source regions influencing air masses measured at Welgegund.

Rain events with similar cloud base height (CBH) air mass- and below-cloud air mass histories indicated the influence of point sources and/or source regions over which these air masses passed. Rain events for which back trajectory sets for both the CBH and the below-cloud related air mass, passed over the region east of Welgegund, where major pollutant point source are located, indicated the influence of anthropogenic related pollutants (i.e. SO_4^{2-} , NO_3^-). In contrast, for rain events where both back trajectory sets originated from the relatively cleaner western sector, lower ionic concentrations were measured. The efficient scavenging or washout effect by rain was also demonstrated for two rain events occurring on two consecutive days, which had similar back trajectories. The build-up of pollutants during winter was also indicated by the ionic concentrations measured for a winter rain event. The influence of veld fires close to and distant from Welgegund was also indicated.

The results from this pilot study clearly highlighted the key influence of air mass history on rainwater chemistry. The method must be further developed by incorporating more event-based parameters such as synoptic weather patterns, precipitation type and rain intensity. Statistical clustering of parameters will also give more insight into the complex integrated processes that affect the eventual rainwater chemistry. Due to the relatively short sampling period considered in this study, the results are not yet statistically significant and therefore an extended sampling period is recommended for future studies.

7. Project evaluation

The successes and shortcomings of this project can be evaluated through relating the overall outcome of this study to each of the objectives listed in Chapter 1. The general aim of this study, to determine the chemical content of rainwater collected at the Welgegund station and to develop techniques that can be used to relate the event-based composition of precipitation with processes that affect it, was achieved through the following specific objectives:

- i. *conduct wet-only precipitation sampling at the Welgegund atmospheric research station over at least one full seasonal cycle;*

This objective was exceeded, since sampling was conducted at Welgegund over a period of 20 months (December 2014 to July 2016). This sampling period allowed the identification of two 10 month periods representing two different wet seasons, which could be compared. However, although this objective was exceeded, a limitation of the study was associated with this relatively short sampling period, which did not allow for advanced statistical analysis.

- ii. *analyse the collected rainwater to determine the chemical content, which entails ion-chromatography (IC) analyses of water soluble species, i.e. nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), formic acid (HCOO^-), propionic acid ($\text{C}_3\text{H}_5\text{O}_2^-$), acetic acid (CH_3COO^-), oxalic acid ($\text{C}_2\text{O}_4^{2-}$), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}), as well as determining pH and electrical conductivity (EC);*

The ionic concentrations for a total of 56 precipitation events were successfully analysed with only 3 rain samples not passing the data quality standards of the WMO GAW precipitation guidelines. The total collection efficiency was 95.8%. It was determined that SO_4^{2-} had the highest concentrations with NO_3^- , Ca^{2+} , NH_4^+ , Na^+ , Cl^- , OA (the sum of HCOO^- , $\text{C}_3\text{H}_5\text{O}_2^-$, CH_3COO^- , CH_3COO^-), Mg^{2+} , K^+ and F^- following in order from highest to lowest concentrations. The ionic concentrations determined in the rainwater collected at Welgegund could also be compared to other wet deposition studies conducted in South Africa. The VWM of ionic species were generally higher during the austral winter months, which was attributed to pollution build-up in the atmosphere due to more pronounced inversion layers and fewer rainfall events occurring. The second defined period (October 2015 to July 2016) was a drier period, which had elevated Ca^{2+} , Mg^{2+} and OA concentrations, as well as a higher mean pH compared to the first defined period. The mean pH for the sampling period

was determined to be 4.65, which is considered to be acidic. The pH frequency distribution showed that most of the events had a pH in the range of 4.0 - 4.8, with 88% of the events having a pH below 5.6.

- iii. *determine the potential acidic contributors and to identify possible neutralising species through the calculation of neutralisation factors;*

It was established that SO_4^{2-} was the main potential mineral acidic contributor with almost double the acidic contribution compared to NO_3^- . Neutralisation factors were determined in relation to NH_4^+ , Ca^{2+} and Mg^{2+} . Terrigenous Ca^{2+} had the highest contribution to the neutralisation of rain for the entire period, which was especially significant for the drier second defined season. The NH_4^+ neutralisation contribution remained relatively consistent throughout the sampling period and was independent of rainfall depth.

- iv. *identify, calculate and categorise specific source contributions (e.g. fossil fuel combustion, marine) through empirical and statistical methods;*

Spearman correlation coefficients were calculated and empirical methods were applied in order to determine the sources of ionic species measured in the rainwater. The ionic composition of the rainwater was categorised into marine, terrigenous or crustal, agricultural, fossil fuel combustion and biomass burning. It was established that fossil fuel combustion had the largest source contribution to the precipitation chemistry, while marine and terrigenous source groups had slightly lower contributions than fossil fuel. Much lower contributions were calculated from agricultural and biomass burning sources in relation to the other sources.

- v. *contextualise precipitation measured at Welgegund with regard to other South African sites;*

Welgegund precipitation chemistry could be compared to other wet deposition studies conducted in South Africa at the South African DEBITS sites, viz. Amersfoort, Vaal Triangle, Louis Trichardt and Skukuza. The ionic concentrations determined for rainwater collected at Welgegund were in the same order as the concentrations of the species measured at the South African DEBITS sites. Similar to Welgegund, SO_4^{2-} and NO_3^- concentrations were also the highest at all four the South African DEBITS sites. However, the ionic concentrations measured in rainwater at Welgegund were generally higher compared to the other sites, with SO_4^{2-} levels being lower compared to SO_4^{2-} concentrations measured only at the industrially influenced Amersfoort site. The general higher concentrations could be attributed to

air masses arriving at Welgegund passing over the major pollution point sources i.e. over mining, industrial and anthropogenic activities in the Bushveld Complex, the Johannesburg-Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld. The average pH was comparable to the average pH values measured at all the South African DEBITS sites.

- vi. *develop a method to identify rain event specific parameters that could affect the chemical composition, which involves cloud base height (ceilometer) and rain intensity (tipping-bucket intensity instruments) measurements in conjunction with air mass history analysis (HYSPLIT_4.8 model back-trajectories);*

A pilot method was successfully developed in order to relate air mass movements associated with the precipitating cloud base height (CBH) and the below-cloud air mass, to the event-based precipitation chemistry. Ceilometer measurements were used to determine CBHs from the average CBHs 2 hours before the onset of the rain event and rain intensity measurements to establish the start times of rain events. Back trajectory analysis was performed with HYSPLIT v4.8 for the CBH and below-cloud air masses. 3 hourly arriving 96-hour back trajectories, which correspond to the afore-mentioned 2 hours before the onset of the rain event, both at CBH, as well as at 100 m above ground level (AGL) was calculated. The height of 100 m AGL was chosen to represent the below-cloud air mass, since it can be assumed that most rain events sampled at Welgegund was formed due to convective processes, which implies that the planetary boundary layer below the cloud base should be well mixed. The back trajectory analyses could then be related to air masses passing over specific point sources and/or source region. Selected case studies were presented that indicated the potential significance of the above mentioned method in order to study event-based precipitation chemistry.

- viii. *make recommendations with regard to future wet deposition measurements at Welgegund and the further development of the above-mentioned pilot method to link rain chemistry with processes that influence it.*

It is recommended that precipitation chemistry and wet deposition studies are continued at Welgegund. Larger datasets will allow for improved source group characterisation through advanced statistical methods, as well as to determine inter-annual variability. It will also contribute to the understanding of long-term trends, as well as determining the changes in atmospheric composition in relation to the changes associated with anthropogenic activities and population growth. Furthermore, in this study, rain samples were collected for two relatively dry years.

Therefore, the chemical analysis cannot be considered to be representative of long-term precipitation chemistry at Welgegund. It is also recommended that wet deposition is combined with long-term dry deposition measurements at Welgegund in order to determine total deposition of species.

The pilot method developed in this study indicated the potential of this method to successfully establish event-based parameters influencing precipitation chemistry. It is recommended that the method must be further developed by relating more event-based parameters such as rain intensity, rain- or cloud type and synoptic weather maps or satellite imagery. Rain intensity measurements, for instance, will give more insight in the relation between scavenging efficiency and rain chemistry. Statistical clustering of these parameters can enlarge the accuracy of source contribution analysis and will also give more insight into the complex integrated processes that affect the eventual rainwater chemistry. The results presented in this study are not yet statistically significant due to the relatively short sampling period considered in this study. It is foreseen that incorporating more parameters for longer measurement periods with this method presented in this study will yield more substantial evidence to the factors influencing precipitation chemistry.

Overall project evaluation

In general it can be concluded that the aim and objectives were successfully achieved in this study. A few shortcomings of the study were identified, which could be addressed through future research. During the development of the pilot method further research opportunities through in-depth application of the method, as well as numerous comparison prospects, were identified. It is the intent of the candidate to pursue the development and exploration of this method through a PhD research study.

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